SELECTED VIBRONIC LEVEL FLUORESCENCE
SPECTRAL STUDIES

The following papers have been presented or published during course of the work:

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Except where reference has been made to the work of others, the work described in this thesis is my own.

The following papers have been presented or published during the course of the work:


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CHAPTER 1

INTRODUCTION

This thesis is concerned with selected vibronic level fluorescence spectral studies of pyrimidine-d₄ and pyrimidine-h₄ and the instrumentation developed to perform the studies.

Selected vibronic level (SVL) fluorescence spectroscopy involves the study of the fluorescence emission of effectively isolated molecules, excited to single vibronic levels of their first excited singlet states. Studies of SVL fluorescence may be divided into three categories: (relative) quantum yield studies, lifetime (time-resolved) studies and - the prime concern of this thesis - spectral (wavelength resolved) studies.

In combination, such studies can yield a wealth of information on radiative and nonradiative processes in the excited states of a molecule, on its electronic, vibrational and rotational energy states and on the interactions between these states.

It has only been during the past decade, with the advent of new technology and techniques, that the potential of SVL fluorescence spectral measurements to elucidate details of molecular spectroscopy and probe excited state relaxation processes in "large" (e.g. benzene) polyatomic molecules has been exploited. Information on anharmonicities and vibrational level assignments in ground and excited electronic states, vibronic couplings, Franck-Condon factors, intramolecular and environmentally induced electronic, vibrational and rotational excited state relaxation processes has been obtained, for example. The principles and various applications of SVL fluorescence spectral studies are discussed in chapter 5.

Even with the advantages afforded by current technology, measurements of SVL fluorescence spectra still provide a considerable experimental challenge, especially if aspects of the spectroscopy of a molecule are to
be examined in detail. The most time consuming part of the project was the design, construction and refinement of the vapour phase fluorimeter. An overview of the fluorimeter is given in chapter 2; in chapters 2 and 3, the instrument is described in detail and the principles of its construction and use are discussed. To enable studies of fluorescence from effectively isolated molecules and of the dependence of fluorescence on collisional interactions down into the pressure region where collisional perturbations of an excited molecule are insignificant for the duration of its excited state lifetime, a fluorimeter must be capable of maintaining low sample pressures at least for the duration of data collection. The pressure requirements for performing such investigations on different types of molecules are discussed in chapter 2. Special attention was given to the vacuum aspects of the multi-pass cell in which the fluorescent sample is maintained at low pressure. The high to ultra-high vacuum techniques employed in its construction are discussed in detail in chapter 2. Other aspects of the experimental system which are given special attention in chapters 2 and 3 are: a 3-lens coupling scheme for efficient transfer of fluorescence from the multi-pass emission cell to the analysing monochromator, alternative fluorescence excitation and collection methods to those employed currently, methods used to compensate for fluctuations in excitation intensity with time, gated detection of fluorescence, the significance of pulse pileup in data collected using photon counting and the processing and presentation of data.

For the relative intensities of vibrational bands of SVL fluorescence spectra to be correct, which is necessary if such spectra are to be used in the examination of, for example, Franck-Condon factors and vibronic coupling mechanisms, recorded intensities must be corrected for changes in the spectrometer throughput, detector sensitivity, and the efficiency
of fluorescence collection with wavelength. Chapter 4 describes the method used to correct fluorescence spectra for the spectral response of the fluorimeter and the verification of the accuracy of the method. Correction factors were found to differ appreciably in the wavelength range 320-430 nm. It was shown that, in such fluorimeters, variations with wavelength in the efficiency of transfer of fluorescence from the multi-pass cell to the analysing spectrometer can be considerable.

In chapter 5, the applications of SVL fluorescence spectral studies in elucidating details of molecular spectroscopy and in probing excited state nonradiative processes are surveyed and the principles of interpretation of SVL fluorescence spectra, particularly those relating to the SVL spectra of pyrimidine, are discussed.

In chapter 6, fluorescence spectra from several SVL's of pyrimidine-\(d_4\) vapour are analysed and compared with those of pyrimidine-\(h_4\) as reported and analysed by other workers [Knight, Lawburgh and Parmenter, 1975]. The general features of the pyrimidine-\(h_4\) and -\(d_4\) spectra are similar, the spectra being dominated by long progressions in two ring-stretching vibrations and there being no evidence of vibronic coupling involving either the ground or first excited singlet states. However, the spectra of pyrimidine-\(d_4\) are less congested than the spectra of pyrimidine-\(h_4\) because, whereas in pyrimidine-\(h_4\) both modes forming long progressions are involved in ground state Fermi resonances, in pyrimidine-\(d_4\) they are not and because fewer modes are active in forming progressions in pyrimidine-\(d_4\) than in pyrimidine-\(h_4\). Therefore, with structure at displacements as large as 7000 cm\(^{-1}\) from the excitation positions being securely identifiable in the spectra of pyrimidine-\(d_4\), it has been possible to examine Franck-Condon factors and anharmonicities in greater detail for pyrimidine-\(d_4\) than for pyrimidine-\(h_4\).
Franck-Condon factors observed in fluorescence from the zero point level were used to establish the displacement parameters required for calculation of Franck-Condon factors in fluorescence from other levels using the Harmonic Oscillator approximation. From an analysis of the Franck-Condon factors for the fluorescence spectrum of pyrimidine-d$_4$, generated by pumping the first member of the most intense upper state progression in absorption, this progression was identified as $12^1_n$. Observed intensities for the $12^1_n$ progression were in good agreement with calculated intensities, but, as with the $12^0_n$ progression in the zero point level fluorescence spectrum, the parameters for the displacement of the corresponding normal coordinate, $v_{12}$, between the ground and excited states were found to be markedly different for pyrimidine-d$_4$ and pyrimidine-h$_4$.

If a member of an excited state Fermi resonance pair is pumped, the mixed nature of the excited state may be reflected in the structure and intensity distribution of the resultant fluorescence spectrum. Franck-Condon factors observed in pyrimidine-d$_4$ fluorescence from a pair of levels involved in excited state Fermi-resonance were shown to be in agreement with calculated Franck-Condon factors when the anharmonic coupling was taken into account.

Evidence of ground state Fermi resonance interactions comes from multiplet structure in SVL fluorescence spectra and from weak hot bands in absorption spectra. From an analysis of the multiplet structure of some of the hot bands in the high resolution absorption spectrum of pyrimidine-d$_4$, Innes, McSwiney, Simmons and Tilford (1969) concluded that mode $v''_{6a}$ of pyrimidine-d$_4$ was involved in a Fermi resonance interaction and that mode $v''_{6a}$ of pyrimidine-h$_4$ was also. Close scrutiny of the $6a'^0_{1}$ bands in the zero point level fluorescence spectra of pyrimidine-d$_4$ and
pyrimidine-h$_4$ in this work showed, however, that the conclusions of Innes et al. (1969) applied to pyrimidine-h$_4$ but not to pyrimidine-d$_4$, the case for which detailed evidence had been provided. Examination of the perturbation theory treatment used by Innes et al. (1969) showed that it involved inconsistencies when applied to the pyrimidine-d$_4$ data but not when applied to the pyrimidine-h$_4$ data. Calculations showed that the magnitude of the corresponding Fermi resonance interaction in pyrimidine-d$_4$ was such that there should be no evidence of it in the SVL fluorescence spectra.

Evidence is presented in chapter 6 that fluorescence spectra of pyrimidine-d$_4$ become diffuse more rapidly than those of pyrimidine-h$_4$ as the excitation energy is increased.

Upon excitation of different regions of the origin band of pyrimidine-d$_4$, different fluorescence band profiles were observed indicating that fluorescence was occurring from nonequilibrium distributions of rovibronic levels.

The excited state photophysics of pyrimidine is of interest because it displays intermediate case nonradiative decay behaviour and because its fluorescence is possibly more sensitive to collisional quenching than is the fluorescence of any other intermediate case molecule. In chapter 7, classification of nonradiative transitions is discussed, studies of pyrimidine photophysics are reviewed, and theories used to interpret the intermediate case decay behaviour of pyrimidine are outlined. Studies of collisional quenching of pyrimidine-d$_4$ and pyrimidine-h$_4$ fluorescence and attempts to observe vibrational relaxation in pyrimidine-d$_4$ and electronic energy transfer from pyrimidine-d$_4$ to pyrimidine-h$_4$ are also described in this chapter.
When the excited state decay data of intermediate case molecules are analysed within the framework of the most commonly used theoretical model, it is found that the number of states effectively coupled to the initially excited state, responsible for the nonradiative dissipation of the excitation energy, far exceeds the number of available triplet vibronic states even though it has been shown that intersystem crossing is the almost exclusive pathway of non-fluorescent decay in many of these molecules, especially pyrimidine. This has led several authors to propose that, for intermediate case molecules, the dissipative coupling occurs between rovibronic states with rotational effects playing an important role in the collisional quenching of their fluorescence. The discrepancy between the number of effective dissipative states and the number of available triplet vibronic states may be greater for pyrimidine than for any other intermediate case molecule examined so far.

Despite the difference in the intervals between the rotational levels of pyrimidine-\textsubscript{d4} and pyrimidine-\textsubscript{h4}, no such rotational effects are apparent from comparison of the fluorescence quenching data obtained in this work for the two molecules. No significant difference was observed in the rate constants for the self quenching of the zero point level fluorescence of pyrimidine-\textsubscript{d4} and pyrimidine-\textsubscript{h4}, nor was there any appreciable difference in the rate constants for quenching of the zero point level fluorescence of the two molecules by cyclohexane. The absence of exact resonance between the levels of the colliding molecules was found to have a very large effect, however.

At the pressures used, there was no evidence of excited state vibrational energy redistribution in the zero point level fluorescence of pyrimidine-\textsubscript{d4} or of electronic energy transfer from pyrimidine-\textsubscript{d4} to pyrimidine-\textsubscript{h4}. 
While the experimental system for performing SVL spectral measurements was being developed, a study of position dependent deuterium effects on the vapour phase fluorescence lifetime of phenanthrene was conducted but is not treated in this thesis. Fluorescence lifetimes of phenanthrene-\text{h}_{10}, -d_{10}, 2,4-d_{2}, 1,3-d_{2}, 9,10-d_{2}, 2,4,5,7-d_{4} and 1,3,6,8-d_{4} excited at 337 nm and 316 nm with an excitation bandpass of 25 cm$^{-1}$ were measured. A preliminary paper on part of this work is appended (Appendix A8).
CHAPTER 2

DESIGN AND CONSTRUCTION OF SVL FLUORIMETER. I. OPTICAL AND VACUUM ASPECTS

An overview of the vapour phase fluorimeter is given at the start of this chapter. The fluorescence excitation, collection and transfer optics are described and alternative methods of fluorescence excitation and collection in such systems considered. The vacuum requirements of the system are discussed and relevant aspects of vacuum technology presented. The chapter concludes with a description and an assessment of the performance of the stainless steel multi-pass emission cell used to perform the fluorescence spectral measurements of chapters 6 and 7. A gold-plated aluminium multi-pass cell that was found to be unsatisfactory is also discussed.
2.1 INTRODUCTION

A. Historical

The major aim of this project was to establish a system for obtaining SVL fluorescence spectra. It was initiated by a former PhD student of this laboratory and the system he envisaged is described in his thesis [Nott, 1975]. When I inherited the project, the mirrors for the multi-pass optical systems had been obtained and preliminary drawings for an aluminium sample compartment (or multi-pass cell) which was to provide the necessary low pressure conditions and contain the multi-pass optics were in preparation.

The system eventually developed in the course of this project represents a considerable improvement on that initially contemplated. The most beneficial changes made were the replacement of the gold-plated aluminium multi-pass cell with a stainless steel one to ensure the maintenance of stable low pressure conditions for the duration of experiments and the introduction of dual channel gated detection systems to enhance the S/N ratio and to correct for fluctuations in the excitation intensity. During the project, several originally unavailable major items of equipment were incorporated into the system to extend its capabilities. These included a tunable dye laser, a capacitance manometer, a digital charge integrator and an intelligent graphics display terminal with paper tape reader and digital plotter.

B. System overview

A frequency-doubled, pulsed, tunable, dye laser excites fluorescence from a low pressure (~ 0.02 torr) gas sample contained in a stainless steel multi-pass White/Welsh cell. Pressure in the cell is monitored by a Baratron capacitance manometer. Fluorescence is directed via three lenses...
into a Spex 1 m Czerny-Turner scanning (in stepper mode) spectrometer which isolates the fluorescence bandpass ($\Delta \lambda$) to be viewed at wavelength $\lambda$ by the photomultiplier tube (PMT). Fluorescence intensity is determined by single photon counting (SPC) or by counting the digitised charge of the PMT photocurrent using a digital current integrator (DCI). By means of a TIMER, the counting period and hence the dwell time of the spectrometer at each $\lambda$ can be either kept constant or controlled so that the same total laser intensity irradiates the sample at each $\lambda$. Each SPC or DCI signal is relayed via an appropriate DELAY to a COUNTER which is enabled only for a limited period of time ($\sim 1 \mu s$) after each laser pulse by a GATING MODULE. At the end of each counting period, the number of fluorescence signals accumulated in the COUNTER is output to paper tape (and via a D/A CONVERTER to a chart recorder) and the spectrometer is advanced, under the control of a SPEX INTERFACE MODULE, to the next wavelength interval. When the required wavelength is attained, the SPEX INTERFACE MODULE furnishes signals to reinitiate the cycle: one to reset the COUNTER that accumulates the fluorescence signals and one to restart the TIMER that determines the duration of the counting periods. The COUNTER is disabled during the "down" period of the cycle.

After the scan of the wavelength region of interest is complete, the paper tape output is read via an on-site paper tape reader and intelligent display terminal into a central computer where the data are edited, smoothed and corrected for the spectral response of the fluorimeter system, cumulative intensities are tallied and tabulated to assist in evaluating band intensities and plot files are generated. Spectra can be displayed on the terminal or plotted on an on-site plotter or on the central computer's plotters.

As well as providing a means of obtaining SVL fluorescence spectra of near-isolated large ($\sim$ benzene) polyatomic molecules, this system can
be used to monitor quantitatively the effect of collisional perturbations on the fluorescence emission and considerably facilitates data analysis and the presentation of spectra.

C. Format of discussion

Details of the design, construction and operation of the fluorimeter system are provided in chapters 2 and 3. This chapter (2) deals with the excitation and collection optics, the optics used to transfer fluorescence from the cell to the analysing monochromator and vacuum aspects of the system (in particular of the vacuum chamber housing the multi-pass optics). Chapter 3 is concerned with the excitation source, the electronics, and data handling and describes the general procedures adopted in collecting the fluorescence data.

2.2 OPTICAL ASPECTS OF FLUORIMETER

To obtain highly resolved fluorescence spectra of molecules in the low pressure vapour phase, the optical arrangement for fluorescence excitation, collection and transfer to the scanning monochromator must be extremely efficient.

2.2.1 EXCITATION OPTICS

An ingenious system of mirrors as suggested by White (1942) and slightly modified by Bernstein and Herzberg (1948) is used to enhance the absorption of excitation radiation within the volume viewed by the fluorescence collection optics. The features of this system were fully described in the original papers and Atkinson, Parmenter and Schuyler (1974) have detailed its application to SVL spectroscopy.

Figure 2.1 shows an arrangement of White excitation optics to achieve twelve traversals of the volume between the mirrors. Three
Figure 2.1. White optics for multipass excitation. Numbers refer to number of traversals.

concave spherical mirrors A, B and C of equal radius of curvature $r$ have their centres of curvature at $a$, $b$ and $c$ respectively. Collimated light (a laser beam) entering the system via the notch in mirror C (point 0) and impinging upon mirror A undergoes multiple reflections as indicated. When properly arranged, the system maintains the spot size of the incoming beam since the mirrors act to focus the beam as illustrated in figure 2.2. Positions of successive images are determined by the principle that the angle of incidence equals the angle of reflection. The normal to the surface at the point of incidence is the line to the centre of curvature of the mirror. For rays of light travelling near the optical axis of a spherical mirror of large radius of curvature these points can be located by the rule that object and image points lie on a straight line whose midpoint is at the centre of curvature, i.e. in figure 2.1, $Pa = aQ$. It is obvious that this can apply strictly only when $r \to \infty$ and $aP \to 0$. For example, it is shown in Appendix A2(i) that, according to simple geometry, if in figure 2.1 the common radius of curvature ($r$) is 100 cm, $Mc = 1.5$ cm and $aP = 2.5$ cm, then $aQ$ is 2.5009 cm. For the dimensions of the system
being described, \( r = 13 \text{ cm}, \quad M_c = 1.5 \text{ cm} \) and \( aP = 2.5 \text{ cm} \), \( aQ = 2.5548 \text{ cm} \). This departure from the ideal situation is not the limiting condition in the performance of the White optics though in general its effect should be considered as the radius of curvature is reduced and as more traversals are attempted.

**Figure 2.2.** Focusing action of mirror system. Dashed lines represent normals to mirror surfaces.

Alignment of the excitation optics proceeds as follows. Mirror C is adjusted so that a laser beam directed through the centre of the 2 mm slit between mirrors A and B is reflected in mirror C so as to retrace its path exactly. A piece of thin transparent plastic is an aid in determining this. The laser beam is then directed onto the centre of mirror A via the notch in mirror C and mirror A is adjusted to give its first reflected image just below the notch in mirror C opposite the entry point, i.e. at point 2. The beam then reflects automatically to the centre of mirror B and mirror B is adjusted so that a pattern such as that in figure 2.1 starts to form on mirror C. By turning mirror B by small amounts about an axis perpendicular to the plane of the page, the number of images on mirror C and therefore the number of traversals can be changed. The separation of the centres of curvature of mirrors A and B (points a and b in figure 2.1) determines the number of traversals in the system. If \( m \) is the number of images of the beam formed between the symmetrical notches in the top section of mirror C, then the number of traversals is \( 4m + 4 \).
The closer a is to b the greater the number of traversals up to the limit where the spot images on C just start to overlap.

With the mirror system on a common base, alignment can be accomplished initially at a location remote from the sample cell with the aid of a He-Ne laser. The procedure is not critical and alignment can be checked when the rest of system has been aligned with the dye laser. The observation port at the top of the cell (plates 2 and 4) affords a view of the mirror surfaces; thus the dye laser beam position can be adjusted to optimise alignment or to alter the absorption path length while the system is in operation.

From the above considerations it is evident that, apart from reflection losses, the limit on the number of traversals is determined by the diameter of the entering beam and its proximity to the edge of mirror C, the number of images that can be accommodated on mirror C and hence its breadth, and by how closely the mirror system approaches the ideal situation of infinite radius of curvature and coaxial rays. Thus, by focusing the incoming laser beam to a smaller diameter it is possible to achieve more traversals. This has been found to be impractical because the positioning of the necessary lens is very critical and difficult to reproduce and because of the consequent extra reflection loss. In the present cell with dimensions as given in figure 2.1, 44 traversals* can be achieved comfortably. Many more traversals have been reported for similar mirror systems of much larger size (e.g. 90 traversals for \( r = 62.5 \text{ cm} \) [White, 1942] and 144 traversals with \( r = 22 \text{ m} \) [Bernstein and Herzberg, 1948]).

Assuming no absorption loss and a reflectivity of 90% (\( R = 0.90 \)) for the aluminium coated mirrors, the intensity of a beam after 44 traversals

\[ I = I_0 \left( \frac{R}{R_0} \right)^{44} \]

* Given by \( 2(m + 1) \) where \( m \) is the number of images of the excitation beam on mirror C.
(43 reflections) of the White mirror system will be 1.1% of its intensity on entry. If $R = 0.90$ and 2% of the radiation is absorbed per transversal ($T = 0.98$), the White system alone should increase the absorption and hence the fluorescence intensity by a factor of $8.4^\star$ over that of a single pass system. If the reflection loss at each mirror could be reduced to 0.5% (i.e. $RT = 0.975$), the enhancement factor becomes 27 which illustrates the importance of having and maintaining highly reflective mirror surfaces. Multi-layer dielectric mirror coatings have reflectivities $> 99\%$ in their design wavelength interval.

The White and Welsh (section 2.2.2) multi-pass optics used in the aluminium and stainless steel cells are shown in plates 2 and 5: plate 2 shows the White excitation optics in operation. The same mirrors were employed in both cells but, before being used in the stainless steel cell, they were recoated with aluminium and a proprietary protective dielectric film by Varian Pty Ltd (Melbourne).\*\* As the photographs show, the mirrors were mounted differently in the two cells. Further details on the mountings for the optics in the stainless steel cell are given in section 2.3.4.

2.2.2 COLLECTION OPTICS

Figure 2.3 represents schematically the "split-cone" arrangement of mirrors, after the design of Welsh, used to increase the efficiency of fluorescence collection [Welsh, Cumming and Stansbury, 1951; Welsh,

\* Given by $\frac{(RT)^{44}}{RT - 1} - 1$; if $I_0$ is the intensity of the laser beam on entry to the multi-pass system, the intensity of the beam on exit from the system after $2n$ traversals is $I_0T^{2n}R^{2n-1}$, the intensity absorbed on the $(2n)$th traversal being $I_0T^{2n-1}R^{2n-1}(1-T)$.

\*\* Thanks to Mr Graham Plant.
Four concave spherical mirrors (D, E, F, G) of equal radius of curvature are positioned so that mirrors F and G have a common centre of curvature (f, g) in the middle of the slot between mirrors D and E whereas mirrors D and E are "crossed" in that their centres of curvature lie on the inside edges of the diagonally opposite mirrors G and F respectively (points d and e). F and G are equivalent to a single spherical mirror with a transparent slot. Fluorescence originating in the volume between the pairs of mirrors emerges through the slot between F and G.
The action of this mirror system in enhancing the efficiency of light collection has been explained in detail by Welsh et al. (1951, 1955), Rich and Welsh (1971a,b) and Stoicheff (1954, 1959, 1962) and only a relatively brief treatment will be given here. Consider the system operating in reverse, with a cone of light entering between mirrors F and G and filling rear mirrors D and E (figure 2.4). D and E form a series of slot images $S_1, S_1', S_2, S_2'$ etc., on the front mirrors G and F with successive reflections appearing on alternate sides of the slot and farther away from the slot till they "walk off" the edge of the mirrors. Thus the whole volume is filled with light. In the forward operation of the system, only light from points within the cone of observation (shaded region of figure 2.5) can leave the system directly via the slot without reflection. What the multiple reflection system does is to collect many cones of light that would not emerge directly and focus them on the gap between the mirrors. For any point P within the cone of observation, in addition to the direct cone, figure 2.6(a), many more indirect cones originating at P can be brought into the cone of observation after 1, 2, 3 ... reflections (figures 2.6(b), (c), (d)). Thus, the greater the number of reflections possible the greater the number of cones originating at P.

Figure 2.5. Cone of observation.
that can be collected and the greater the collection efficiency, the enhancement factor being given by 

\[ 1 + R + R^2 + R^3 + \ldots \]

where \( R \) is the reflectivity of the mirrors. Fluorescence originating from points outside the cone of observation may also be collected after reflections. Thus fluorescence generated in the volume will be fed by multiple reflections into the slot between \( F \) and \( G \) and leave the system. The number of reflections is directly related to the number of slot images that can be accommodated on front mirrors \( F \) and \( G \) which is determined by the ratio of the width of the mirrors to the slot width. Emission enhancement approaches 

\[ \frac{1}{1 - R} \]

as more slot images are accommodated on mirrors \( F \) and \( G \) and

\[
\sum_{i=0}^{n} \frac{R^i}{1 - R} = \frac{1 - R^n}{1 - R} \quad \text{for } R < 1 \text{ and as } n \to \infty
\]
therefore depends upon the reflectivity of the mirrors and the number of images contained on the front mirrors. Welsh et al. (1951) reported an enhancement factor of 7 in the visible region for aluminium coated mirrors and Stoicheff gains of 30 ($R = 99\%$ and 20 slot images) and up to 40 with high reflectance dielectric multilayer coatings [Stoicheff, 1954, 1959].

Alignment of the Welsh mirrors is undertaken with the mirror system remote from the sample cell. With the mirror pairs separated by their common radius of curvature, a laser beam is directed through the centre of the slot between mirrors D and E onto the centre of mirror G. G is adjusted to reflect the laser beam along its path of entry. F is adjusted similarly. The laser beam is then directed through the gap between F and G and the process is repeated. A quartz halogen lamp directed along the cell axis and focused on the gap between F and G is then used to illuminate D and E. With D masked, E is adjusted to give the first image of the slot between F and G on the inside of mirror F in a symmetrically vertical position. E is then masked and D is adjusted in an analogous manner. The mirrors are now aligned so that F is imaged exactly onto G and vice versa. E is then unmasked and, if alignment is complete, contiguous images of the slot between F and G should completely cover the surfaces of mirrors F and G. As alignment is approached successively more images of the slot appear on F and G.

2.2.3 FLUORESCENCE TRANSFER OPTICS

A. Introduction

A disadvantage in the use of multi-pass White/Welsh mirror systems to excite and collect fluorescence is the difficulty of optically coupling a large fraction of the fluorescence to the scanning spectrometer because the emission emanates from a relatively large volume. In gas phase Raman
spectroscopy, a similar difficulty is circumvented to some extent since the advent of the laser by confining the scattering region to a small volume \(< 10^{-7} \text{L} \) outside [e.g. Classen et al., 1969, Barrett and Weber, 1970; Hickman and Liang, 1972; Kiefer et al., 1972; Brodersen and Bendtsen, 1973; Hill and Hartley, 1974], or even inside [e.g. Neeley et al., 1972; Hickman and Liang, 1973], the laser cavity and dispensing with multi-pass collection optics. The geometry of the focused laser beam in the excitation region and the optics used for collecting the scattered light still require special attention to achieve optimum performance because the scattering volume, though small, is a spatially "extended" very intense Raman source [Barrett and Adams, 1968].

Weber (1979), in reviewing high resolution Raman spectroscopy, says that, although there are many possible arrangements of the illuminating beam within the Raman cell and of the imaging optics "there is no clear decision possible at the moment of the best possible arrangement".

Nielson (1930, 1947) determined the conditions for optimum transfer of light from an extended volume to a spectrometer using a single condensing lens but, to avoid vignetting at the collimating mirror of the spectrometer, a second collecting lens is necessary. The convenient two-lens arrangement of Callomon (1956) for efficient transfer of light from a White/Welsh cell to a spectrometer is widely used in vapour phase fluorescence systems and is described below. Shaw (1978) has reported a 40% improvement in transfer efficiency over the Callomon system with a three-lens arrangement. The latter is also described.

* Of course laser excitation sources have also been used with multi-pass Raman cells in Raman spectroscopy [e.g. Fletcher and Rayside, 1974]: dual multi-pass Raman cells designed especially for extracavity [e.g. Weber et al., 1967] and intracavity [Berger et al., 1973] operation have been reported.
The design equations of a particular coupling scheme largely determine the focal lengths and apertures of the lenses used, but in selecting the components for and assessing the performance of a scheme, several additional factors should be considered: focal lengths change with wavelength, spectrometer slit widths are varied to alter the fluorescence collection bandpass, reflection losses occur at each lens and generally increase as the focal length decreases, standard lenses are usually much cheaper than custom made ones. Ease of access of the optical components of the system and the spectrometer controls, the spatial requirements of the overall system and relative ease of adjustment (e.g. for operation in different wavelength intervals) may also be important criteria. Even at the design wavelength and slit widths, compromise in the choice of various parameters of a coupling scheme may be necessary and optimum performance only obtained upon varying the positions of lenses and inter-element distances about their calculated values.

B. Callomon (1956) coupling scheme

Figure 2.7(a) shows a vertical plane along the optic axis of this scheme and figure 2.7(b) a horizontal plane. To limit transfer loss, the aperture stops as well as the apertures of the Welsh cell/spectrometer combination are matched by focusing the rear mirrors of the Welsh cell onto the collimating mirror of the spectrometer and the exit slot of the Welsh cell onto the entrance slit of the spectrometer. The exit slot of the Welsh cell WW is at the principal focus of lens $L_2$ (focal length $f_2$) rendering light from points near the optic axis parallel. Lens $L_1$ (focal length $f_1$) refocuses this light at the entrance slit of the spectrometer SS. Thus slot WW is imaged onto slit SS, the magnification being given by $M = \frac{f_1}{f_2}$. From the geometry of ray tracing, the numerical apertures of the Welsh cell $(NA)_W$ and the spectrometer $(NA)_S$ are matched by setting
Figure 2.7(a). Callomon coupling scheme. Vertical plane along the optic axis. Dashed lines illustrate the geometry of ray tracing for determining the location of image.

Figure 2.7(b). Callomon coupling scheme. Horizontal plane along the optic axis. Dashed lines represent use of the full width of the Welsh cell rear mirrors in determining (NA)_W. See text.
the ratio of the focal lengths of lens $L_2$ and lens $L_1$ to

$$\frac{(NA)_w}{(NA)_S} = \frac{2w/f_2}{s/f_S} = \frac{f_1}{f_2} = M$$

magnification of image of WW on the spectrometer slit

$$\text{(2.1)}$$

since, from figure 2.7(b),

$$(NA)_w = z/f_2 \text{ and } (NA)_S = z/f_1$$

$$\text{(2.2)}$$

This determines the ratio of the focal lengths of the lenses and the magnification of the exit slot image on the spectrometer slit. Lens $L_2$ also forms an image, QQ, of the rear mirrors of the Welsh cell at an intermediate point between lenses $L_2$ and $L_1$ and lens $L_1$ images QQ onto the collimating mirror of the spectrometer. The separation of lens $L_1$ and $L_2$ ($q_1 + q_2$) is obtained by applying the thin lens formula twice

$$\frac{1}{f_2} = \frac{1}{f_2 + \frac{\lambda}{w}} + \frac{1}{q_2}$$

$$\text{(2.3)}$$

$$\frac{1}{f_1} = \frac{1}{q_1} + \frac{1}{f_1 + \frac{\lambda}{S}}$$

$$\text{(2.4)}$$

so that

$$q_1 + q_2 = f_1 + f_2 + f_1^2/\lambda S^2 + f_2^2/\lambda w^2$$

$$\text{(2.5)}$$

The necessary apertures ($\phi$'s) for the lenses are obtained from the geometry of ray tracing (figures 2.7(a), (b)).

Ideally, the geometry of the Welsh mirror system should be matched to the spectrometer so that the exit slot is imaged, according to the above criteria, exactly onto the spectrometer slit (widths and heights). Often, however, a compromise must be made, with either just the widths or
just the heights being matched. Matching of the other dimension is possible by using a cylindrical lens in front of the spectrometer slit.

If the fluorescence collection bandpass is to be varied the spectrometer slit width has to be changed. The choice here has been to match slot and slit widths for the maximum slit width used (vide infra).

The Callomon coupling scheme is readily adjusted to accommodate changes in focal lengths with wavelength since (i) the ratio of the focal lengths of lenses \( L_1 \) and \( L_2 \) remains constant with changes in wavelength and (ii) the positions of the lens and spectrometer can be easily changed.

There is also some flexibility in the choice of lenses (\( f \)'s and \( \phi \)'s) (only the ratio of lens focal lengths is restricted by the design equations), no special spatial requirements (e.g. necessarily large \( q_1 + q_2 \)) and no need for lenses to occupy relatively inaccessible positions.

Table 2.1 Dimensions of the fluorescence collection Welsh cell and spectrometer. Symbols from figures 2.7(a), (b).

**WELSH CELL:**

<table>
<thead>
<tr>
<th>Dimension</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Combined dimensions of rear mirrors</td>
<td>width (2w)</td>
</tr>
<tr>
<td></td>
<td>height (w)</td>
</tr>
<tr>
<td>Distance from rear mirrors to apex of cone of observation (( \xi_W ))</td>
<td>\sim 13.3 cm</td>
</tr>
<tr>
<td>Slot width (variable)</td>
<td>\geq 1 mm</td>
</tr>
<tr>
<td>Slot height</td>
<td>3 cm</td>
</tr>
<tr>
<td>Numerical aperture of Welsh cell (NA)(_W)</td>
<td>\sim 0.226</td>
</tr>
</tbody>
</table>

**SPECTROMETER:**

<table>
<thead>
<tr>
<th>Dimension</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Collimating mirror</td>
<td>width (s)</td>
</tr>
<tr>
<td></td>
<td>height (s)</td>
</tr>
<tr>
<td>Distance from slit to collimating mirror (( \xi_S ))</td>
<td>100 cm</td>
</tr>
<tr>
<td>Slit width (variable)</td>
<td>0-3 mm</td>
</tr>
<tr>
<td>Slit height (variable)</td>
<td>0-3 cm</td>
</tr>
<tr>
<td>Numerical aperture of spectrometer (NA)(_S)</td>
<td>\sim 0.051</td>
</tr>
</tbody>
</table>
From the dimensions of our Welsh cell and spectrometer given in table 2.1, a value for \( M = \frac{(NA)_W}{(NA)_S} \) of 4.2 is obtained. This would result in much overspilling of light at the spectrometer entrance slit. Since it is expected, however, that more light departs directly through the exit slot of the Welsh cell from inner regions of its rear mirrors because of the multiple reflection action of mirror system and the concentration of excitation light in the middle of the cell, a compromise* has been made in considering only half the available width of the Welsh cell rear mirrors in calculating \((NA)_W\) (i.e. the solid rather than the dashed lines in figure 2.7(b)). This results in a magnification factor of 2.2 and enables closer matching of the Welsh cell slot to the spectrometer entrance slit. Details of the Callomon coupling scheme as used here with the aluminium multi-pass cell are listed in table 2.2.

Restrictions imposed by the focal lengths of the available lenses prevented strict adherence to the scheme. For the stainless steel multi-pass cell we use a coupling scheme similar to that suggested by Shaw (1978) and described below.

Table 2.2 Parameters of Callomon coupling scheme used with aluminium multi-pass cell. Symbols from figure 2.7(a).

<table>
<thead>
<tr>
<th>Lens ( L_1 ):</th>
<th>( f_1 = 36 \text{ cm}, \phi_1 = 4 \text{ cm} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lens ( L_2 ):</td>
<td>( f_2 = 15 \text{ cm}, \phi_2 = 4 \text{ cm} )</td>
</tr>
<tr>
<td>Separation of lenses ( (q_1 + q_2) )</td>
<td>85 cm</td>
</tr>
</tbody>
</table>

C. Three-lens coupling scheme of Shaw (1978)

In an endeavour to capture more of the fluorescence radiation emerging directly without reflection from the Welsh cell, Shaw (1978) has

* There are few alternatives. For example, \( M \) cannot be reduced by increasing \((NA)_S\) or by reducing \( \phi_W \).
used an arrangement of three lenses as shown in figure 2.8. The focal length of lens $L_1$ is $f_1$. Lenses $L_1$ and $L_2$ are placed at the entrance slit of the spectrometer and the exit slot of the Welsh mirrors respectively; lens $L_0$ is at the focus of lens $L_1$. $L_2$ images the rear mirrors of the Welsh system in lens $L_0$, $L_1$ renders light from its focus at $L_0$ parallel and $L_0$ images the exit slot of the Welsh system onto the spectrometer entrance slit. Two limiting conditions which are mutually exclusive in our system, apply: (i) collecting light from the full height of the exit slot and (ii) collecting light from all the rear mirrors of the Welsh cell. The necessary design equations for this coupling scheme are similar to those for the next coupling scheme to be discussed.

![Figure 2.8. Shaw coupling scheme. wrm = Welsh cell rear mirrors; scm = spectrometer collimating mirror; $S_1$ = Welsh cell exit slot; $S_2$ = spectrometer entrance slit; L's = lenses; f's = focal lengths.](image)

**D. Modified three-lens coupling scheme of Shaw (1978)**

Figures 2.9(a), (b) and (c) show a variant of the three-lens coupling scheme described above. The difference is that lens $L_0$ is not at the focus of lens $L_1$ and lens $L_1$ images $L_0$ onto the collimating mirror
Figure 2.9. (a) Horizontal view of 3-lens coupling scheme.

(b) Vertical view of 3-lens coupling scheme. Dashed lines from full width of Welsh cell rear mirrors show overspill of light at lens $L_0$.

(c) Vertical and part of horizontal view (dotted) of 3-lens coupling scheme(ii). $(NA)_W = n \sin \theta_W$; $(NA)_S = n \sin \theta_S$
of the spectrometer. This scheme achieves the same effect as the Callomon system in that the rear mirrors of the Welsh cell are imaged onto the collimating mirror of the spectrometer and the exit slot of the Welsh cell is imaged onto the entrance slit of the spectrometer. The two limiting cases defined in section C above will be discussed separately.

(i) Collecting light from the full height of the exit slot, figures 2.9(a), (b): \( L_0 \) images \( S_2 \) onto \( S_1 \) with magnification \( M_0 \) where

\[
M_0 = \frac{x_1}{x_2} = \frac{h_1}{h_2} \frac{\text{(slot height)}}{\text{(slit height)}}
\] (2.6)

For the numerical aperture of lens \( L_0 \) to match the numerical aperture of the spectrometer

\[
\frac{\phi_0}{\phi_1} = \frac{\varnothing}{H}
\] (2.7)

The focal lengths of lenses \( L_0, L_1, L_2 \) are obtained from the thin lens formula viz.:

\[
\frac{1}{f_0} = \frac{1}{x_1} + \frac{1}{x_2}, \quad \frac{1}{f_1} = \frac{1}{h_1} + \frac{1}{H}, \quad \frac{1}{f_2} = \frac{1}{h_2} + \frac{1}{L}
\] (2.8)

The slot and slit heights are matched by this scheme and, by making it variable, the slot width can be matched to a chosen slit width.

Table 2.3 Dimensions of fluorescence system for three-lens coupling scheme. Symbols from figures 2.9(a), (b).

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( m )</td>
<td>30 mm</td>
</tr>
<tr>
<td>( w = 2m )</td>
<td>60 mm</td>
</tr>
<tr>
<td>( L )</td>
<td>160 mm</td>
</tr>
<tr>
<td>( h_2 )</td>
<td>30 mm</td>
</tr>
<tr>
<td>( w_2 )</td>
<td>&gt; 1 mm</td>
</tr>
<tr>
<td>( g )</td>
<td>102 mm</td>
</tr>
<tr>
<td>( H )</td>
<td>1030 mm</td>
</tr>
<tr>
<td>( h_1 )</td>
<td>20 mm</td>
</tr>
<tr>
<td>( w_1 )</td>
<td>0.3 mm</td>
</tr>
</tbody>
</table>
With the dimensions of our Welsh cell and spectrometer (table 2.3), the image of the rear mirrors overspills lens $L_0$ when equations 2.6-2.8 are satisfied. The width of this image is given by $i = 2m\lambda_2/L$ and the height by $i/2$. Table 2.4 case (i) gives a representative set of values with $\phi_0 = 40$ mm. An estimate of the loss at $L_0$ is given by the loss factor $LF$ which equals the ratio of the aperture of lens $L_0$ to the width of the image of the rear mirrors on $L_0$, i.e. $\phi_0/i = 2mH_2/gLh_1$.

Table 2.4 Specifications for three-lens coupling scheme for $\phi_0 = 40$ mm. Symbols from figures 2.9(a), (b) and from text.

<table>
<thead>
<tr>
<th>Case</th>
<th>$\phi_0$</th>
<th>$f_0$</th>
<th>$f_1$</th>
<th>$f_2$</th>
<th>$l_1$</th>
<th>$l_2$</th>
<th>$M$</th>
<th>$i$</th>
<th>$j$</th>
<th>$LF$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i)</td>
<td>40</td>
<td>242</td>
<td>290</td>
<td>127</td>
<td>404</td>
<td>606</td>
<td>0.67</td>
<td>227</td>
<td>20</td>
<td>5.68</td>
</tr>
<tr>
<td>(ii)</td>
<td>40</td>
<td>84</td>
<td>290</td>
<td>64</td>
<td>404</td>
<td>107</td>
<td>3.79</td>
<td>40</td>
<td>114</td>
<td>5.69</td>
</tr>
<tr>
<td>(i')</td>
<td>40</td>
<td>242</td>
<td>290</td>
<td>127</td>
<td>404</td>
<td>606</td>
<td>0.67</td>
<td>114</td>
<td>20</td>
<td>2.84</td>
</tr>
<tr>
<td>(ii')</td>
<td>40</td>
<td>140</td>
<td>290</td>
<td>91</td>
<td>404</td>
<td>213</td>
<td>1.89</td>
<td>40</td>
<td>57</td>
<td>2.84</td>
</tr>
</tbody>
</table>

(ii) Collecting light from all of the rear mirrors of the Welsh cell, figure 2.9(c): To match the numerical apertures of the Welsh cell $(NA)_W$ and the spectrometer $(NA)_S$, $(NA)_W$ and $(NA)_S$ are matched to the numerical aperture of lens $L_0$ viz.:

\[
(NA)_W = \frac{w/2}{L}, \quad (NA)_S = \frac{a/2}{H}
\]

\[
(NA)_W = \frac{\phi_0/2}{l_2/2}, \quad (NA)_S = \frac{\phi_0/2}{l_1/2}
\]

Lens $L_0$ images $S_2$ onto $S_1$ with magnification $M_0$ given by

\[
M_0 = \frac{l_1}{l_2} = \frac{wH}{gL} = 2mH/gL
\]
giving an image height \( j \) at the entrance slit of \( M_0 h_2 \). Focal lengths are obtained from the thin lens formula as in case (i). In this scheme the whole of the rear mirrors of the Welsh cell is imaged onto the collimating mirror of the spectrometer but, with the dimensions of our system, (table 2.3), the image of slot \( S_2 \) overspills the entrance slit \( S_1 \). Table 2.4 case (ii) gives a representative set of values with \( \phi_0 = 40 \text{ mm} \). The loss factor, \( LF \), applies to the image of the height of \( S_2 \) on \( S_1 \), i.e. \( j/h_1 = 2mHh_2/gLh_1 \). With a magnification of 3.8 for lens \( L_0 \), it is physically impossible to match the widths of \( S_2 \) and \( S_1 \).

It is apparent that for the same aperture for lens \( L_0 \), the loss factors by the above definitions are identical for cases (i) and (ii) and that they are large for the dimensions of our system. A compromise, identical to that made in implementing the Callomon coupling scheme, is to neglect the contribution to the light emerging from the rear mirrors of the Welsh cell made by the outer halves of the widths of these mirrors. This is based on the expectation that more light emerges from the central halves than from the outer halves of the rear mirrors (i.e. from an area of combined width \( w/4 + w/4 \) equal to the height of the rear mirrors, \( m \)).

When this restriction is applied to case (i), the values of \( f_0, f_1, f_2, \delta_1 \) and \( \delta_2 \) calculated with \( \phi_0 = 40 \text{ mm} \) (table 2.4, case (i')) are unchanged but the loss factor is reduced two-fold since only half the width of the rear mirrors is considered to contribute to the size of the image of these mirrors in lens \( L_0 \). Similarly, with only half the width of the rear mirrors contributing to \( (NA)_W \) of case (ii), the magnification of the slot \( S_2 \) on \( S_1 \) is reduced by a factor of two with equations (2.9) and (2.10) becoming

\[
(NA)_W = \frac{w/4}{L} = \frac{m/2}{L} \quad (2.12)
\]
It is then also physically possible to match the widths of the exit slot of the Welsh cell (w₂) and the spectrometer entrance slit (w₁) by setting the slot width to w₁/M. Table 2.4 case (ii') lists values calculated with φ₀ = 40 mm and w₁ = 3 mm using the new condition. If the exit slot of the Welsh cell is set at 1.6 mm, the only contribution to the loss factor, LF, is from overspilling of the image height of S₂ on S₁.

The equations defining the parameters for optimum transfer of fluorescence light from the Welsh cell to the spectrometer do not determine uniquely the focal lengths f₀, f₁, f₂ and so additional factors were considered in selecting lenses L₀, L₁, L₂. Lenses are less expensive if available commercially as standard items. Reflection losses are lower for longer focal length lenses and can be reduced by anti-reflection coating. Distances l₁ and l₂ should be such as to permit convenient location of the spectrometer and enable easy access to equipment. Focal lengths obtained from the design equations should apply to the wavelength region of the fluorescence radiation.

From the lens maker's formula

\[
\frac{1}{f} = (n - 1) \left( \frac{1}{r₁} - \frac{1}{r₂} \right)
\]

(2.14)

(where n is the refractive index at wavelength λ and r₁, r₂ are the radii of curvature of the first and second surfaces of the lens), the focal length of a lens, f, at wavelength λ can be related to its focal length, f', at wavelength λ' by the equation

\[
f' = \frac{(n - 1) f}{(n' - 1)}
\]

(2.15)

where n' is the refractive index at λ'. Table 2.5 provides a listing of the refractive index of Suprasil 1 synthetic fused silica at various wavelengths can be made by adjusting the parameters of the optical system to match the exit slot of the Welsh cell with the entrance slit of the spectrometer.
wavelengths [Melles Griot, 1975], and figure 2.10 shows the dependence of the focal length on the wavelength for a Suprasil 1 lens of focal length 100 mm at 587 nm. It is evident that the focal length changes by about 4% between 587 and 347 nm and by about 5% between 300 and 450 nm.

Table 2.5 Refractive index, n, of suprasil 1 fused silica at various wavelengths [Melles Griot, 1975]

<table>
<thead>
<tr>
<th>nm</th>
<th>n</th>
<th>nm</th>
<th>n</th>
<th>nm</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>202.54</td>
<td>1.54717</td>
<td>307.59</td>
<td>1.48575</td>
<td>435.83</td>
<td>1.46669</td>
</tr>
<tr>
<td>226.50</td>
<td>1.52299</td>
<td>334.15</td>
<td>1.47976</td>
<td>486.13</td>
<td>1.46314</td>
</tr>
<tr>
<td>248.20</td>
<td>1.50841</td>
<td>346.69</td>
<td>1.47748</td>
<td>546.07</td>
<td>1.46007</td>
</tr>
<tr>
<td>265.36</td>
<td>1.49994</td>
<td>361.17</td>
<td>1.47503</td>
<td>587.56</td>
<td>1.45847</td>
</tr>
<tr>
<td>289.36</td>
<td>1.49098</td>
<td>404.65</td>
<td>1.46961</td>
<td>656.27</td>
<td>1.45637</td>
</tr>
</tbody>
</table>

The effect of change in focal length with wavelength upon the three-lens coupling scheme is best illustrated by an example. If the focal lengths for case (ii') of table 2.4 refer to 587 nm, it is necessary to investigate how well the design conditions are satisfied at 347 nm, where the focal lengths become:

\[ f_0' = 134 \text{ mm}, \quad f_1' = 279 \text{ mm}, \quad f_2' = 88 \text{ mm}. \]

If the separations \( \xi_1 \) and \( \xi_2 \) are adjusted so that, with the focal lengths \( f_1' \) and \( f_2' \) above, the rear mirrors of the Welsh cell are imaged on lens \( L_0 \) which is imaged onto the collimating mirror of the spectrometer then \( \xi_1' = 382 \text{ mm} \) and \( \xi_2' = 195 \text{ mm} \). However, the numerical aperture combination (NA)_S, (NA)_W is no longer matched since \( \xi_1'/\xi_2' = 1.96 \) compared with the required 1.89 and lens \( L_0 \) does not image \( S_2 \) on \( S_1 \) exactly since the focal length required for this, with the above values of \( \xi_1' \) and \( \xi_2' \), would be 129 mm compared with 134 mm for \( f_0' \). Thus, although the design equations do not apply exactly, some compensation for change in focal length with wavelength can be made by adjusting separations \( \xi_1 \) and \( \xi_2 \).
Figure 2.10. Change in focal length of lens with wavelength (relative to a focal length of 100 at 587 nm).

To assist in selecting lenses L0, L1 and L2, the values of f₀, f₁, f₂, λ₁ and λ₂ were calculated for ϕ₀ values ranging from 25 mm to 50 mm in 0.5 mm increments using the equations of cases (i) and (ii') in a simple computer program. The resultant focal lengths were compared with those for commercially available standard lenses taking into account the different reference wavelengths used by various manufacturers in specifying focal lengths for "quartz" lenses. Examples of this are given in table 2.6.

Table 2.6 Reference wavelengths used by various manufacturers in specifying lens focal length

<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>Material of construction</th>
<th>Reference wavelength</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hereaus</td>
<td>Suprasil 1</td>
<td>546 nm</td>
</tr>
<tr>
<td>Melles Griot</td>
<td>Suprasil 1</td>
<td>587 nm</td>
</tr>
<tr>
<td>Micro Controle</td>
<td>Spectrosil B</td>
<td>258 nm</td>
</tr>
<tr>
<td>Oriel</td>
<td>Fused silica UV grade</td>
<td>589 nm</td>
</tr>
<tr>
<td>Spindler and Hoyer</td>
<td>Spectrosil B</td>
<td>245 nm</td>
</tr>
<tr>
<td>Unique Optical Company</td>
<td>Fused silica</td>
<td>589 nm</td>
</tr>
</tbody>
</table>
The specifications for the lenses chosen are given in table 2.7. These comply reasonably well with the requirements of case (ii') above. All three lenses are coated with high efficiency broadband anti-reflection HEBBAR™ multilayer coatings (Melles Griot), designed to minimize reflectance over the interval 400-720 nm and for use at 0° incidence, and consist of Suprasil 1 synthetic fused silica.* The manufacturers (Melles Griot) claim this to be the best grade of synthetic fused silica commercially available for ultraviolet and visible applications. It offers both the highest transmission (92%-95% from 200 to 600 nm) and very low fluorescence levels (∼0.1% that of fused natural quartz excited at 245 nm). It does not fluoresce at all at excitation wavelengths longer than 290 nm.

Table 2.7 Specifications of the lenses chosen for the three-lens coupling scheme. (f = focal length, φ = aperture). Units mm. All lenses are of Suprasil 1 synthetic fused silica.

<table>
<thead>
<tr>
<th>Lens</th>
<th>f (587 nm)</th>
<th>Type</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>L₀</td>
<td>150 ± 5%</td>
<td>50 Symmetric bi-convex</td>
<td>Melles Griot (standard lens)</td>
</tr>
<tr>
<td>L₁</td>
<td>300 ± 5%</td>
<td>25 Plano-convex</td>
<td>Melles Griot (standard lens)</td>
</tr>
<tr>
<td>L₂</td>
<td>94.5 ± 5%</td>
<td>35 Symmetric bi-convex</td>
<td>Melles Griot (custom made)</td>
</tr>
</tbody>
</table>

Spherical aberration can be minimised by suitable choice of lens shape for the particular conjugate ratio (object to image distance ratio).

* Synthetic fused silica, formed by chemical combination of silicon and oxygen, is not to be confused with fused quartz which is made from natural crystals. It is far purer than fused quartz and thus assures higher ultraviolet transmission, better homogeneity and freedom from striae or inclusions. It also has the added advantages of increased hardness and resistance to scratching and much higher resistance to radiation darkening [Melles Griot, 1975].
A symmetric bi-convex lens is suitable for the ratio 1:1 and a plano-convex lens is suitable for the image ratio 0 or $\infty$ when used with the convex side towards the parallel beam [Spindler and Hoyer, 1976].

These lenses were initially placed to give optimum transfer of fluorescence from the Welsh cell to the spectrometer (according to the conditions of case (ii')) at a wavelength of 346 nm. Separations $l_1$ and $l_2$ were set so that the combination of lenses $L_1$ and $L_2$ imaged the Welsh cell rear mirrors onto the spectrometer collimating mirror; the values obtained are listed in table 2.8.

Table 2.8 Specifications of coupling scheme used for 346 nm light. Symbols defined in figures 2.9(a), (b). Units mm.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f_0$</td>
<td>144</td>
</tr>
<tr>
<td>$f_1$</td>
<td>288</td>
</tr>
<tr>
<td>$f_2$</td>
<td>91</td>
</tr>
<tr>
<td>$l_1$</td>
<td>400</td>
</tr>
<tr>
<td>$l_2$</td>
<td>210</td>
</tr>
<tr>
<td>$\phi_0$</td>
<td>40</td>
</tr>
</tbody>
</table>

For optimum match of the numerical apertures $(NA)_W$ and $(NA)_S$, it is required that $l_1/l_2$ equal 1.89. This system gives a reasonable match with $l_1/l_2$ being 1.91. Furthermore, for exact imaging of $S_2$ on $S_1$, $f_0$ should be 138 mm using the values calculated for $l_1$ and $l_2$ compared with the actual focal length of 144 mm. Prior to aligning the Welsh mirror system its exit slot was set at 1.6 mm.

Positioning of the three lenses was not altogether straightforward. Lens $L_2$ had to be placed inside the vacuum compartment directly in front of the exit slot of the Welsh mirrors and supported by a stable mount which allowed easy adjustment of the lens position for alignment purposes. Lens $L_1$ was positioned as close as possible to the entrance slit of the spectrometer by building its support into the slit housing.
The lens system was aligned using a He-Ne laser directed through the centres of the slots of the mirror pairs of the Welsh system and into the spectrometer. Lenses \( L_1, L_2 \) and \( L_0 \) were then added successively and alignment restored after each addition. Proper functioning of the lens system was verified initially by directing light from a neon lamp into the exit slit of the spectrometer and observing the resultant image on the rear mirrors of the Welsh cell for 3 mm slit widths. Final alignment was achieved by varying \( l_1 \) and \( l_2 \) so as to maximize the fluorescence signal from the \( 12^0_{-1} \) peak of pyrimidine-\( h_{10} \) excited at 31072.7 cm\(^{-1}\), which occurs at 333 nm.

Compared with the Callomon coupling scheme, the three-lens coupling arrangement allows less flexibility in the choice of lenses, is less readily adjusted especially with one lens, \( L_2 \), being located inside the sample compartment, and presents greater construction difficulties (associated with the location and support of lenses \( L_1 \) and \( L_2 \)). Since it consists of three rather than two lenses, it is probable that it is more expensive and that its transfer efficiency is more affected by reflection losses and is more susceptible to changes in wavelength. However, it has greater potential to trap directly emerging fluorescence and Shaw (1978) reported a similar three-lens coupling scheme to be 40% more efficient than a Callomon coupling scheme. The relative efficiencies of the Callomon and our three-lens coupling schemes have not been examined in our fluorescence system.

2.2.4 FUTURE POSSIBILITIES

As indicated earlier, associated with the technique of exciting fluorescence by multi-passing a laser beam through a finite volume of sample gas is the difficulty of optically coupling a large fraction of the resultant fluorescence to the spectrometer. We have used a Welsh mirror
system and special lens coupling schemes to enhance fluorescence capture efficiency. Another possibility, akin to techniques successfully applied in vapour phase Raman spectroscopy, would be to reflect the laser beam many times through the same point, with the beam focused at the point and to collect fluorescence over a large solid angle with a lens of short focal length, focused at the point of high excitation density. Two possible schemes will be outlined. A disadvantage of such arrangements in single photon fluorescence excitation experiments would be the higher probability of non-linear absorption effects due to the high radiation densities.

(a) One simple possibility, based on the method of illumination employed by Kiefer et al. (1972) in vapour phase Raman scattering experiments to obtain a gain factor of about 20 compared to a single pass system, is illustrated in figure 2.11. The incident laser beam passes close to one edge of mirror $M_1$, comes to a focus very close to the centre
of curvature of the two concentric spherical mirrors $M_1$ and $M_2$ and hits the opposite edge of mirror $M_2$. By alternating reflections at $M_1$ and $M_2$, excitation light is concentrated at two points straddling the common centre of curvature $C$. These two points can be made to approach $C$ and each other very closely; with highly reflective mirror surfaces and many passes of the system (determined by the breadth of the mirrors and the spacing of successive images on the mirrors), excitation can be concentrated in a very small region. Fluorescence coming directly from this region is supplemented by fluorescence reflected back by the spherical mirror $M_3$, and the combined emission is gathered and transferred to the spectrometer by lenses $L_1$ and $L_2$. Mirror $M_3$ has the same radius of curvature and centre of curvature as mirrors $M_1$ and $M_2$, point $C$ is at the focus of lens $L_1$ and lens $L_2$, located at a distance equal to its focal length from the entrance slit, is chosen so that its numerical aperture equals that of the spectrometer.

(b) Several schemes for concentrating excitation light at a point as described by Hill and Hartley [Hill and Hartley, 1972; Hartley and Hill, 1972; Hill and Hartley, 1974] could also be exploited for vapour phase fluorescence work. All of these use a unique property of ellipsoidal mirrors, viz., light brought to one focus will be reflected alternately through the two foci and collapse to the major axis. The most recent of these schemes (yielding an experimental gain of 93 in a Raman scattering application), consists of an on-axis ellipsoidal mirror facing a coaxial flat-spherical mirror combination positioned at the minor axis and is illustrated in figure 2.12. The same system of fluorescence collection could be employed as indicated in figure 2.11 for case (a). The stainless steel sample compartment could readily accommodate schemes such as (a) and (b) in which excitation is concentrated within and fluorescence sampled from a very small volume.
Figure 2.12. Alternative excitation scheme according to Hill and Hartley (1974).

In systems such as (a) and (b) above, where the excitation light is concentrated at a point, it does not seem feasible to combine the technique of focusing this point onto the entrance slit of the spectrometer with the multi-reflection capture technique of Welsh and simultaneously realize the full potential of both techniques. As indicated in figures 2.13a,b,c, the difficulty arises from the impossibility of imaging fluorescence emerging as parallel rays from $s_2$ (originating at point C) and emission diverging from $s_2$ (in a cone defined by the solid angle subtended at $s_2$ by $I_w$) without loss onto the spectrometer slit $s_1$.

2.3 VACUUM ASPECTS OF FLUORIMETER SYSTEM

2.3.1 INTRODUCTION

Subsequent to its excitation to a specific distribution of rovibronic levels, a molecule may undergo nonradiative relaxation processes, some or all of which may be induced or enhanced by environmental perturbations, fluoresce or do both. Therefore, to ensure that fluorescence can be observed from the initially excited rovibronic distribution and
Figure 2.13. (a) 3-lens coupling scheme with the focus of lens $L_2$ at the centre of the Welsh cell. Optics are aligned to image rear mirrors of Welsh cell ($I_w$) into $L_0$ ($I_0$) and thence to collimator of spectrometer ($I_s$). A large portion of light emanating from the centre of the Welsh cell directly is lost.

(b) 2-lens coupling scheme with the focus of lens $L_1$ at the centre of the Welsh cell. Rear mirrors of Welsh cell ($I_w$) are imaged at QQ and thence on the spectrometer collimator ($I_s$) but slot $S_1$ is not imaged on slit $S_2$.

(c) 2-lens coupling scheme with focus of lens $L_1$ at exit slot and not at the centre of the Welsh cell. Solid lines horizontal view, dashed lines vertical view. $I_w$ is imaged at QQ and thence at $I_s$ and slot $S_2$ is imaged at slit $S_1$. 
that the effects of even weak environmental influences on this distribution can be monitored, it must be possible to keep a major fraction of the excited molecules free from the environmental perturbations that affect their excited state photophysics (i.e. maintain essentially isolated molecule conditions) for the duration of their excited state lifetimes.

The pressure and sample compartment size necessary to achieve essentially isolated molecule conditions depends on the molecule being studied.* In some cases, $S_1$ excited state nonradiative processes can be induced by very weak perturbations (in effect by long range encounters), rate constants for the processes being many times the hard sphere collision rate calculated from the kinetic theory of gases. In other cases some nonradiative processes (e.g. vibrational relaxation) are apparently only brought about by head-on collisions, rate constants being much smaller than the calculated gas kinetic rate. The following examples illustrate these points.

(a) For SO$_2$, it was found that large fluorescence cells must be used to prevent significant wall deactivation of the long lived molecules otherwise incorrect values ($< 1$) for the fluorescence quantum yield are obtained, even at pressures down to $10^{-6}$ torr, and that the fast component of the observed dual fluorescence decay is quenched with extra-ordinary efficiency [Rao et al., 1969, 1970; Horowitz and Calvert, 1972; Sidebottom et al., 1972; Calvert, 1973; Hui and Rice, 1973; Brus and McDonald, 1973, 1974]. However, Holtermann, Lee and Nanes (1980), though confirming that the fluorescence quenching of SO$_2$ was very efficient, established recently that the biexponential nature of the SO$_2$

* The classification of molecules into small, intermediate case and statistical limit classes, according to the type of photophysical behaviour they display when excited to their first excited singlet states ($S_1$), is discussed in section 7.1A; the various nonradiative decay processes that compete with fluorescence are discussed in section 5.3II.
fluorescence decay observed in the earlier experiments (lifetimes 50-60 µs and 200-600 µs) was also the result of an experimental artefact: the excitation bandpasses employed were too large and the spectral resolution of the emission was inadequate. Holtermann et al. (1980) found that the decay of rotationally resolved fluorescence from selected rovibronic levels of SO₂ is single exponential (zero-pressure lifetime 13 µs), that the rate constant for quenching this emission (the sum of rate constants for rotational, vibrational and electronic quenching) is about 8 times the gas kinetic collision rate but that, if the fluorescence emission is not resolved, the decay is double exponential with lifetimes consistent with those reported earlier. Vibrational relaxation is evident in SVL fluorescence spectra of SO₂ at ~10⁻³ torr [Kent, O’Dwyer and Shaw, 1974].

(b) The long components of the dual exponential fluorescence decays of the dicarboxyls glyoxal, methylglyoxal and biacetyl are very severely quenched, rate constants being as large as 8 times the hard sphere collision rate [Coveleskie and Yardley, 1975a,b; van der Werf, Schutten and Kommandeur, 1976; van der Werf and Kommandeur, 1976; Beyer, Zittel and Lineberger, 1975; Beyer and Lineberger, 1975; Zittel and Lineberger, 1977]. It has been necessary to employ pressures as low as 10⁻⁵ torr to study these quenching processes. Pressures of ~10⁻⁴ torr were required to obtain true resonance fluorescence spectra from selected rovibronic levels of glyoxal [Parmenter and Rordorf, 1978; Rordorf, Knight and Parmenter, 1978]. In such low pressure studies, flow systems have been used to maintain the required pressures and to avoid sample contamination by photochemical decomposition products.

(c) In larger molecules such as benzene and naphthalene, bimolecular quenching processes have to compete with significant intramolecular
nonradiative relaxation processes and collisional dependence of
fluorescence is only observed at pressures above $\sim 5 \times 10^{-3}$ torr
[Spears and Rice, 1971; Stockburger, Gattermann and Klusman, 1975].
Vibrational relaxation becomes evident in SVL spectra of these compounds
at pressures greater than $\sim 0.1$ torr.

(d) There have been several cases in which the true $S_1$ excited state
photophysical behaviour of a molecule has only been revealed when studies
were extended to the low pressure region. Biexponential decays and
lifetimes longer than the calculated radiative lifetime, characteristics
of intermediate case and small molecule limit nonradiative decay
behaviour, were reported for benzophenone in studies conducted at pressures
of $1-10^{-4}$ torr [Busch, Rentzepis and Jortner, 1971; Hochstrasser and
Wessel, 1973; Zevenhuijzen and van der Werf, 1977]; but studies of the
time-resolved emission from benzophenone excited under molecular beam
conditions, where isolated molecule conditions were ensured (average
separation between nearest neighbours $\sim 10^4$ Å), showed that benzophenone
decay fits the statistical limit classification expected for so large a
molecule: decays were single exponential with lifetimes being less than
the calculated radiative lifetime [Naaman, Lubman and Zare, 1978]. For
pyrene, a short component in its fluorescence decay was observed at $10^{-3}$
torr but not at $10^{-1}$ torr [Werkhoven, Deinum, Langelaar, Rettschnick and
van Voorst, 1971, 1975] and the case of pyrazine is described in section
7.1c.

Strictly collision free conditions have often had to be sacrificed
so that SVL fluorescence spectra of the desired S/N ratio and resolution
could be obtained and data have generally been collected at pressures of
about 0.01-0.1 torr. At these pressures, the vibrational structure of SVL
spectra is not affected by $S_1$ vibrational relaxation in molecules in which
collaboration induced $S_1$ intramolecular vibrational energy transfer is a significant nonradiative process such as benzene and aniline [Parmenter, Tang and Ware, 1976; Parmenter and Tang 1977, 1978; Chernoff and Rice, 1979b] or by electronic and perhaps rotational relaxation in molecules in which these are the dominant collision induced nonradiative decay processes such as $\sigma$-triazine and pyrimidine [Knight and Parmenter, 1979; Knight, Lawburgh and Parmenter, 1975].

The pressures at which environment-induced nonradiative processes become significant can be estimated by applying the kinetic theory of gases. The average number of hard sphere collisions experienced by a molecule per second, $Z_1$, is given by

$$Z_1 = \sqrt{2nNd^2c}$$

where $N$ is the number of molecules per cm$^3$, $d$ is the molecular diameter in cm ($\pi d^2$ is termed the collision cross section) and $c$ is the average speed in cm s$^{-1}$. If the pressure $P$ is in torr,

$$N = 9.66 \times 10^{18} \frac{P}{T}$$

where $T$ is the temperature. The average speed* is given by

$$\overline{c} = 100 \left(\frac{8RT}{\pi M}\right)^{1/2}$$

where, if $R = 8.314$ joules K$^{-1}$ mole$^{-1}$, $M$ is the molecular weight in kg mole$^{-1}$. Therefore, if a molecule has an excited state lifetime $\tau$, the number of hard sphere collisions per lifetime is $Z_1\tau$; in the time $\tau$ after excitation, 63% of the excited state molecules which are to fluoresce

* $\overline{c}$ is $(8/3\pi)^{1/2} = 0.921$ times the r.m.s. speed.
have done so.* If $S_1$ nonradiative transitions can be induced by long range encounters, the hard sphere diameter $d$ can be replaced by an effective collision diameter $d_{\text{eff}}$ in determining pressures for isolated molecule conditions. The relationship between $P$, the lifetime $\tau$, the number of collisions in an excited state lifetime $Z_{\text{eff}} \tau$, and $d_{\text{eff}}$ is illustrated in figure 2.14 for a molecule of molecular weight 150 g. The pressure required for keeping a molecule collision free for a time $t$ (i.e. only one collision on average in time $t$) is given by

$$P \leq \frac{T}{(\sqrt{2\pi}) 9.66 \times 10^{18} d_{\text{eff}}^2 / ct}$$ (2.19)

The sample compartment size required to maintain isolated molecule conditions can be estimated from the mean free path, $\lambda$, the average distance a molecule travels between effective (perturbing) encounters:

$$\lambda = \frac{c}{Z_{\text{eff}}} = (\sqrt{2\pi N d_{\text{eff}}^2})^{-1}$$ (2.20)

Application of equations (2.19) and (2.20) shows that deactivation of excited molecules by collisions with the walls of the sample compartment should be insignificant compared with collisional deactivation in the gas phase in all but the smallest of containers except for very long lived species. For example to keep a molecule with $M = 50$ g and $d_{\text{eff}} = 10$ Å isolated for 100 ns at 293 K, the pressure required would be < 0.19 torr and the average distance travelled between encounters would be $3.5 \times 10^{-3}$ cm but to keep the same molecule isolated for 100 µs would require a pressure of < $1.9 \times 10^{-4}$ torr at which $\lambda$ would be 3.5 cm.

* The proportion of excited state molecules which are to fluoresce that have done so after time $n\tau$ is given by $1 - e^{-n}$. 
Figure 2.14. The relationship between pressure, lifetime $\tau$, effective collision diameter $d_{\text{eff}}$ and the number of collisions per lifetime $Z_{\text{eff}}^{\tau}$ for a molecule of molecular weight 150 g.
Because the sample compartment is kept isolated* from the pumping system during fluorescence measurements, it must have very low leak rate \( Q \).

For a well designed and constructed vacuum chamber, the major contribution**† to the leak rate at pressures greater than \( \sim 10^{-9} \) torr should be from outgassing*** (rate \( Q_D \)). For such a chamber the pump-down time and ultimate pressure should be determined by the nature and

* Even if a flow system is used or the fluorescence cell is re-evacuated several times in the course of data collection [e.g. Gattermann and Stockburger, 1977] the same requirement applies.

** Other sources of gas in an evacuated chamber at \(< 10^{-4} \) torr (volume gas removed) are actual leakage into the chamber of gas from the surrounding atmosphere (rate \( Q_L \)), the vapour pressure of the constituent materials (rate \( Q_V \)) permeation through the chamber walls (rate \( Q_P \)). In a clean system comprised of materials of very low vapour pressure and having relatively small actual leaks, \( Q_L, Q_V \) and \( Q_P \) are insignificant compared with \( Q_D \) until pressures in the UHV region (\(< 10^{-9} \) torr) are approached. \( Q = Q_D + Q_L + Q_V + Q_P \).

† Unless otherwise stated information given in this and the following two paragraphs is compiled from Roth (1976), Wheeler (1972) and Green (1968).

*** An equilibrium is very rapidly established for any clean surface exposed to the atmosphere (e.g. the time required for monolayer formation is about 2 ns at 760 torr [Barrington, 1963]) when the number of molecules striking the surface equals the number of molecules leaving. When this equilibrium is disturbed by removal of the bulk gas, the gas which was previously adsorbed or absorbed begins to desorb. The generation of gas resulting from the desorption is known as outgassing. The previously adsorbed (physically sorbed or chemisorbed) gas is from one to several monolayers thick (7-8 monolayers of water may be sorbed during air exposure) and, in the case of metals and glasses but not polymers, makes by far the dominant contribution to \( Q_D \) until, at high enough vacuum (\(< 10^{-9} \) torr), release of sorbed gas is virtually complete. De-adsorption is similar in mechanism and effect to permeation. Even the number of molecules involved in monolayer formation is appreciable. For example, the number of molecules in a monolayer of air (average molecular diameter 3.72 Å) covering the internal surface of a 1 cm³ cubical volume is \( \sim 4 \times 10^{15} \) which would result in a pressure increase of 0.13 torr if all the molecules were released simultaneously [Barrington, 1965].
ultimate rate of its outgassing since the pressure in the chamber is
given by

\[ P = \frac{Q}{S_{\text{eff}}} \]

(2.21)

where \( S_{\text{eff}} \) is the effective pumping speed at the chamber. For example, the ultimate outgassing rate per cm\(^2\) of internal surface of an empty 5\(\times\)10 cm high 25 cm diameter cylindrical chamber would have to be

\(< 4 \times 10^{-10} \text{ torr litre cm}^{-2} \text{ s}^{-1} \) (cf. values of table 2.9) for the pressure increase in the chamber when isolated to be less than \( 5 \times 10^{-4} \) torr per hour. With an ultimate leak rate of \( 5 \times 10^{-4} \) torr/hour and \( S_{\text{eff}} = 7 \times 10^{-4} \) s\(^{-1}\), the ultimate pressure in the chamber would be \( 10^{-7} \) torr.

Outgassing is a surface phenomenon and \( Q_0 \) depends on the nature of the surface (material, pretreatment, cleanliness), its temperature and the nature of the surface coverage. Initially at multi-layer coverage, \( Q_0 \) is a function of the relatively weak gas-to-gas binding energies but, as monolayer coverage is approached, it becomes a function of the higher physiosorption and the much higher chemisorption desorption energies. After the weakly bound outer layers of the sorbed gas are stripped away, log-log graphs of \( Q_0 \) vs. time are approximately linear. The copious outgassing that occurs initially from untreated aluminium surfaces is attributed to the thick porous layers of oxide that may increase its effective surface area many hundreds of times. The very sensitive dependence of \( Q_0 \) on temperature may be used to drastically reduce the time for outgassing. It is found that bake-out results in outgassing rates which are lower by factors of \( > 10^5 \) than those produced after pumping for the same time without bake-out, the ultimate \( Q_0 \)'s being limited by de-absorption and permeation. Although the outgassing rates that apply after bake-out can be achieved in theory by prolonged pumping, in practice the time required may be prohibitively long.
Outgassing rates for various materials are usually expressed in terms of the specific outgassing rate per unit area and, because of the time dependence of $Q_D$, values for unbaked materials are usually quoted at specific times after the start of pumping. Often no distinction is made between outgassing, volatilisation and permeation. There are considerable variations in the outgassing rates determined by different workers as illustrated by the chart in Roth (1976), p. 142. Some of the literature values for the materials of interest in this work are presented in Appendix 2 (ii). Table 2.9 shows that bake-out can reduce the outgassing rates applying after several hours pumping of degreased surfaces by many orders of magnitude. Longer pumping times at the bake-out

<table>
<thead>
<tr>
<th>Material</th>
<th>Outgassing rate* (a)</th>
<th>Lowest reported outgassing rate (b)</th>
<th>Bake-out temperature(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrex</td>
<td>$10^{-8}$</td>
<td>$10^{-17}$</td>
<td>450</td>
</tr>
<tr>
<td>Stainless steel</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Copper</td>
<td>$10^{-7}$-$10^{-9}$</td>
<td>$10^{-14}$</td>
<td>400</td>
</tr>
<tr>
<td>Aluminium</td>
<td></td>
<td></td>
<td>400</td>
</tr>
<tr>
<td>Viton</td>
<td>$10^{-7}$</td>
<td>$10^{-10}$</td>
<td>200</td>
</tr>
</tbody>
</table>

* In torr litre cm$^{-2}$ s$^{-1}$

temperatures are required if milder temperatures are employed. Strausser (1968) reported that final outgassing rates for stainless steel after a prolonged 150°C bake-out ($4 \times 10^{-12}$ torr litre cm$^{-2}$ s$^{-1}$) are approximately the same as after a shorter 300°C bake-out and alleged that bake-out above 150°C is not necessary for UHV systems. The lowest outgassing rate
reported for stainless steel ($\sim 10^{-14}$ torr litre cm$^{-2}$ s$^{-1}$) was obtained when a bake-out under UHV at 1000°C followed a 12 h bake-out at 400°C (which gave a rate of $10^{-12}$ torr litre cm$^{-2}$ s$^{-1}$) [Calder and Lewin, 1967].

A report on vacuum aspects of vapour phase fluorimeter systems was compiled by the author [O'Brien, 1978]. Vacuum systems and sample compartments used by other workers in the field to achieve effectively isolated molecule conditions for different types of molecules, are surveyed in a discussion of the requirements of a generally applicable SVL fluorimeter system. The performance of the initial (aluminium) cell is assessed, alternative sample compartments considered and reasons given for the choice of a stainless steel one. A considerable amount of material* on features of vacuum technology considered relevant to the project was presented with the intention of providing a reference for subsequent workers in the laboratory. The article contains recommendations on suitable construction materials, selection of components, cleaning procedures, degassing, permanent seals (brazing and tungsten-inert-gas (TIG) welding practices), demountable seals and techniques for avoiding virtual leaks. The table of contents of the report is reproduced in Appendix 2(iii).

2.3.2 ALUMINIUM MULTI-PASS CELL

The initial multi-pass cell, based on the compact crossed-cell of Atkinson, Parmenter and Schuyler (1974), was made of aluminium and is shown in plates 1 and 2. The mirror mounts are secured to a removable and relocatable platform seated on the base plate and the space between

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* Derived in part from experience but mainly from the following sources: Roth (1966, 1976), Ophel (1973a,b; 1974), Barrington (1963), Holland, Steckelmacher and Yarwood (1974), Wheeler (1972), and Sullivan and Schultz (1966).
Plate 1
the two Viton O-rings forming the vacuum seal between the base plate and the lid is evacuated to backing pump pressure to provide a guard vacuum. The four Suprasil I quartz windows and the large (10 mm thick 160 mm clear diameter) glass viewing port were cemented to the lid with Varian Torr Seal*, a solvent free epoxy resin. The aluminium mirror mounts, platform, base plate and lid were electroplated commercially with a 3 μm layer of gold in an attempt to reduce the porosity of the aluminium [Nott, 1975] and, by preventing the formation of surface oxide, reduce the outgassing. The external diameter of the cell is 275 mm, its enclosed volume 1.8 l and its internal surface area 2.4 x 10^3 cm², 90% of which is aluminium. At the time the performance of the cell was being investigated, the pressure in the cell could only be monitored (and then only indirectly) when the brass bellows isolation valve, fitted directly to the base plate, was open.

The leak rate of the cell could only be measured indirectly [Steele, 1976]. Measurements were performed using an Alphatron ionization gauge (Varian NRC 821) and were conducted when the system had apparently attained its ultimate pressure (invariably after several days pumping) and when no leaks could be detected**. Values for the leak rate ranged from 2 x 10^-5 to 3.3 x 10^-7 torr litre s⁻¹, the average being 4 x 10^-6 torr litre s⁻¹ if the maximum and minimum values were rejected. The average and minimum leak rates correspond to pressure rises of 0.2 torr and 0.016 torr per day respectively and were considered unacceptably high for a general purpose multi-pass cell, as it was anticipated that data collection times of many hours and sample pressures of < 0.01 torr would be required.

* Outgassing rate after 1 h and 40 h pumping of 1 x 10⁻⁵ and 7.5 x 10⁻⁷ torr litres cm⁻²s⁻¹ respectively and bakeable to 120°C [Varian data sheet].

** Leak testing was carried out using helium in a fine jet as probe gas and a Dynavac cold cathode ionisation gauge as detector.
The average and minimum leak rates measured for the cell correspond to outgassing rates per cm$^2$ of internal surface of $1.7 \times 10^{-9}$ and $1.4 \times 10^{-10}$ torr litre cm$^{-2}$s$^{-1}$ which compare very favourably with those in the literature for unbaked aluminium after many hours under vacuum (table 2.9 and Appendix 2(ii)). All attempts to bake-out the cell at mild temperatures ($\sim 50^\circ C$) in order to reduce the outgassing rate resulted in cracks occurring in the Torr Seal cementing the quartz windows to the lid, presumably because of the difference in the expansion coefficients of quartz and aluminium. Surface adsorbed gas can be very easily removed by relatively short and mild baking even if the equivalent of more than 100 monolayers of gas must be driven off. Bills (1969) and Elsey (1975a) demonstrate this and the effect of different desorption energies on degassing times in model calculations of pump-down curves.

The long pumping times required to achieve ultimate pressure after the cell was vented to the atmosphere suggests that the gold plating did not reduce the outgassing of the aluminium and the experience of other workers at this university also suggests that the gold plating is porous. Nickel-plating of aluminium with coatings thicker than 8 µm has been found to be very effective in reducing the outgassing of aluminium to the extent that nickel-plated (18 µm) aluminium is comparable if not superior to stainless steel in pump-down tests [Ophel, 1974, p.28]. Some sections of the gold plating on the aluminium cell appeared to corrode suggesting that the plating was defective in these places. Successful electroplating of aluminium is generally difficult because of recalcitrance of the surface oxide and the rapidity with which the cleaned metal reoxidises. Ophel (1973b) attributes most plating failures to undercleaning or to occlusions or porous defects in the metal being treated. Field and Weill (1951) identify several difficulties in electroplating aluminium including
the presence of gas in the metal or in the plating, presence of solution retained in the pores of the metal, failure of aluminium to alloy with the plating and the presence in the deposit of pinholes which allow subsequent corrosion.

The failure to obtain lower leak rates by prolonged pumping (weeks) and the shape of the pressure vs. time curves during leak testing (cf. Roth, 1976, p.430) suggest that either undetectable leaks in the vacuum seals and/or that leaks through the chamber wall were significant. It is possible that "stringers" in aluminium act as real leakage paths just as in the case of stainless steel (Section 2.3.3). They are produced when the inclusions, gas pockets, etc. which form as the molten metal solidifies, are rolled or extruded into long fine capillaries during the metal fabrication process. Such porosity in conventional vacuum materials (stainless steel, aluminium, etc.) is "well known to electron-tube and vacuum-equipment manufacturers ... from painful direct experience" and special material processing is necessary to limit the presence of real leaks of $10^{-7}$-$10^{-12}$ torr litre s$^{-1}$ through 1 cm thick sections of metal cut perpendicular to the direction of rolling [Bills, 1969]. The aluminium block from which the cell was made was not vacuum melted or specially forged and the chamber wall was as thin as 0.5 cm in places.

The performance of the aluminium cell is consistent with the expectations of experienced workers in vacuum technology who, in general, have not recommended aluminium for high/ultra high vacuum work [e.g. Roth, 1966, p.45; Wheeler, 1972]. Stainless steel has for many years been considered the best metal for constructing vacuum vessels and components. For example, Roth (1976) contends that the only metals suitable for high vacuum work are "stainless steels, high nickel alloys and OFHC copper" and for vacuum envelopes recommends only rolled or forged metal and not
castings which can be permeable and Holland et al. (1974) advise that "to attain pressures below $7.5 \times 10^{-7}$ torr, certainly below $7.5 \times 10^{-9}$ torr, and especially if the evacuated chamber is to be isolated from the pumps subsequent to processing, bake-out of the chamber is essential ... the recommended chamber materials being either borosilicate glass or stainless steel (300 series)."

Aluminium has been considered a rather poor metal for the construction of vacuum vessels and has been largely neglected in vacuum technology mainly because it has a reputation as a porous, gas-filled material [Espe, 1966, p.324], and has relatively low strength at high temperature. It is also difficult to weld, nearly impossible to braze [Roth, 1966, pp.68-69] and it is difficult to make bakeable all-metal leak tight seals between aluminium flanges. However, as pointed out by Bills (1969) and Elsey (1975b) for example, the difficulties associated with the use of aluminium as a vacuum material are not insurmountable and because aluminium has a lower hydrogen solubility than any of the commonly used metals for vacuum system construction and a hydrogen permeability at room temperature about $10^7$ times lower than for 300 series stainless steels [Bills, 1969], it can be a useful UHV material. After the initial removal of surface adsorbed gas, outgassing of metals is controlled by the diffusion of gas, predominantly $H_2$, out of the bulk. The gas is mainly that taken up during the molten stage and entrapped when the melt solidifies but gases can also permeate into the solid metal and though permeation is relatively low at room temperature it increases exponentially with temperature and may set an upper temperature limit for baking. Since the rate of diffusion varies exponentially with temperature, the gas concentration in the bulk metal can be reduced very dramatically by high temperature (≥ 420°C) baking. For example, Calder and Lewin (1967)
calculated that, neglecting the permeation of hydrogen, a 1 h bake at 1000°C is as effective as a 24 h bake at 420°C or a 2500 h bake at 300°C in reducing the gas content of 2 mm thick stainless steel sheet such that its contribution to the outgassing rate is about $10^{-16}$ Torr litre cm$^{-2}$s$^{-1}$. Stainless steel contains large amounts of hydrogen and at room temperature the diffusion of hydrogen is fast enough to limit the pressure attainable but slow enough to prevent its concentration being significantly depleted in a reasonable time. In principle, the outgassing rate of stainless steel can be reduced to the steady state permeation rate of H$_2$ ($\sim 5 \times 10^{-17}$ Torr litre cm$^{-2}$s$^{-1}$ at room temperature) if it is pumped and baked in situ for a prolonged period of time ($\approx 24$ h) at $\sim 420$°C or if, prior to assembly, components are baked for a few hours at 1000°C in a vacuum furnace in which the hydrogen partial pressure is $\lesssim 1 \times 10^{-4}$ Torr, and then baked in situ for a short time at $\sim 250$°C to remove surface adsorbed gases [Elsey, 1975b; Weston, 1975]. However, though there is a report of an outgassing rate of $5 \times 10^{-16}$ Torr litre cm$^{-2}$s$^{-1}$ [Strausser, 1967], the lowest outgassing rate for stainless steel following the above severe degassing routines is usually $1 \times 10^{-14}$ Torr litre cm$^{-2}$s$^{-1}$ [Calder and Lewin, 1967; Elsey, 1975b]. The solubility of hydrogen (and nitrogen) in aluminium is relatively high for the melt but drops precipitously for the solid and the sharp drop is believed to account for the observed porosity and high gas content [Bills, 1969]. However, vacuum melted aluminium should have a greatly reduced porosity and a low gas content and so should only require bake-out at relatively low temperatures to remove surface adsorbed gas for the ultimate outgassing rates (determined by the H$_2$ permeation rate and hence lower than for those of stainless steel) to be attained. In practice, outgassing rates as low as the lowest outgassing rates obtained for stainless steel have been achieved for aluminium following relatively mild and short duration bake-out.
Moraw (1974) obtained outgassing rates after bake-out in vacuum at 100°C for 20 h of $4 \times 10^{-14}$ torr litre cm$^{-2}$s$^{-1}$ for aluminium and $1 \times 10^{-12}$ torr litre cm$^{-2}$s$^{-1}$ for stainless steel. This compares with typical values for stainless steel after normal (250-300°C for 24 h) bake-out of $2-3 \times 10^{-12}$ torr litre cm$^{-2}$s$^{-1}$ [Calder and Lewin, 1967; Young, 1969]. Young (1969) also found that the outgassing rate of aluminium of $4 \times 10^{-13}$ torr litre cm$^{-2}$s$^{-1}$ after only a 15 h 250°C bake compared favourably with the lowest values he observed for stainless steel, $3-4 \times 10^{-13}$ torr litre cm$^{-2}$s$^{-1}$ after prolonged baking at 450°C, i.e. different from those of Calder and Lewin (1967). With the apparatus used by Young (1969), however, it was only possible to determine outgassing rates down to about $3 \times 10^{-13}$ torr litre cm$^{-2}$s$^{-1}$ so the values reported were at the detection limits. Elsey (1975b), in reviewing published outgassing rates, observed that different workers have obtained very different outgassing rates for materials apparently the same and attributes some of the variations to differences in the method of measurement but most to differences in the state of the samples at the start of testing.

2.3.3 STAINLESS STEEL MULTI-PASS CELL

The stainless steel multi-pass cell finally developed during this project and used in the fluorescence studies of pyrimidine-d$_4$, is shown in plates 3, 4 and 5. The technical drawings for the stainless steel chamber are reproduced in Appendix A2(iv) a-e. The techniques, materials and components employed were such as to ensure high to ultra high vacuum performance but, in addition, the chamber was designed with flexibility of use in mind. It is large enough and has sufficient viewing ports for different excitation and collection optics to be employed, for fluorescence to be collected via three different windows and for absorption measurements.
Plate 3
to be performed. There are two sample admission ports and a second large port in the base plate to enable attachment of, for example, a needle valve to control the flow of material into or out of the cell.

The components and materials used in the construction and assembly of the cell and its attachments are specified in table 2.10. All demountable seals except the large one between base plate and lid are either Varian Conflat copper (OFHC) gasket seals or Cajon VCR nickel gasket seals. The viewing ports for the transmission of the exciting light are at special angles to minimise reflection losses; they needed to be trued-up after welding. Connection to the vacuum line is via a 1½" UHV valve mounted at the 1½" port near the centre of the base plate. Near the edge of the base plate is a second 1½" port positioned so that a Granville-Phillips Series 203 variable leak valve (0.4 to 10⁻¹¹ litre s⁻¹) can be connected between the cell and the vacuum line (figure 2.18). This valve could provide a means of regulating the flow of material into or out of the cell, for example, to compensate for the outgassing rate of the cell, regulate the pressure of an exposed high pressure sample, vary sample pressure at a constant rate, operate a continuous flow system, etc. Currently the port is blanked off. One of the three ports with VCR Cajon fittings in the base plate (only two are shown in the drawings of Appendix A2(iv)) is for connection of the Baratron sensor head for direct monitoring of cell pressure; the other two are for sample admission.

The seal between the lid and base plate of the cell presented some problems. Commerically available Conflat flanges were too small to accommodate the cell's optics and though Wheeler flanges of appropriate size could be obtained commercially they were considered too expensive. It was decided to use a simple seal consisting of a metal gasket compressed between flat stainless steel flanges with no grooves or steps machined in
Table 2.10 Components and materials of the multi-pass cell and its attachments

<table>
<thead>
<tr>
<th>Component</th>
<th>Specifications, features</th>
</tr>
</thead>
<tbody>
<tr>
<td>Windows for transmission of excitation light and emission</td>
<td>4 x sapphire 1&quot; clear diameter viewing port on 2 3/4&quot; OD Conflat flange; Varian 954-5035; &gt; 80% transmission from 0.25 to 5.5 μ; bakeable to 450°C; suitable for use to below 10⁻¹¹ torr.</td>
</tr>
<tr>
<td>Observation window</td>
<td>7056 glass 4&quot; clear diameter viewing port on 6&quot; OD Conflat flange; Varian 754-5128; &gt; 80% transmission from 0.32 to 2.7 μ; bakeable to 400°C; suitable for use to below 10⁻¹¹ torr.</td>
</tr>
<tr>
<td>Conflat flanges</td>
<td>2 3/4&quot; OD rotatable and non-rotatable for 1/4&quot; OD tubing (Varian 954-5071, -5072, -5076, -5077) and 6&quot; OD non-rotatable for 4&quot; OD tubing (Varian 954-5080); with matching screws, nuts and washers; OFHC copper gaskets; bakeable to 500°C; suitable for use to below 10⁻¹³ torr.</td>
</tr>
<tr>
<td>Chamber isolation valve</td>
<td>1/2&quot; Viton sealed inconel bellows UHV valve with 2 3/4&quot; rotatable Conflat flanges; Varian 951-5091; bakeable to 200°C; no leaks detectable at 1.5 x 10⁻¹⁰ torr litre s⁻¹ sensitivity through valve seat when closed; conductance 42 litre s⁻¹; suitable for use to below 10⁻¹³ torr.</td>
</tr>
<tr>
<td>Sample admission port valves</td>
<td>Nupro SS-4BK 316 stainless steel bellows valve with Kel-F gasket and stem insert and Swagelok connections; soft sealing seat suitable for repetitive dead tight shut-off operation; maximum temperature rating 150°C; no leak detectable at 3 x 10⁻⁹ torr litre s⁻¹ sensitivity through valve envelope or valve seat when closed; test ports at seals; suitable for UHV applications.</td>
</tr>
<tr>
<td>Base plate, large flange and top plate</td>
<td>Cross-forged type 304 stainless steel</td>
</tr>
<tr>
<td>Chamber walls</td>
<td>16 SWG (0.064&quot;) type 316 stainless steel</td>
</tr>
<tr>
<td>1/4&quot; fittings on base plate</td>
<td>3 x Cajon VCR type 316 stainless steel vacuum couplings - gland (SS-8-VCR-3), female nut (SS-8-VCR-1), nickel gasket (SS-8-VCR-2) male nut (SS-8-VCR-4), elbow (SS-8-VCR-9); no axial clearance needed for disassembly; no detectable leakage at 3 x 10⁻⁵ torr litre s⁻¹ sensitivity; test port at seal; maximum temperature rating 537°C; suitable for UHV applications.</td>
</tr>
<tr>
<td>Sample storage vessels</td>
<td>2 x 1/4&quot; OD tube consisting of Pyrex glass and stainless steel brazed to a 1/4&quot; VCR gland (SS-4VCR-3) to enable easy attachment and detachment to sample admission valves via Cajon VCR coupling - female nut (SS-4VCR-1), nickel gasket (SS-8-VCR-2), male nut (SS-4-VCR-4).</td>
</tr>
<tr>
<td>1/4&quot;, 1/2&quot; tubing</td>
<td>Type 316 seamless extruded so as to be suitable for use with Swagelok fittings</td>
</tr>
<tr>
<td>Line coupling Baratron to cell</td>
<td>1/4&quot; and 1/2&quot; tubing as above; Cajon VCR vacuum couplings as above plus VCR Tee (SS-8-VCR-T); Swagelok couplings; Nupro SS-8BK stainless steel bellows valves (features identical to SS-4BK valve) for 1/4&quot; tubing.</td>
</tr>
</tbody>
</table>
their surfaces, so that a variety of materials could be used as gaskets and there would be no special constraints on the size or location of the gasket. Such seals have been successful in vacuum applications [Roth, 1966, p.361]. Care has to be taken in the selection of the stainless steel from which flanges and plates are machined [Geyari, 1976]. Voids and inclusions formed in the steel during casting can result in microscopic leak paths as illustrated in figure 2.15. These potential leak paths can be avoided in stainless steel sheets and extruded tubing made from ordinary stock because the pores run in the roll direction, i.e. parallel
to the surface, and so can be stopped up in properly made weld joints. Various processing techniques can be used to restrict the size of pores in flange material. Varian uses cross-forging to break up and re-orient any leak paths in the billets used to make their larger flanges but refused to supply any of their cross-forged stock either as raw or machined material. Varian were willing to custom build the cell, as per the drawings in Appendix A2(iv) a-d, at their Palo Alto, California plant for $8750 delivery time being 3 months [Bill Judson, Varian, Sydney, 22.2.78]. Since at the time the cost and delay were considered unacceptable, it was decided to have the cell built in the mechanical workshop of the Research School of Physical Sciences, A.N.U.* Three plates (approx. 12" x 3/4") of supposedly cross-forged stainless steel** were procured from ASSAB (Sydney) to provide the material for the large rotatable flange, base plate and top plate of the cell shown in drawings a-d of Appendix A2(iv). The author only became aware that the material supplied was not cross-forged when the machinist reported that it was difficult to obtain the required surface finish for the large flat seal because of flaws in the stainless steel***. On inspection ASSAB agreed that the plates were not cross-forged and, though the cell was almost complete, it was decided that, since the commercial flanges and glands already welded to the chamber wall and the base plate could be salvaged, it would be more prudent to start again using cross-forged material to avoid the possibility of porosity problems with the initially supplied material.

* Thanks to Mr Colin Steele of the R.S.Phys.S. workshop who permitted this.

** The order specified "cross-forged type 304 stainless steel suitable for ultra-high-vacuum application".

*** It transpired that the machinist had known from the outset that the plates supplied were not cross-forged but was unaware that they were supposed to be cross-forged.
material. Modifications (Appendix A2(iv)e) were made to the original design for the base plate and large flange to better utilise the three replacement cross-forged blanks which were much larger than requested and to provide a greater possible sealing area. The flange is rotatable and the sealing surfaces were polished manually using progressively finer grades of wet and dry silicon carbide. A shallow groove was machined in the surface of the base plate to indicate the inner limit for the position of the gasket. The nuts, bolts and washers used in the main seal are of stainless steel (a type in the 300 series) so that their thermal expansion matches that of the flanges.

All permanent joints in the cell were argon-arc (tungsten-inert-gas, TIG) welded. The well-established principles of weld joint design and construction (mass equilization, relief grooves, surplus material, good fits, sharp welding edges, compatibility of materials, vacuum side or 100% penetration weld, cleanliness) explained by Sullivan and Schultz (1966) were followed where practicable. Adherence to these principles, some of which are illustrated in figure 2.16, preserves smooth internal surfaces, avoids trapped voids which could be the source of virtual leaks and reduces the chance of distortion and cracking due to thermal expansion and contraction because the least amount of current can be used, heating can be restricted to a small localised zone and release of stresses developed in the steel as the weld forms is assisted. In some of the joints the requirement of mass equalisation was not strictly observed so that sufficient material remained for faulty welds to be corrected without making major alterations to the cell. Leaking welded seals are seldom repaired by rewelding. It is usually necessary to remove them and prepare and weld fresh joints. The main cylindrical wall of the cell consists of stainless steel sheet rolled to the appropriate diameter and seam-welded. Other (1½" and 4" OD) tubing used in constructing the cell
Figure 2.16. TIG welding principles.

was purchased seam-welded. Welds cap the ends of the sheets and so stop up any potential microscopic leak paths.

Mirrors A, B, C, D, E of figures 2.1 and 2.3 were mounted on a stainless steel rotatable table with legs of adjustable length standing in locating holes in the base plate (plate 5). The gold plated aluminium carriage of the aluminium multi-pass cell was retained for the large mirror (C) but carriages for the other mirrors were of brass and enabled the lateral positions of the mirrors to be varied, as indicated in figure 2.17. This was necessary in order to obtain optimum performances from the mirror systems. All mirrors were glued to stainless steel backing plates and were spring-mounted on three adjustable screws using the point-groove-flat
principle (figure 2.17) to enable smooth variation in the orientations of the mirrors during alignment and to ensure that the positions of mirrors could be rigidly maintained whatever their orientation. To facilitate alignment of the cell's optics with the external optics and to ease construction tolerances, the cell can be rotated in its support stand and its vertical position can be varied (± 2 cm), there being sufficient freedom and flexibility in the vacuum lines connected to the cell to compensate for the adjustments. Vents to potential trapped voids (e.g. bases of screw wells) were drilled to avoid virtual leaks.

Pressure in the cell is directly monitored by the MKS Baratron capacitance manometer specified in table 2.11. For the studies described here, a non-bakeable, differential sensor head (145 BH-1) with a full range of 1 torr was used. (A bakeable (450°C) differential sensor head (94 BH-1000) with a full range of 1000 torr became available subsequently).
Capacitance manometers measure true pressure (deflection of a metal diaphragm), the pressure measured being totally independent of gas composition whereas most other gauges measure some property of the gas related to pressure (e.g. ionisation) and so the values they give depend on gas composition.

Table 2.11 Capacitance manometer specifications (MKS Baratron)

Components: MKS Electronics Unit (Type 170M-6B)

MKS Differential Sensor Head -1 torr full range, temperature regulated at 49°C (Type 145 BH-1)

MKS Analog Meter (Type 170M-26B)

(Fluke 8012A 3½ digit Digital Multimeter used in addition to display the output of the Electronics Unit digitally)

Accuracy:

\[ \pm 0.08\% \text{ at 0.1-1 torr} \]
\[ \pm 0.09\% \text{ at } 10^{-2} \text{ torr} \]
\[ \pm 0.15\% \text{ at } 10^{-3} \text{ torr} \text{ at } 25 \pm 0.5°C \]
\[ \pm 1.2\% \text{ at } 10^{-4} \text{ torr} \]
\[ \pm 10\% \text{ at } 10^{-5} \text{ torr} \]

Zero/Span temperature coefficient: \( < 3 \times 10^{-6} \text{ FS/°C} \)

Resolution and Ultimate Sensitivity: \( 2 \times 10^{-6} \text { torr} \)

Maximum temperature rating: 70°C

A CEC Primary Pressure Standard in the Electron and Ion Diffusion Laboratories, A.N.U. was used to check the calibration* of the gauge used.

* Thanks to J. Gascoigne of the Electron and Ion Diffusion Unit, Research School of Physical Sciences, A.N.U., who performed the check.
in this study for the range 0.077-1 torr. Typically, the manufacturer calibrates gauges in a similar way for the pressure range 0.1-1 torr and assumes them to be linear down to the lowest pressures which can be read (≈ 1 x 10^{-6} torr) [Van Zyl, 1976]. Loriot and Moran (1975) found that, in the pressure range 2 x 10^{-4} - 5 x 10^{-6} torr, an almost identical Baratron capacitance manometer to that used in this study displayed excellent linearity and had an accuracy of 2% plus 4 x 10^{-7} torr.

To perform absolute pressure measurements with the Baratron differential gauge, the pressure on the reference side of the diaphragm must be much lower than the pressure being measured; in order to zero the Baratron gauge, it must be possible to expose the measurement and reference sides of the diaphragm to the same pressure. The configuration used is shown in figure 2.18. A Dynavac CG2 cold cathode ionisation gauge is used to monitor the pressure on the reference side of the sensor head. Components and materials are specified in table 2.10. Readings in the lowest pressure range were markedly affected by vibrations in the connecting tubing and it appears that thermal expansion and contraction of rigid connecting tubing can result in appreciable zero drifts [MKS Baratron representative]. Therefore, the sensor head should be connected to the vacuum system and the cell via flexible couplings and not supported by its ports. Because of the electronics associated with it, the 145 BH sensor head cannot be heated to more than 70°C but it is designed to keep outgassing to a minimum [MKS Baratron].

As the Baratron sensor head and the cell are at different temperatures, T_m (49°C) and T_c (22°C) respectively, the pressure in the cell \( P_c \) may differ from that measured by the gauge \( P_m \) due to the effect of thermal transpiration. The difference depends on \( T_m, T_c \) and the ratio, \( \gamma \), of the diameter, 2a, of the connecting tubing between the cell and the sensor head to the mean free path, \( \lambda \). There are two
limiting cases (i) \( y \to \infty \) (collisions between molecules predominant over collisions with the tubing walls) where

\[
\lim_{y \to \infty} (P_m - P_c) = 0 \tag{2.22}
\]

and (ii) \( y \to 0 \) (molecular flow conditions) where

\[
\lim_{y \to 0} \left( \frac{P_c}{P_m} \right) = \left( \frac{T_c}{T_m} \right)^{\frac{1}{2}} \tag{2.23}
\]

In between these limits, the thermal transpiration ratio, \( \frac{P_c}{P_m} \), is best obtained from semiempirical equations [Dushman, 1962, p. 59] such as that proposed by Liang (1955) a more general form of which is [Miller, 1963]:

\[
1 - \left( \frac{P_c}{P_m} \right) = \left[ 0.03 y^2 + 0.245 y + \frac{1 + 2.5y}{1 + 2y} \right]^{-1} \tag{2.24}
\]

However, since the measurement error due to thermal transpiration is at the most 4.3\% \((T_m = 322 \text{ K}, T_c = 295 \text{ K in equation (2.23)) and is always less than the stated accuracy of the gauge (table 2.11) - for example, with 2a = 5 mm, equation (2.24) gives \( \frac{P_c}{P_m} \) values for pyrimidine \((d = 5.7 \text{Å})\) of 0.99997 at 1 torr and 0.957 at \( 10^{-5} \) torr - pressure measurements were not corrected for the effect of thermal transpiration.

As only modest bake-out temperatures were possible for the cell (because of its contents) and its attachments, they were scrupulously cleaned. Cleaning techniques for various materials are given in the literature [e.g. Roth, 1966, 1976]. Newly made stainless steel components were divested of the scale around their weld joints by immersions in hot \((70^\circ \text{C}) 1:1 \text{ HCl} \) combined with steel wool scouring and then subjected to the following cleaning sequence: vapour degreasing with trichloroethylene, alkaline degreasing with hot \((80^\circ \text{C}) \) solution of trisodium phosphate \((2\%)\),
Figure 2.18. Vacuum system associated with the multi-pass cell.
rinse in hot tap water, rinse in 1:1 HCl at 70°C, hot and cold tap water
rinses, rinse in demineralised water, rinse in ethanol, oven drying.
For small items a 5 ℓ beaker on a hot plate and a condenser (a coil of
copper tubing through which cooling water flowed) which was lowered 3 cm
into the beaker, constituted the vapour degreaser. Large items were
vapour degreased in a 44 gallon drum with a heating belt (1000 W,
Electro-Flex Heat Inc.) around the outside of its base and copper cooling
coils around the inside walls for the top 20 cm.

The vacuum system associated with the cell and Baratron pressure
gauge is shown in plate 6, the major components being specified in figure
2.18. On the high vacuum side of the fine pump it is stainless steel,
demountable seals being 2 3/4" OD Varian Conflat, Cajon VCR or Swagelok
permanent joints being argon-arc welded. The liquid nitrogen trapped
water cooled baffled DC 705 oil diffusion fine pumping system is extremely
clean and is capable of achieving ultimate pressures ~ 10^-8 torr [Varian].
A system, designed and developed during the project in collaboration
with David Llewellyn of the Electronics workshop, for automatically
maintaining the cryotrap in liquid nitrogen is described in Appendix A2(v).
The calculated [Guthrie and Wakerling, 1949] effective pumping speed at
the cell is 5 litres s^-1 for air under molecular flow conditions. Gold,
indium and Viton O-rings have been tried as gaskets for the main seal.
Viton O-rings proved to be the most convenient and reliable and were used
in all performance tests and experiments reported in this thesis. It
was difficult to obtain a completely leak free seal with the 0.02" cross-
section gold wire* used and indium seals** were extremely difficult to

* Ends welded together in a small oxyacetylene torch while being held
together by a pair of clamps [Hawrylak, 1967]; annealed by heating to a dull
red heat for a few minutes in a furnace at 700-800°C. Suggested surface
finish for gold wire sealing with flat flanges is 4-8 μin [Roth, 1966, p.399].
** Ends overlapped and cold welded as the flanges were brought together.
1.5 mm diameter and compressed to 15-20% of this. Melts at 156°C.
remove after use since the indium welded the stainless steel. Leak
testing was done using helium as test gas and a cold cathode gauge and
a mass spectrometer* as sensors. A hood in the form of a plastic garbage
bin proved useful in checking for smaller leaks. Subsequently, the
presence of leaks could be established by monitoring the rate of pressure
increase in the system using the Baratron pressure gauge. A small leak
in the seam weld of the main chamber wall was sealed using Edwards
silicone leak sealant. Vapour degreasing removes this sealant. With the
Viton O-ring main seal and/or the cell's internal optics in position,
the cell was only baked out at temperatures up to 150°C.

Leak rates routinely observed for the cell are \( \leq 5 \times 10^{-4} \) torr/day.
A typical pressure vs. time plot for the isolated cell is given in
figure 2.19. As the enclosed volume is 7.4 \( \ell \) and the exposed surface area
is 4600 cm\(^2\), 90\% of which is stainless steel, this leak rate corresponds
to an outgassing rate per cm\(^2\) of exposed surface of \( \leq 9 \times 10^{-12} \) torr
litre cm\(^{-2}\)s\(^{-1}\). This compares with outgassing rates reported for unbaked
stainless steel after 48 h pumping of 1-5 \( \times 10^{-11} \) torr litre cm\(^{-2}\)s\(^{-1}\)
[Barton and Govier, 1970; Elsey, 1975b]. The slightly lower value
obtained may be attributed to reabsorption and the fact that 1400 cm\(^2\)
of the exposed surface area is due to completely enclosed objects. The
pressure at the position of the CG2 ionization gauge on the reference
side of the Baratron sensor head is maintained at \( < 10^{-7} \) torr according

* Thanks to Steve Robertson and Dr Neil Daly of the Chemistry Department
for the use of a quadrupole mass spectrometer (EAI QUAD 150A).

** The system is kept evacuated when not being used but leak rates
of this magnitude are observed between experiments in which the cell is
filled with pyrimidine at pressures of up to 1 torr 12 h after evacuation
of the cell commences and without any baking. Bake-outs (\( \leq 150^\circ C \) for 18 h)
were only employed to obtain leak rates of this magnitude within 30 h of
the system being fully exposed to the atmosphere.
Figure 2.19. Increase of pressure with time within the stainless steel multi-pass cell.

to the ionization gauge (off scale). From the measured outgassing rate and the calculated pumping speed at the cell, the ultimate pressure for the cell is estimated to be $8 \times 10^{-9}$ torr.

It has been found that absorption of some samples into the Viton O-ring has a marked effect on system pressure. Figure 2.20 illustrates the effect for pyrimidine. (In contrast to this, hardly any absorption effect has been observed for cyclohexane). Consequently, an economical alternative to Viton for the main seal is desirable. Copper wire may be suitable; Beaver (1980) describes how solid copper electrical utility
wire can be used in place of gold wire O-ring type gaskets in metal vacuum systems.

Figure 2.20. Effect on the pressure in the stainless steel cell of adsorption and absorption of pyrimidine into the O-ring and onto the internal surfaces.

The leak rate of $\leq 5 \times 10^{-4}$ torr/day compares with the best leak rates found in the literature for multi-pass cells of $3 \times 10^{-4}$ torr/hour [Weisshaar, Baronavski, Cabello and Moore, 1978], $2 \times 10^{-4}$ torr/hour [van der Werf and Kommandeur, 1976] and $\leq 5 \times 10^{-4}$ torr/day [Parmenter et al., 1978]. The latter was obtained for an aluminium multi-pass cell equipped with indium seals and baked for 48 h at 70°C. With the stainless steel multi-pass cell described here, the maintenance of the required
degree of isolation for molecules in SVL studies has been relatively
easy. Spectra collection times of several days have been possible for
samples at pressures \( \sim 0.01 \) torr; measurements can be made on a single
sample for 2-3 weeks at pressures \( \sim 0.1 \) torr; and pressure dependent
fluorescence studies have been conducted at pressures down to \( 5 \times 10^{-4} \)
torr. The excellent, reliable pressure holding capability of the stain-
less steel cell and the stability afforded the enclosed optics by its
considerable mass (55 kg) are major reasons for the convenience with
which SVL fluorescence spectral measurements can be performed in this
laboratory.
CHAPTER 3

DESIGN AND CONSTRUCTION OF SVL FLUORIMETER. II. EXCITATION SOURCE, ELECTRONICS, DATA PROCESSING AND PRESENTATION

The specifications and performance characteristics of the excitation source are given and the methods used to compensate for fluctuations in excitation intensity are described. The gated photon counting and charge integration fluorescence detection systems are described and compared. The problem of pulse pileup in data collected using photon counting is examined. Computer processing and presentation of the data is described. Configurations of electronic modules that can be used to obtain data and those employed in the studies described in chapters 4, 6 and 7 are specified. Details of sample handling, excitation wavelength selection and system stability are given.
3.1 INTRODUCTION

The excitation source for SVL fluorescence spectral measurements should be sufficiently monochromatic for a single $S_1$ vibrational level to be populated exclusively, tunable so that excitation can occur to different SVL's in $S_1$ and intense enough to yield well-resolved fluorescence spectra from the low pressure vapour phase samples in reasonable time but not so intense that non-linear absorption effects become significant. The response and sensitivity of the detection and recording system should be such that each fluorescence photon issuing from the fluorescence analysing monochromator at wavelength $\lambda$ and reaching the detector will register as such (i.e. each should contribute equally to the cumulative intensity at $\lambda$). Furthermore, to obtain a true fluorescence spectrum, compensations must be made for fluctuations in excitation intensity occurring throughout the recording of the spectrum and for variation in the response of the fluorimeter system with wavelength. Data should be recorded in a form which permits their easy analysis, correction and presentation.

In the following paragraphs, details concerning the excitation source, fluorescence detection, compensation for fluctuations in excitation intensity and data handling for the fluorimeter system developed during this project are given and illustrated by reference to studies of pyrimidine-$d_4$ and -$h_4$. Information on the origin and treatment of the samples used in those studies is contained in a miscellaneous section at the end of this chapter.

3.2 EXCITATION SOURCE

The frequency doubled tunable dye laser excitation source for the fluorimeter system is specified in table 3.1. Figure 3.1 shows the optical configuration for directing the laser beam into the multi-pass cell.
Figure 3.1. Optical configuration for exciting fluorescence and monitoring the excitation intensity.
and for monitoring the excitation intensity. Table 3.1 also lists the
dyes used and the maximum possible pulse energies that could be employed
in the pyrimidine-d₄, -h₄ studies. Even if the laser was performing
optimally, the energy of the excitation pulses entering the multi-pass
cell were probably an order of magnitude less than the typical values
listed for the 310-322 nm range. Transmission losses are ∼ 50% and the
operating voltage for the nitrogen laser was 15% below that suggested*
resulting in a reduction of ∼ 20% in the intensity of the dye laser's
doubled beam. Though the maximum pulse energies occur at a repetition
rate of ∼ 15 Hz, the laser was operated at 40 Hz, with a consequent
reduction of ∼ 40% in pulse energies of the doubled beam, because the
maximum fluorescence intensity was obtained at 40 Hz. The output of the
laser dyes also diminishes appreciably with time spent in the dye cell,
pump and reservoir and not just with time in service. Tests showed that
non-linear absorption effects were insignificant in the pyrimidine studies.
While fluorescence was being generated from the 0° level of pyrimidine-d₄,
the excitation intensity was varied by inserting different combinations
of OX1 and UG2 filters in the laser beam and it was found that the
fluorescence intensity was directly proportional to the excitation
intensity. Measurement of the fundamental beam pulse energy at 640 nm
with a Molectron pyroelectric joulemeter (model J3) which became available
at the end of the pyrimidine studies indicated that the excitation pulse
energies employed for the pyrimidine studies were probably much less
than 1 µJ**.

* With a view to prolonging the life of the N₂ laser's thyratron,
storage capacitor, etc. Continuous operation for many hours was necessary
in collecting spectra. The N₂ laser has operated for a total of more than
1200 hours.

** Under the operating conditions employed for the pyrimidine studies,
the energy of the fundamental beam at the entrance window to the multi-
pass cell for a 70362 dye solution which had seen considerable service
Table 3.1 Dye laser specifications\(^a\)

<table>
<thead>
<tr>
<th>Description</th>
<th>Molectron UV400 nitrogen laser pumped DL200 dye laser with DL070 frequency doubler and DL080 intracavity linear polarizer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bandwidth</td>
<td>0.4 cm(^{-1})*</td>
</tr>
<tr>
<td>Wavelength reproducibility</td>
<td>0.01 nm</td>
</tr>
<tr>
<td>Wavelength stability</td>
<td>0.01 nm/°C</td>
</tr>
<tr>
<td>Pulse half-width</td>
<td>5-7 ns for fundamental beam, 2.5-3.5 ns for frequency doubled beam</td>
</tr>
<tr>
<td>Output pulse energy at 580 nm (fundamental)</td>
<td>340 µJ</td>
</tr>
<tr>
<td>Output pulse energy at 290 nm (doubled)</td>
<td>8 µJ</td>
</tr>
<tr>
<td>Output power at 580 nm</td>
<td>55 kW</td>
</tr>
<tr>
<td>Details for excitation of pyrimidine-d(_4), -h(_4) (310-322 nm)</td>
<td></td>
</tr>
<tr>
<td>Dyes</td>
<td>Molectron 70361 (rhodamine B) and 70362 (rhodamine B and cresyl violet perchlorate)</td>
</tr>
<tr>
<td>Fundamental pulse energy (power)</td>
<td>150-250 µJ (25-40 kW)</td>
</tr>
<tr>
<td>Frequency doubled pulse energy (power)</td>
<td>1-6 µJ (30-200 W)</td>
</tr>
</tbody>
</table>

\(^a\) From specifications and tuning curves given in Molectron brochures. Output power is derived from pulse energy by dividing by the pulse half-width.
* Others would have 0.6 cm\(^{-1}\) [Nutt, 1980].

The laser wavelength was determined using the 1 m Spex fluorescence spectrometer with the scattered laser light from the multi-pass cell as sample. When pumping sharp absorption features it is important that the wavelength of the excitation source be very stable especially when data was about 9% of the typical performance value given by Molectron. With the \(\text{N}_2\) laser operated at 20 Hz and its suggested voltage, the fundamental beam on exit from the dye laser was about 18% of Molectron's typical value. The energy of the frequency doubled beam pulses could not be determined with the joulemeter and the read-out devices available.
collection occurs over several days. In cases where the wavelength region of excitation was rescanned at the completion of data collection, the same excitation wavelength was invariably obtained. To check in greater detail the wavelength stability of the laser under conditions similar to those during data collection, the wavelength of the laser, set at the same wavelength according to the wavelength counter, was determined at moderately high resolution (spectrometer bandpass 2.4 cm\(^{-1}\)) on three different days. On each occasion the dye laser output was maximised before commencing the scan and the dye laser settings (wavelength, mirror tilts, etc.) were changed slightly between the scans to simulate the conditions of data collection*. The results of the check, given in figure 3.2, show that the excitation profile is spectrometer bandpass limited but that the peak intensities all occur within a 0.05 Å (0.4 cm\(^{-1}\)) region. Thus the wavelength stability of the dye laser appears to be completely adequate for SVL fluorescence studies**.

As Molectron claimed an amplitude stability of \(\pm 5\%\) for the dye laser, it was initially thought that constant excitation intensity could be achieved by using constant excitation times. It soon became apparent, however, that long term fluctuations in the excitation intensity were much larger than \(\pm 5\%\) and that it would be necessary to compensate for these fluctuations to obtain true fluorescence intensities. Part of the problem is that the angle of the KDP doubling crystal requires periodic adjustment to maintain maximum conversion efficiency. This may be

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* Data for long duration scans were often collected over several days, but not continuously. Scans were interrupted for \(\text{N}_2\) cylinder changes, frequently to maximise the dye laser output, overnight and even for dye changes.

** Even the relatively small differences observed can be attributed more to irreproducibilities in the spectrometer wavelength (e.g. resettability \(\pm 0.3/3\) Å according to Spex test report) than to laser wavelength instability.
Figure 3.2(a),(b),(c). Illustration of the wavelength stability of laser excitation beam. Spectrometer bandpass 2.4 cm$^{-1}$, step size 0.4 cm$^{-1}$, NSM=3, constant time (60 s) collection intervals. Cell contained 0.07 torr pyrimidine-d$_4$ (transparent to laser wavelength) to enhance scattering of laser light into the spectrometer. Peak intensities at (a) 30976.1 cm$^{-1}$, (b) 30976.3 cm$^{-1}$, (c) 30976.5 cm$^{-1}$. 
indicative of changes in the laser wavelength induced by thermal or vibrational intracavity disturbances but, as already noted, relatively crude tests of the dye laser's wavelength stability have not revealed any fluctuations outside the manufacturers specifications. Pulse-to-pulse variation in the intensity of the dye laser was observed to be about ± 5% for the fundamental beam but much higher (about ± 15%) for the frequency doubled beam. Examples of long term (hours) fluctuations in the intensity of the frequency doubled beam are shown in figure 3.5 (a), (b). Other workers have also reported poor pulse-to-pulse intensity reproducibility for dye lasers [e.g. Ritz, Wallan and Morris, 1978].

For continuous monitoring of laser intensity during data collection two systems, designated A and B, were used each relying on the integration of the photocurrent of a photomultiplier tube (PMT) detector using an Ortec 439 Digital Current Integrator (DCI) or a PMT charge integrator (PCI) built in the department for the purpose and described later. In system A the laser excitation intensity was monitored indirectly by using a 6256S PMT situated at the Pyrex observation port of the multipass cell (figure 3.1) to measure the total fluorescence intensity through an aperture to confine the emission collected to that emanating from the centre of the cell and to reduce the intensity of fluorescence reaching the PMT and a BG12 filter to cut out stray room light, the dye laser's fundamental beam* and any excitation light (≈ 320 nm) not absorbed by the Pyrex window. In system B the laser excitation intensity was monitored directly by the 6256S PMT or a 1P28 PMT which viewed the reflection of the dye laser beam from the sapphire entrance window through a series of roughened quartz plates and 1 cm diameter apertures (to diffuse and attenuate the laser beam) and 7-54 filters (to exclude the fundamental beam) (figure 3.1). The PMT's were operated near the voltages

* Use of the 7-54 filter in the dye laser to cut out the fundamental also reduced the intensity of the frequency doubled beam used for excitation by about 5-10% and so was avoided.
recommended by the manufacturers* with the anodes at ground potential and the cathodes at high negative potential as recommended for fast-pulse light applications [e.g. RCA, 1970, p.107] and were wired for current operation (no load resistor at anode). To assure proportionality between the anode current and the incident light flux, at least for the range of intensities encountered, anode currents were kept as low as consistent with accurate intensity measurement of individual laser pulses and, as recommended for pulsed operation, higher voltages and/or decoupling capacitors were used for the last few dynodes near the anode**.

* Though use of PMT's at low operating voltages is appealing when the level of light available is high since the dark current can be kept low, constant and easily balanced out, it should be avoided if linearity of the output current with light input is required. For the anode current to be proportional to the cathode illumination, the cathode and dynode currents should always be in the region of saturation. The saturation current of the dynodes is always reached under normal operating conditions even at the highest permissible luminous flux (but see a later note), but for the cathode current to be saturating throughout the working range, an adequately high electric field in the cathode (K) to first dynode (D1) region must be maintained by providing the recommended K-D1 voltage. For many PMT's this is higher than the voltage between successive dynodes (except perhaps those near the anode). To assure an adequate K-D1 voltage regardless of change in overall voltage (to control the gain), use of a Zener diode to hold the critical voltage constant is recommended by manufacturers. At low operating voltages, ohmic leakage is the predominant source of dark current and results in a steady d.c. current. As the operating voltage is increased to the normal value, gain-proportional thermionic emission of electrons becomes the main component of the dark current and, being variable, cannot be easily balanced out as can the ohmic leakage. It is usually advantageous to operate a PMT in a range where the thermionic component is dominant because in this range the S/N ratio of the tube is maximum [RCA, 1970; Philips, 1970; EMI, 1975].

** As the source of electrons for the multiplier effect is the divider current, it is necessary for it to be large compared with the dynode current if fluctuations in gain due to variation in the dynode potentials with different incident light fluxes are to be avoided. For continuous operation, the divider current (I_d) should be at least 100 times the anode current (I_a) for non-linearity due to variation of the dynode voltages to be less than 1% since the change in gain with varying cathode illumination is approximately proportional to I_a/I_d. In pulsed operations in which the average anode current is orders of magnitude less than a peak pulse current (≤ 100 ns), the fluctuations in gain can be restricted, (i.e. dynode potentials can be maintained at nearly constant values) without resorting to very high divider current by use of charge storage
Gain changes due to fatigue are also minimized by keeping the anode current as low as possible* though there were some indications of a fatigue effect for system B. The photon counting technique reduces the effect of fatigue since count rates are much less affected by changes in gain than is the output current, however, photon counting is inapplicable in this case because of distortion due to pulse pileup. To avoid gain fluctuations due to variations in the overall supply voltage the PMT's were powered by Fluke stabilised power supplies**.

Capacitors at the last few dynode stages near the anode. The divider current need only be sufficient to provide the average anode current and recharge the capacitors; the high peak currents required during the large amplitude light pulses may be supplied by the capacitors. Capacitors are not required across those dynode stages at which the peak dynode current is less than 1/10 of the average divider current. At the peak currents of pulsed operation, nonlinearity may also arise from the effects of space charge saturation in the region of the last few stages of PMT's. This may be avoided by increasing the interstage voltages near the anode by use of a tapered divider circuit. Space charge effects may be ignored in the earlier stages because of the low current densities there and intermediate stages usually operate satisfactorily from uniformly distributed voltages which can be varied over a wide range [RCA, 1970; Philips, 1970; EMI, 1975].

* Apart from being applied to the sensitivity loss that occurs when excessively large currents flow for long times, thought to be due to erosion of the dynode surfaces during periods of heavy electron bombardment, the term fatigue is also applied to the poorly understood increases or decreases in gain that occur, to differing extents, in all PMT's even at the lowest anode currents. This effect decreases with the anode current and the rate of change of gain diminishes as exposure time increases. Coates (1975) cites a case of the anode current of a PMT illuminated with light of constant intensity changing by 8% after a 15 min exposure even when operated at about 18 nA anode current. At 5 nA anode current the change was only 2% and increasing the temperature from -20°C to room temperature resulted in a 2-fold decrease in the change. Changes decreased markedly for room temperature operation after 20 min illumination, there being no apparent change for 6 nA operation after 20 min.

** The gain of a PMT is critically dependent on the supply voltage, the percentage change in gain being approximately 10 times the percentage change in supply voltage [RCA, 1970].
Linear operation of the PMT's was confirmed even for incident light levels higher than those permitted in experiments; when the excitation intensity was reduced by known amounts by inserting UG11 and OX1 filters in the frequency doubled laser beam, the output currents of systems A and B decreased by a commensurate amount. System B also showed a linear response to the fundamental beam, despite its much higher intensity, Kodak filters 11, 78A, 78C and 85 being used to attenuate the fundamental beam.

System A provides a better measure of the excitation intensity reaching the fluorescent sample than system B since slight variations in beam position (which are observed) and any shifts in wavelength from the selected wavelength of excitation will be reflected in the overall fluorescence intensity and hence the output of system A and not system B. System A was always used when collecting fluorescence spectra to ensure that excitation intensity was the same at each collection interval of the spectrum. However, when equal excitation intensities are required for different fluorescent samples (pressures, species) or at different excitation wavelengths, system A cannot be used. In obtaining data for pressure dependence studies (chapter 7), system B (with a 1P28 PMT detector) was used in compensating for fluctuations in excitation intensity. There were indications that PMT fatigue could be significant in these experiments, so to minimize the effect the PMT was conditioned prior to the start of an experiment by illuminating it for 30 min under the operating and intensity conditions to be used in the experiment and by conducting the series of intensity vs. pressures measurements constituting the experiment, as rapidly as possible. Use of a silicon photodiode instead of a PMT in system B was investigated in an attempt to avoid long term changes in gain in the detector. Operated in the photovoltaic mode (zero bias), silicon photodiodes have features desirable for this
application; they offer the possibility of better short and long term stability and linearity over a wider dynamic range than PMT's and no hysteresis or memory effects [EG and G, 1976; Kelly and Duda, 1974]. A UDT PIN 5/UV photodiode with high responsivity in the uv region and a HP 5082-4220 PIN photodiode with window removed to enhance its uv sensitivity were tried using a simple circuit (figure 3.3) in which the signal current is fed to an operational amplifier. They were unsatisfactory for long term monitoring* of the excitation beam intensity, however, because their output varied markedly with the position of the laser beam on the active area (5 x 10^-2 and 2 x 10^-3 cm^2) - they were too insensitive to permit the use of a diffuser for smoothing variations in the intensity distribution across the active area - and because the photodiode/amplifier combination used was not sufficiently stable.

The DCI produces an output signal for every 10^-10, 10^-8 or 10^-6 coulombs of charge accumulated. Use of a charge storage capacitor was sometimes necessary in the 10^-10C/pulse range to maintain linear operation.

* In photoconductive mode they afforded a good view of pulse-to-pulse intensities on a CRO.
when the maximum digitising rate (1 KHz) for this range was exceeded.*

Output of the DCI can be inhibited so the DCI was only gated on for a selected time period before and after each laser pulse to reduce the contribution of PMT dark current to the output. When the DCI is used to ensure that the excitation intensity at each collection interval is the same, its output signals are fed to an Ortec 719 Timer operated as a preset prescaler. When the number of DCI output signals accumulated in the Timer reaches a pre-set number, the Timer generates a pulse which notifies other modules that fluorescence collection at the particular spectrometer wavelength is complete. The PCI stores the charge of PMT anode pulses in a capacitor until a preselected voltage is reached whereupon it produces an output signal and the charge on the capacitor is dumped to earth. The PCI (circuit figure 3.4) has additional features to those of the PMT anode pulse integrator of Beddard and Williams (1975) upon which it was based in that, as well as providing an output pulse at the end of each integration period, the PCI enables/inhibits other modules according to its own status (by means of IC 7400 which is connected as a bistable) and is re-started by a signal supplied by the Spex control unit upon completion of the Spex wavelength advance. Whenever possible, the DCI was used in preference to the PCI when compensating for fluctuations in excitation intensity since it gave a continuous indication of excitation intensity (via a second digital output plus a counter), could be gated to minimize the contribution of the dark current and operated more reliably than the PCI.

* Linearity checks for the DCI and PCI were made by comparing the frequency and time respectively of their outputs at different range settings of the DCI and PCI, given the same anode current input.
Figure 3.4. Circuit diagram for PMT CURRENT INTEGRATOR (PCI).
Figure 3.5 illustrates the results of using constant excitation intensity collection intervals (c), ensured by use of system A with the DCI, and collection intervals of constant time (a), (b), when the same fluorescence signal is observed at each collection interval. It demonstrates the necessity of using constant excitation intensities at each collection wavelength if true fluorescence intensities are to be obtained with the fluorimeter and the effectiveness of the method used to achieve this. Correction of the resulting spectra for the spectral response of the fluorimeter is discussed in chapter 4.

3.3 FLUORESCENCE DETECTION

Photon counting has been shown both theoretically and experimentally to be superior to other detection techniques for low light levels [Niemczyk and Ettinger, 1978]. Many authors have pointed out the inherent advantages of photon counting compared with other photon measurement techniques in spectrometric systems (high sensitivity, ability to discriminate against dark current not originating at the photocathode resulting in an effective orders of magnitude reduction in the dark current, relative insensitivity to change in detector gain, system stability against drift, virtual elimination of reading error, processing of information by digital circuitry which (a) makes it less susceptible to long term drifts and 1/f noise and thus enables much longer averaging times than would be feasible with dc detection and (b) leaves it in computer compatible form) which, at low light levels, result in a higher S/N for the photon counting technique than for other methods of detection [Ingle and Crouch, 1972a; Franklin, Horlick and Malmstadt, 1969; Jones, Oliver and Pike, 1971; Oliver, 1977]. However, the general maxim applies to low light fluxes uniformly distributed in time and not necessarily to fluorescence generated by high intensity pulsed (~ 3 ns) excitation where photon counting may be inappropriate because of pulse pileup (signals
Figure 3.5. Illustration of the long term fluctuations in excitation intensity and the effectiveness of system A (see text) in compensating for the fluctuations during data collection. Monitoring the intensity of the $6a_1^0a_2^0$ band of fluorescence from the $O^0$ level of pyrimidine-$d_4$ at (a) 0.03 torr, constant time collection intervals of 8 s; (b) 0.18 torr, constant time collection intervals of 12 s; (c) 0.18 torr, constant excitation intensity collection intervals.
arriving at intervals shorter than the resolution time of the single photon counting instrumentation) even though the average intensity of emission (signals per unit time) is very low (e.g. 40 Hz). Unless dead time compensation or mathematical correction techniques are used [Ash and Piepmeier, 1971; Ingle and Crouch, 1972b], pulse pileup limits the linear range of photon counting to relatively low light levels; dc techniques are capable of measuring light levels several orders of magnitude greater than can be measured without pulse pileup in photon counting [Ingle and Crouch, 1972a]. In the fluorimeter system described, fluorescence intensities are normally measured by photon counting but a digital current integration system has been developed for use with intensities which would cause significant pileup with the photon counting technique.

For a Poisson source with a mean intensity decaying exponentially with time, the fraction of pulses missed due to pileup [Harris and Selinger, 1979] is

\[ 1 - \frac{\mu_c}{\mu_0} = 1 - \exp\left[-F \left(1 - \exp\left(-\frac{T}{\tau}\right)\right)\right] \]  

(3.1)

where \( \frac{\mu_c}{\mu_0} \) is the fraction of pulses received by the detection system that are registered (\( \mu_0 \) is the true count rate in the absence of pileup), \( F \) is the mean number of counts received by the detector per (laser) excitation flash, \( T \) is the extended dead time* of the instrument and \( \tau \) is the (single exponential) fluorescence lifetime of the sample. Equation (3.1) was not used to correct spectra obtained by photon counting for pileup but to determine the collection efficiencies at which pileup is insignificant. Use of equation (3.1) to estimate the probability of

* i.e. the dead time extends for a constant time beyond the arrival of the last signal whether or not this occurred while a signal was already being processed; apparently a straightforward analysis was only possible for a detector with an extended dead time.
pileup for the fluorimeter system described is not strictly appropriate because the excitation pulse, though very short, is not a delta pulse and the instrumental dead time is non-extended (though, ignoring other factors, the probability of pileup is lower than predicted from equation (3.1) if the dead time is non-extended). A practical constraint on the utility of equation (3.1) may be ignorance of $\tau$ for the sample at the pressure used. Curves illustrating the influence of the various parameters in equation (3.1) on the fraction of the total possible number of received fluorescence photons that are processed are given in figure 3.6. An instrumental dead time of 10 ns was assumed as a 100 MHz discriminator and a 100 MHz counter are employed in the fluorimeter system. The curves show that the probability of pileup is relatively insignificant, $\leq 5\%$, when the ratio of counts processed/s to excitation flashes/s, $F$, is less than 5% for samples with lifetimes $> 3$ ns (i.e. most species in the vapour phase) and that for short lived species ($\leq 25$ ns) the probability of pileup increases dramatically as $F$ increases beyond 10%.

When the probability of pileup for fluorescence data collected by photon counting is considered insignificant, the photon counting system of figures 3.8(a), (b), (c) can be employed. An EMI 9789QA PMT housed in a Products for Research (PR) refrigerated (-20°C) chamber (PR TE-102) and wired for photon counting (interchangeable socket with PMT base SCH-1722-01) serves as detector and photon counts are accumulated in an Ortec 770 COUNTER. On other occasions, to avoid the problem of pileup, the anode current of the 9789QA PMT wired for current mode of operation (base SCH-820-82) is integrated and digitised by the Ortec 439 DIGITAL CURRENT INTEGRATOR (DCI) already described, the digital output being accumulated in the COUNTER (figure 3.8(d)).
Figure 3.6. Plots of $\mu_c/\mu_0$, the fraction of pulses received by a detection system that are detected, vs. $F$, the mean number of counts received by the detector per excitation flash for different fluorescence lifetimes, $\tau$, and an extended dead time of 10 ns.
When dealing with low average light levels, background effects, due to PMT dark current or other sources, can be very significant. For example, the background count rate for the 9789QA PMT even when cooled to -20°C is ~5 Hz which, at the collection efficiencies necessary to ensure low pileup probability, would dwarf the number of true fluorescence counts/s in all but the strongest fluorescence peaks. Minimisation of background effects will improve the S/N ratio and so assist in distinguishing small peaks from baseline fluctuations in spectra but is also essential when fluorescence data are collected over constant excitation intensity intervals if large variations in the background contribution to the overall intensities at different collection intervals (brought about by variations in the duration of the intervals) are to be avoided.

To minimise the effect of randomly occurring noise pulses, advantage was taken of the pulsed nature of the excitation source. A simple GATING MODULE (circuit figure 3.7) was built which, upon receipt of an initiation pulse from a 1P28 PMT viewing the dye laser cavity via a light pipe, generates three variable width pulses which are used to enable the 770 COUNTER and the 439 DCI; outside the gating period the 770 and 439 modules are inhibited by the GATING MODULE. The occurrence of two of these pulses (both 0.6-14 µs) is conditional upon the GATING MODULE being enabled by an interval pulse from the TIMER or the PCI so that accumulation of fluorescence signals does not occur between collection intervals while the spectrometer is being advanced and data are being output. The other gating pulse (6-170 µs or 65-1800 µs, switch selectable) is generated after each laser pulse and serves only to gate the DCI when the DCI is being used with laser intensity monitor A or B to maintain the same excitation intensity for each fluorescence collection interval. With the configuration of PMT's, cables and modules used, fluorescence signals and gating pulses were synchronised by delaying (delay cables) the
Figure 3.7. Circuit diagram for GATING MODULE.
fluorescence signals. Further variation in the widths of the gating pulses can be achieved by simple changes in the circuit. In principle it is possible to select various sections of the fluorescence decay profile for analysis by judicious choice of delays and gating intervals, however, this has not been pursued.

Gating the 770 and 439 modules with 0.6-14 µs pulses should reduce a background count rate of 5 Hz to $1 \times 10^{-4} - 3 \times 10^{-3}$ Hz for a laser repetition rate of 40 Hz. Reductions in background of this order are observed when the spectrometer slits are closed. The background in fluorescence spectra, however, is expected to be greater than $10^{-3}$ Hz. For example, emission of wavelengths other than that selected by the analysing monochromator but scattered into the PMT will arrive at the correct time to be processed and recorded and so enhance the background. However, as can be judged from the spectra presented later, the gated detection system reduces background to an insignificant level (0-5 counts per 40 s collection interval).

3.4 SIGNAL PROCESSING and DATA HANDLING

Some of the configurations (of electronic modules) which can be used to obtain fluorescence spectra are given in figures 3.8(a)-(d), the special features of each configuration being listed in table 3.2. These configurations are designated (a), (b), (c), (d). The functions of all but two of the modules have already been described or are obvious.

The 719 TIMER has two modes of operation. Operated as a timer to give constant time collection intervals (figure 3.8(b)), it generates a stop pulse a pre-set time after it receives a start pulse. When the TIMER operates as a pre-set prescaler, the stop pulse is generated after a pre-set number of pulses has been received through the external (EXT) input.
Table 3.2 Features of configurations (a)-(d), schematised in figures 3.8(a)-(d), which can be used to obtain fluorescence spectra

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Detection system</th>
<th>Collection intervals</th>
<th>Excitation intensity monitor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>Photon counting</td>
<td>Constant excitation intensity</td>
<td>Total fluorescence intensity (system A)*; 6256S PMT with DCI</td>
</tr>
<tr>
<td>(b)</td>
<td>Photon counting</td>
<td>Constant time</td>
<td>-</td>
</tr>
<tr>
<td>(c)</td>
<td>Photon counting</td>
<td>Constant excitation intensity</td>
<td>Laser intensity (system B)*; 6256S or 1P28 PMT with DCI</td>
</tr>
<tr>
<td>(d)</td>
<td>Current integration</td>
<td>Constant excitation intensity</td>
<td>Laser intensity, (system B)*; 6256S or 1P28 PMT with PCI</td>
</tr>
</tbody>
</table>

* Excitation intensity monitoring systems A and B described in text, section 3.2.
Figure 3.8(a)-(d). Configurations which can be used to obtain fluorescence spectra. Features of each configuration are listed in table 3.2.
Figure 3.8(b)

* wired for photon counting
Spex 1704 Spectrometer
Spex 17515 Stepper Motor Control
Spex Interface Module
Facit 4023 Paper Tape Reader
Tektronix 4051 Terminal
Tektronix 4662 Plotter

EMI 6256S Ortec 439 Ortec 719 Timer
Ortec 719 Timer
Facit 4070 Paper Tape Punch
UNIVAC 1108 Computer
Calcomp 960 Plotter

IP28 PMT (Initiation)
Ortec 417 Discriminator
Gating Module
Anker Lassfolk 7023-8 Serialiser

EMI 9789QA PMT in PR TE-102 Refrigerated Chamber (Fluorescence monitor)
Ortec 436 Discriminator
Ortec 770-02 Counter
HP 580A D/A Converter
Chart Recorder

Delay

START IN
STOP OUT
READY
EXT
INTERVAL
0.2-3.5 µsec GATE

Figure 3.8(c)

* wired for photon counting
Figure 3.8(d)

* wired for charge accumulation (anode open circuit)
It is used in this mode when constant excitation intensity collection intervals are required, the external pulses being the digitised output from the 439 DCI when it is used to integrate the anode current of the PMT monitoring the excitation intensity (figures 3.8(a),(c)).

The SPEX 17515 STEPPER MOTOR CONTROL (SSMC) and SPEX INTERFACE MODULE (SIM) are used to obtain spectrometer wavelength advances of the requisite size at the completion of each fluorescence collection interval. The spectrometer can be stepped (forwards or backwards) continuously under control of the SSMC which, in its scan mode, provides pulses continually to the stepper motor. The scan rate (1 step/pulse) is determined by the step size and the frequency of pulses delivered by the SSMC. When the SSMC is operated in external mode, however, the spectrometer makes one step for each external pulse the SSMC receives, the maximum step size/pulse being only 1/12 Å. The SIM (circuit figure 3.9), designed and constructed in collaboration with Barry Machan of the Chemistry department Electronics workshop was used in conjunction with the SSMC in its external mode to enable spectrometer advances greater than 1/12 Å at the end of each fluorescence collection interval. Without impairing the normal functions of the SSMC, its continually generated pulses are rerouted to the SIM where, upon receipt of a Spex advance pulse, a train of 12, 48 or 72 of the rerouted pulses is directed to the stepper motor, according to the setting of the SIM. These settings (1 Å, 4 Å and 6 Å) refer to the spectrometer step size when the Spex scan rate is set at its maximum, 1000 Å/min. The step sizes can be subdivided by factors of 2, 5, 10, 20, 100, 200 and 500 by changing the Spex scan rate from the 1000 Å/min setting. Under SSMC-SIM control, the stepping rate is still controlled by the SSMC steps/second setting (x 12, 48 or 72). Upon completion of the spectrometer advance, the SIM generates a positive pulse
Figure 3.9. Circuit diagram for SPEX INTERFACE MODULE (SIM).
to restart the TIMER and a negative pulse to restart the PCI. START, STOP and RESET switches are also provided for the SIM. Upon completion of data collection for each fluorescence spectrum, a check was made that the number of data recorded matched exactly the number expected for the wavelength region scanned and the step size used; invariably the SSMC-SIM spectrometer advance system was found to have performed without fault.

As the statistical error in the number, \( N \), of accumulated fluorescence counts is \( \sqrt{N} \), the greater the number of counts collected per wavelength interval the less noisy appears that section of a fluorescence spectrum (figure 3.10). Boxcar integration overcomes the noisy appearance to some extent by averaging the results of a pre-selected number of collection intervals. In the fluorimeter system described, a moving-point averaging scheme** in the computer plotting program can be employed to smooth spectra. To ensure that this is done without detriment to the fluorescence structure, step sizes are arranged to be \( \leq 0.2 \) the size of the fluorescence collection bandpass***. The number of data values used to form each average in the moving-point averaging scheme is denoted by "NSM" throughout this thesis****. The remarkable effectiveness of the scheme in eliciting otherwise poorly

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* \( N \) is an estimate of a Poisson distributed quantity and the standard deviation in this estimate is \( \sqrt{N} \). If there are m estimates of a Poisson distributed quantity with individual values \( N_i \) the standard deviation in their average \( \bar{N} \) is \( \sqrt{\bar{N}}/\sqrt{m} \).

** i.e. 2 or more successive intensity values, \( Z_i \) and \( Z_{i+1} \) say, are averaged to produce \( Z_i' \) then values \( Z_{i+1}' \) and \( Z_{i+2} \) are averaged to produce \( Z_{i+1}'' \), etc.

*** "It is customary to allow at least four steps per spectral slit width" - Spex Instruction Manual.

**** e.g. a 3 point moving average \( \equiv \text{NSM} = 3 \).
Figure 3.10. Illustration of the dependence of noise on the number of counts accumulated per collection interval. Fluorescence from $0^0$ level of pyrimidine-$d_4$ at 0.14 torr. Collection bandpass 20 cm$^{-1}$, step size 3.2 cm$^{-1}$, NSM=1, constant excitation intensity collection intervals.
defined structure is illustrated in figure 3.11. Long term variations in
the excitation intensities are more readily apparent once the data have
been smoothed (figure 3.12 cf. figure 3.5).

All pyrimidine-d₄ spectra that were analysed in detail (figures 6.3,
6.12, 6.13, 6.19) were obtained using photon counting, configuration (a).
In collecting spectra a compromise has to be made between collection time,
resolution and insignificant pulse pileup. The choice here has been to
have F, the mean number of pulses received by the detection system per
excitation pulse*, approximately equal to unity for the most intense
peak of a spectrum. Pyrimidine-h₄ lifetime data have been used to obtain
a rough indication of the maximum extent of pileup in the spectra referred
to above. Pileup is greatest at the strongest peak in each spectrum.
Decay of pyrimidine-h₄ (and presumably pyrimidine-d₄) is biexponential
consisting of a short (1-3 ns) state dependent, pressure independent
component and a long (~ 1 μs at zero pressure) state and pressure dependent
component; the integrated intensity of the short component ranges from a
very minor fraction of the total intensity to the dominant fraction
depending on the level excited and the pressure [Spears and El-Manguch,
1977; Uchida, Yamazaki and Baba, 1976, 1978]. Equation (3.1) does not
apply to biexponential decays though a weighted average of $\mu_C/\mu_0$
values determined for each component separately using equation (3.1), the weight-
ing coefficients being the proportions of each component in the decay,
agrees very well with $\mu_C/\mu_0$ values calculated using the corresponding
equation to equation (3.1) for a biexponential decay (columns 13, 14 cf.
columns 9, 10 in table 3.3). The equation of Harris and Selinger (1979)
for the fraction of pulses missed due to pulse pileup in the case of a
Poisson source with mean intensity decaying as a sum of exponentials can be

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* In practice the mean number of pulses registered per excitation pulse
is used for F.
Figure 3.11. Effectiveness of curve smoothing in eliciting poorly defined structure. Higher resolution scan of "12" fluorescence band of pyrimidine-d₄ at 0.15 torr following excitation at 31158 cm⁻¹ (0⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻˓
Figure 3.12(a)-(c). Curves of figure 3.5(a)-(c) after smoothing. NSM=12.
expressed in the form

\[ 1 - \frac{\mu_c}{\mu_0} = 1 - \exp[-F(1 - \frac{\exp(-T/\tau_1)}{1 + R_{12}^{-1}} - \frac{\exp(-T/\tau_2)}{1 + R_{12}})] \]  

(3.2)

where \( R_{12} \) is the contribution of component 1 relative to that of component 2, \( \tau_1 \) and \( \tau_2 \) are lifetimes and \( \frac{\mu_c}{\mu_0} \), \( F \) and \( T \) have the same meaning as in equation (3.1). Equation (3.2) was used to calculate \( \frac{\mu_c}{\mu_0} \) at the strongest peak (apart from the excitation position) of each spectrum using values of \( R_{12} \) obtained from the results of (i) lifetime and (ii) quantum yield studies; the \( R_{12} \) (i) values are probably better because lifetime data are usually more reliable than quantum yield data. Results are given in table 3.3 (columns 9 and 10). Because the instrumental dead time is non-extended and because the lifetimes of pyrimidine-d_4 are expected to be larger than those of pyrimidine-h_4 due to the normal isotope effect [Avouris, Gelbart and El-Sayed, 1977], these results probably represent overestimates of pileup in the strongest peaks. They do, however, indicate that pileup could only be significant for the strongest peaks of the 6a\(^1\) and 12\(^1\) spectra. The effect of pileup diminishes rapidly as \( F \) decreases: at \( F \) values one-half those in table 3.3, \( \frac{\mu_c}{\mu_0} \) (i) values (i.e. \( D(i) \) values in table 3.3) are restored to 0.97, 0.88 and 0.80.

Charge integration fluorescence detection, configuration (d), was not as suitable as photon counting for obtaining fluorescence spectra of adequate resolution. The DCI permits long collection times (as it constantly digitises incoming charge) and allows pulse pileup* to be

* i.e. if the PMT generates the same average charge per incident photon for closely arriving photons. A charge storage capacitor on the input of the DCI was used to prevent losses due to the maximum digitising rate of the DCI being momentarily exceeded for closely arriving anode pulses.
Table 3.3 Fraction of counts reaching the detection system that are registered for the strongest peaks in the spectra analysed in chapter 6

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>Figure</th>
<th>$P^a$</th>
<th>$F^b$</th>
<th>$\tau_L^c(\mu s)$</th>
<th>$\tau_S^c(ns)$</th>
<th>Proportion, $R_L^d$</th>
<th>$D^e$ from eqn (3.2)</th>
<th>Wt. Mean$^g$ of $D_L$ and $D_S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0$^o$</td>
<td>6.3</td>
<td>0.017</td>
<td>1.1</td>
<td>0.43</td>
<td>2.7</td>
<td>28 (i) 13 (ii)</td>
<td>0.94 (i) 0.91 (ii)</td>
<td>0.98 0.35 0.95 0.93</td>
</tr>
<tr>
<td>6$^a_1$</td>
<td>6.12</td>
<td>0.06</td>
<td>0.8</td>
<td>0.14</td>
<td>1.6</td>
<td>2.6 (i) 1.3 (ii)</td>
<td>0.78 (i) 0.70 (ii)</td>
<td>0.95 0.46 0.82 0.74</td>
</tr>
<tr>
<td>12$^l$</td>
<td>6.19</td>
<td>0.07</td>
<td>0.9</td>
<td>0.14</td>
<td>1.3</td>
<td>1.3 (i) 0.8 (ii)</td>
<td>0.65 (i) 0.59 (ii)</td>
<td>0.94 0.41 0.70 0.65</td>
</tr>
</tbody>
</table>

Notes:

- $a$ pressure in torr
- $b$ mean number of counts registered/excitation pulse at the position of maximum intensity for the spectrum
- $c$ lifetimes from Spears and El-Manguch (1977); $L \equiv$ long component, $S \equiv$ short component
- $d$ Proportion of long component to short component from
  
  (i) lifetime data; $R_L = (A_L \tau_L)/(A_S \tau_S)$ where $A_L$, $A_S$ are the pre-exponential factors
  
  (ii) quantum yield data; $R_L = \phi_L(P)/\phi_S$ where $\phi_L(P)$ was obtained from $\phi_L(P) = \phi_L(0)/(1 + 9.3 \times 10^6 \tau_L(0)P)$ [Uchida et al. 1978]
- $e$ $D = \mu_c/\mu_0$; calculated using equation for biexponential decays, equation (3.2)
- $f$ $\mu_c/\mu_0$ values for long and short components calculated using equation (3.1)
- $g$ Weighted mean obtained using $R_L/(1 + R_L)$ and $1/(1 + R_L)$ as weighting coefficients
avoided but does not afford as high sensitivity or as effective noise reduction through gating as the photon counting system. Gating of the DCI acts on the output not the input and this is unsatisfactory for intensities of about 1 photon/excitation pulse at most and an average charge/incident photon* approximately equal to the minimum charge/digitised output of the DCI**. Attempts to reduce noise by gating the PMT input pulses to the DCI using electronic switches in standard configurations were unsuccessful since switching transients contributed a significant amount of charge to the DCI. The charge integration detection system of configuration (d) was used to obtain the fluorescence spectrum from the 12\(^1\) level of pyrimidine-d\(_4\) shown in figure 3.13(a). This is to be compared with the spectrum in figure 3.13(b) recorded under identical conditions but using photon counting for fluorescence detection. The long component of pyrimidine-d\(_4\) fluorescence is expected to be almost completely quenched at the sample pressure employed (0.17 torr pyrimidine-d\(_4\) + 0.17 torr pyrimidine-h\(_4\)) and the results of pileup calculations (table 3.3) suggest that under these conditions the intensities of the stronger bands in the spectrum collected using photon counting (i.e. figure 3.13(b)) may be significantly reduced due to pulse pileup, much more so than for any of the cases considered in table 3.3. However, comparison of the relative intensity distributions in figures 3.13(a) and (b), especially in the region 32000-29500 cm\(^{-1}\), does not reveal any systematic distortions in the intensities of bands in the spectrum collected using photon counting which should be attributed to

---

* Estimated from the shape of the 9789QA PMT anode pulse on a 1GHz HP 1810A Sampling CRO when the PMT viewed a light flux \(\sim 5000\) photons/s.

** i.e. a digitised output may fall due during an inhibit period even though most of the accumulated charge resulted from a photon being incident on the PMT and not from dark current.
Figure 3.13. Fluorescence spectra from the $12^1$ level of pyrimidine-$d_4$ at 0.17 torr with 0.17 torr of added pyrimidine-$h_4$. Collection bandpass 22-11 cm$^{-1}$, step size 3.5-2 cm$^{-1}$, NSM=5, 3.5 µs gating pulses, constant excitation intensity collection intervals of 20-25 s. Collected using (a) charge integration, (b) photon counting fluorescence detection, i.e. configurations (d) and (a) respectively of figure 3.8.
Figure 3.13(b)

Relative Intensity

Wavenumber (cm⁻¹)
pulse pileup*, suggesting that pileup distortion of intensities in the spectra analysed in detail in chapter 6 is insignificant. Comparison of figures 3 (a) and (b) also illustrates the much greater sensitivity and more effective background reduction for the photon counting system than for the charge integration system.

The configurations, designated C1 and C2, which yielded the most consistent results in the studies of fluorescence quenching (chapter 7) were basically configurations (c) and (d) of figure 3.8. A 1P28 PMT (cf. 6256S PMT in figure 3.8 (c), (d)) was used to monitor the laser intensity directly. In configuration C1 the spectrometer was used to isolate and not scan a fluorescence band (i.e. spectrometer wavelength held fixed) and the intensity of that band was measured at various sample pressures using photon counting and constant excitation intensity collection intervals in an arrangement similar to that of figure 3.8 (c). The spectrometer bandpass was kept large (≈ 50 cm⁻¹) to reduce spurious effects due to rotational relaxation [Beyer, Zittel and Lineberger, 1975] and consequently minimum slit heights had to be used to avoid pulse pileup over the range of pressures employed. In configuration C2, the total fluorescence intensity, determined by charge integration of the output of the 6256S PMT at the observation window of the multi-pass cell, was monitored as a function of sample pressure using constant excitation intensity collection intervals in an arrangement similar to that of figure 3.8 (d)**. A variation of configuration C2 was to employ constant time collection intervals and normalise the total fluorescence intensities accumulated during the collection intervals to a constant excitation

* The difference in the background distributions for the two spectra suggests that constant excitation intensity collection intervals were not maintained as well as hoped during the recording.

** With the 6256S PMT replaced by a 1P28 PMT and the 9789QA PMT replaced by the 6256S total fluorescence intensity monitor PMT.
intensity by using the DCI in conjunction with the 1P28 PMT laser intensity monitor to measure the excitation intensity before and after each collection interval.

Each series of fluorescence intensity vs. pressure measurements was performed as quickly as possible (hence fluorescence bands were not scanned) to keep changes in the gain of the 1P28 PMT monitoring the excitation intensity and variations in sample pressure minimal and, at each pressure, data were obtained using both configurations C1 and C2. A configuration similar to that in figure 3.8(d) in which the intensity of a fluorescence band isolated by the spectrometer is monitored using the 9789QA PMT in charge integration mode was not used in the pressure dependence studies.

3.5 MISCELLANEOUS

(a) Samples

Pyrimidine-d$_4$ was prepared from tetrachloropyrimidine (Aldrich Chemical Co.) by Merrick Puza of the Research School of Chemistry, A.N.U. A mass spectrum of the sample used indicated 80% pyrimidine-d$_4$, 10% chloro-, 5% dichloro- and 5% trichloropyrimidine. The impurities did not contribute anything noticeable to the absorption or fluorescence spectra of the sample.

Pyrimidine-h$_4$ (Fluka AG purum) and cyclohexane (Matheson Coleman and Bell, spectroquality) were used as received.

(b) Degassing

All samples were degassed in 10-15 freeze-pump-thaw cycles using liquid nitrogen as coolant in the initial stages and then dry ice. The extent of degassing was checked periodically during the procedure by measuring the pressure rise in the cell over a 2-4 minute interval when
the valve to the vial containing the sample being degassed was opened at the freeze stage of a cycle. Degassing was considered complete when, during such a check, there was no measurable change in the zero pressure reading for the empty cell with the pressure gauge at its most sensitive setting. Apart from being degassed upon initial introduction to the vials, samples were degassed immediately before use in the multi-pass cell.

(c) Sample admission to the multi-pass cell

Controlled admission of sample to the multi-pass cell was facilitated by placing one of a series of slush baths (ice-water (0°C), carbon tetrachloride (-23), 1,2-dichloroethane (-35), chloroform (-64), acetone (-78), [Gunning and Strausz, 1971]) around the sample vial. Usually the cell was filled to a higher pressure than that required and/or was conditioned with a preliminary fill of sample at the required pressure to offset the effect of adsorption and absorption of sample onto the internal surfaces and into the O-ring seal of the multi-pass cell.

(d) Selection of excitation wavelength

The excitation wavelength was selected initially by setting the spectrometer wavelength at the calculated position and maximising the signal from the PMT observing the throughput of the spectrometer by varying the laser wavelength. The procedure was repeated using progressively narrower slit widths. The optimum excitation wavelength for a particular absorption band was achieved by varying the laser wavelength so as to maximise the total fluorescence intensity observed by the 6256S PMT at the observation port of the multi-pass cell and the signal from the PMT viewing the output from the spectrometer set at the expected position of a fluorescence band and used with large slit widths.
(e) System stability

The electronic modules were powered by Ortec NIM bins and the PMT's by Fluke stabilised power supplies to maintain stability in the electronics of the system.

The laser, spectrometer and the optical rails, upon which the optical components (mirrors, lenses) external to the multi-pass cell are mounted, sit on a common $\frac{1}{2}$" thick steel plate which in turn rests on a $\frac{1}{2}$" thick rubber cushion on the bench top. Use of an Aerotech beam director makes alignment of the excitation beam with the excitation optics of the multi-pass cell easy and its rigidity assists in maintaining alignment almost indefinitely. Alignment of the excitation optics was checked periodically by inspection of the images of the fundamental laser beam on the excitation mirrors. Alignment of the cell with the fluorescence transfer optics and the spectrometer was checked frequently by directing a He-Ne laser beam through the gaps between the fluorescence collection mirror pairs and onto a screen placed over the collimating mirror of the spectrometer. The large mass of the cell (~ 55 kg) assists in maintaining alignment.

It was necessary to use a dual stage regulator on the $N_2$ gas cylinder supplying $N_2$ to the $N_2$ laser in order to avoid variation in $N_2$ pressure of the laser as the cylinder pressure changed which occurs if ordinary regulators are used necessitating constant monitoring and adjustment of $N_2$ pressure.
CHAPTER 4

TRANSFORMATION OF RECORDED FLUORESCENCE DATA TO TRUE FLUORESCENCE SPECTRA ON A WAVENUMBER SCALE

For the assessment of Franck-Condon factors and vibronic coupling mechanisms using SVL fluorescence spectra, it is important that the relative intensity of vibrational bands within such spectra be correct. This chapter is concerned with the use of tungsten filament quartz-halogen lamps as standard sources in calibrating a vapour phase fluorimeter having a grating dispersive element, so that fluorescence data recorded on a wavelength scale may be plotted, corrected for the fluorimeter spectral response, in terms of wavenumber. The relative correction factors are found to differ by up to three-fold in the wavelength range 320 to 430 nm. Considerable effort was given to verifying the results because the trend in the calibration curve was not as expected. The desirability of using a vapour phase chemical standard in such calibrations is indicated.
4.1 INTRODUCTION

SVL fluorescence spectra correspond to changes in vibronic levels and the process is quantized. Since the "size" of a quantum is proportional to its frequency, these spectra are more readily characterised/assigned if plotted in terms of frequency or wavenumber (cm$^{-1}$) units rather than in terms of wavelength. When emission intensity is measured by counting photons, these spectra represent the intensity, proportional to the number of quanta emitted per second, within a unit wavenumber interval, versus wavenumber. If $Q_q$ represents the total number of quanta of all wavelengths emitted per second*, $dQ_q/d\nu$ represents the intensity/cm$^{-1}$ at wavenumber $\nu$.

When a grating spectrometer, operated at constant slit widths, is used to record a spectrum, the spectrometer bandpass is virtually independent of wavelength (within one order, cf. table 4.2), and the spectrum is automatically recorded on a scale that is linear in wavelength**. In spectra of both representations, $(dQ_q/d\nu$ and $dQ_q/d\lambda)$, the area under the curve is meant to be proportional to the total rate of emission of all wavelengths measured as quanta per unit time. To convert spectra recorded in terms of unit wavelength to spectra in terms of unit wavenumber and preserve the area under the curve as a valid measure of intensity, it is necessary to multiply the recorded intensity by a scaling factor proportional to the square of the wavelength, $\lambda$, so that the scaled intensities correspond to a constant wavenumber bandpass. This can be represented mathematically*** as

* The subscript $q$ is used to denote a photon quantity.

** i.e. in the "intensity versus wavelength" plot, intensity is proportional to the number of quanta emitted per second per unit wavelength at the wavelength concerned, $dQ_q/d\lambda$.

*** $\lambda$ in cm.
In our system, spectra are recorded in terms of intensity vs. wavelength using a 1 m Spex grating spectrometer at constant slit widths and consequently almost constant wavelength bandpass. Data are recorded digitally on paper tape and, by means of a computer, can be plotted directly as \( \frac{dQ_q}{d\lambda} \) or, after multiplying by the \( \lambda^2 \) scale factor, as \( \frac{dQ_q}{d\nu} \). The resulting graph is the apparent or uncorrected spectrum. To obtain the true spectrum, the apparent spectrum has to be corrected for several wavenumber/wavelength-dependent factors: the quantum efficiency of the photomultiplier (PMT) fluorescence detector, the throughput (including bandwidth) of the spectrometer, and the efficiency of the transfer optics and the multi-reflection collection optics. Thus, if the observed PMT output at wavenumber \( \bar{\nu} \) is \( \frac{dQ_{q,obs}}{d\bar{\nu}} \) or \( \frac{dQ_{q,obs}}{d\lambda} \), then the true emission spectrum \( \frac{dQ_q}{d\nu} \) (or \( \frac{dQ_q}{d\lambda} \)) is related to the apparent emission spectrum as

\[
\frac{dQ_q}{d\nu} = \text{corr}(\bar{\nu}) \frac{dQ_{q,obs}}{d\bar{\nu}} \tag{4.2a}
\]

or

\[
\frac{dQ_q}{d\lambda} = \text{corr}(\lambda) \frac{dQ_{q,obs}}{d\lambda} \tag{4.2b}
\]

where \( \text{corr}(\bar{\nu}) \) and \( \text{corr}(\lambda) \) are the wavenumber and wavelength dependent correction factors respectively. Therefore, if a source \( L_q \) of known spectral distribution, \( \frac{dL_q}{d\bar{\nu}} \) or \( \frac{dL_q}{d\lambda} \), is made to illuminate the entrance slit of the monochromator via the same optical path as taken by the fluorescence emission and the PMT response \( P_q \) is recorded as a function of
wavelength $dP_q/d\lambda$ (which can be converted to $dP_q/d\nu$), correction factors $\text{corr}(\nu)$ and $\text{corr}(\lambda)$ can be determined from equations

\[
\text{corr}(\nu) = \frac{dL_q/d\nu}{dP_q/d\nu} \quad (4.3a)
\]

and

\[
\text{corr}(\lambda) = \frac{dL_q/d\lambda}{dP_q/d\lambda} \quad (4.3b)
\]

The recording of data in digital format makes this problem especially tractable.

Ideally, the source L would be a chemical standard. For solution spectra, various workers have precisely determined the corrected emission spectra of a series of compounds [e.g. see Berlman (1971), Parker (1968), Melhuish (1972) and references therein]; measurement of the uncorrected spectra of these compounds with the instrument to be calibrated permits direct calculation of the relevant correction factors. Using spectra of standard compounds as references and microprocessors, workers can obtain corrected spectra automatically [e.g. Wampler and De Sa, 1971]; correction factors can be updated with ease as better references become available.

It is to be noted that there is a lack of solution emission standards suitable for use in the ultraviolet [Melhuish, 1972]. For the vapour phase, corrected fluorescence spectra which might be used as reference standards have not been established. Where spectra have been corrected, the practice has been to use a calibrated lamp as source [Parmenter, Tang and Ware, 1976] or to use a standard solution in place of the gas sample. To correct spectra in the range 350-460 nm, Shibuya, Harger and Lee (1978)
employed ethanolic solutions of quinine sulphate and sodium salicylate and referenced these to the intensity distributions given by Berlman (1971). Parker (1962) has described a method for calibrating a fluorescence spectrometer so that corrected fluorescence emission spectra in the ultraviolet region can be determined. The method makes use of a Xenon arc lamp as a source of visible and ultraviolet light, a second monochromator to isolate a constant bandpass of this light and a fluorescent screen monitor, calibrated by a ferrioxalate actinometer, to monitor the intensity of the beam emerging from this second monochromator. It was not feasible to employ this method in calibrating our vapour phase spectrofluorimeter.

For use in the visible-ultraviolet, various types of lamps can be obtained commercially as standards of spectral irradiance* or can be calibrated by standards laboratories. Despite the rapid decrease in radiant power towards shorter wavelengths, tungsten-halogen incandescent lamps are now widely used as standards of spectral irradiance in many types of spectroradiometric calibration [Schwiesow, 1973; Gillham, 1977], and we have chosen to use a tungsten quartz-halogen lamp as reference source in correcting fluorescence spectra. Since 1963, at NBS** the standard of spectral irradiance consists of a quartz-iodine lamp with a coiled-coil tungsten filament operated at about 3000 K and calibrated from 250 nm to 2600 nm against a blackbody source [Stair, Schneider and Jackson, 1963]. The maximum uncertainties in the initial results of about

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* For example Optronic Laboratories, Inc. U.S.A. offer tungsten quartz-halogen lamps calibrated from 250 to 750 (2500) nm and deuterium lamps calibrated from 180 to 400 nm.

** U.S. National Bureau of Standards, Washington, D.C.
8% at 250 nm and 3% in the visible have since been reduced to 2% between 250 nm and 350 nm and less than 1% in the visible region [Saunders, Ott and Bridges, 1978].

Use of a tungsten-quartz-halogen lamp as a standard source has several attractive features. (i) In principle, the spectral distribution of a tungsten lamp operated at a colour temperature \( T_C \) can be obtained by multiplying the spectral distribution of a blackbody by the spectral emissivity \( \varepsilon(\lambda) \) of tungsten at the same temperature:

\[
E_d(\lambda) = \frac{2\pi\varepsilon(\lambda)}{\lambda^4[\exp(ch/k\lambda T_C)-1]} = \frac{C_1\varepsilon(\lambda)}{\lambda^4[\exp(c_2/\lambda T_C)-1]}
\]

(4.4)

where, if the wavelength is in metres and \( E_d(\lambda) \) is in photons/s/m\(^2\) then

\[
c_1 = 1.883652 \times 10^9 \text{ m/s}
\]

\[
c_2 = 1.4388325 \times 10^{-2} \text{ m/K}
\]

c, h, k are velocity of light, Planck's constant and Boltzmann's constant respectively [Levi, 1968, 1974]. The emissivity of tungsten at various temperatures has been determined by de Vos (1954) and varies by about 1% in the wavelength range 320 nm to 430 nm [Liberman, 1971] at temperatures around 2800 K though Liberman (1971) urges caution in applying these measurements to arbitrary tungsten lamps. The actual temperature of a tungsten filament lamp is about 125 K less than the colour temperature [Liberman, 1971]. (ii) Schwiesow (1973) has shown that it is feasible to fit tungsten lamp calibration data to an analytic expression similar to equation (4.4) with a linearly and a quadratically varying emissivity factor, making the data very computer compatible. (iii) Experience elsewhere has shown that, when operated at the same current and voltage, the
radiance of these lamps is stable and reproducible to within 1% virtually for the life of the lamp; (iv) that commercial projector lamps are suitable for use as standards; and (v) that the spectral distribution from tungsten lamps of the same type are very similar from 160 nm to 2600 nm [Stair et al., 1963; Stair et al., 1967; Buckley, 1971]. To illustrate the latter point, spectral irradiance data for three General Electric 200 W compact coiled coil quartz-iodine lamps taken from table 1 of Stair et al. (1963) and normalised to have a value of 400.0 at 400 nm are presented in table 4.1 for the range 300-450 nm.

Table 4.1a Relative spectral irradiance data \(^b\) for three 200 W quartz-iodine tungsten filament lamps.

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Lamp (i)</th>
<th>Lamp (ii)</th>
<th>Lamp (iii)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>6.78</td>
<td>6.78</td>
<td>6.76</td>
</tr>
<tr>
<td>320</td>
<td>12.9</td>
<td>13.0</td>
<td>13.0</td>
</tr>
<tr>
<td>350</td>
<td>29.5</td>
<td>29.9</td>
<td>29.7</td>
</tr>
<tr>
<td>370</td>
<td>45.5</td>
<td>46.2</td>
<td>46.1</td>
</tr>
<tr>
<td>400</td>
<td>80.0</td>
<td>80.0</td>
<td>80.0</td>
</tr>
<tr>
<td>450</td>
<td>156</td>
<td>156</td>
<td>156</td>
</tr>
</tbody>
</table>

\(^a\) Adapted from Stair et al. (1963).

\(^b\) In relative power units.

The rather condemnatory comments made by Parker (1968) and Melhuish (1972) concerning the use of tungsten lamps as calibration sources in the ultraviolet region below about 340 nm, because of the low radiant power in the ultraviolet region, would seem to apply (from the references they make and the tenor of their comments) to tungsten filament incandescent lamps. To prolong their life these lamps are filled with an inert gas such as nitrogen or argon to a pressure of about one atmosphere to reduce evaporation of tungsten [Levi, 1968], and are operated at temperatures perhaps no greater than 2470 K [Liberman, 1971]. Brightness loss with age
still occurs from deposition of tungsten on the lamp envelope. With the advent of tungsten filament quartz-halogen lamps, however, in which iodine is added to the lamp atmosphere, much higher operating temperatures (about 3000 K) are possible and thus a relatively large percentage of ultraviolet radiation is emitted. (Figures 4.1a and 4.1b illustrate the shift of emission to the ultraviolet for a blackbody radiator as temperature increases). The high temperature is made possible by the unique chemical action of the iodine vapour*. As a result, the life of a lamp operated at a relatively high temperature is considerably lengthened, blackening of the quartz envelope is prevented and the efficiency of the lamp remains essentially constant throughout its life. Buckley (1971) has demonstrated that a tungsten filament lamp fitted with a sapphire window and operated at 2800 K can be a stable reproducible calibration source even in the vacuum ultraviolet (165-270 nm). Tungsten quartz-halogen lamps are also compact, easy to operate, available in a range of powers, give a continuous spectral distribution uncomplicated by line structure and, with the stability characteristics already mentioned, provide good spectral calibration sources in the range 320 nm to 430 nm even in the form of cheap projector lamps [Stair et al., 1967].

An unattractive feature in the use of tungsten lamps for the calibration of grating instruments operated in orders higher than the first is that, because of the much higher spectral output in the visible region,

---

*Iodine vapour combines with evaporated tungsten and with the relatively cool tungsten deposits on the bulb wall to form volatile tungsten iodide which diffuses to the hot filament where it dissociates; the tungsten is redeposited on the filament and the iodine is free to continue the cycle. The iodine absorbs a small amount of radiation, primarily in the middle of the visible region, giving the light a purplish cast [Levi, 1968; Stair et al., 1963; Liberman, 1971].
Figure 4.1. Spectral distribution for a blackbody at different temperatures; (a) 300-1000 nm, (b) 310-430 nm.
scattering and overlap of light of lower orders presents problems. Though acknowledging that the tungsten quartz-halogen lamps are available for near ultraviolet radiometry, Saunders et al. (1978) have advocated using deuterium lamps in the 200-350 nm region as spectral irradiance standards if interference from long wavelength radiation is significant in the measurement system. Compared with a 1000 W tungsten quartz-halogen lamp, a typical 30 W deuterium lamp has about the same spectral irradiance at 260 nm but a factor of 100 lower spectral irradiance at 350 nm and a factor of 1000 lower at 550 nm [Saunders et al., 1978].

4.2 CALIBRATION WITH A G.E.C. 200 W TUNGSTEN LAMP SOURCE

Initially, in investigating the spectral response of the fluorimeter, a 200 W (8.33A) G.E.C. quartz-iodine lamp with a coiled-coil tungsten filament, similar to those employed by Stair et al. (1963) at NBS in establishing a new standard of spectral irradiance, was used as a standard. It was hoped that by measuring the temperature of the filament with an optical pyrometer, the relative spectral distribution of the lamp could be obtained from equation (4.4) to give $dL_q/d\lambda$ of equation (4.3b). Additionally, if a similar operating temperature to that of the lamps of Stair et al. (1963) (about 3000 K) could be achieved, their irradiance values might be used, given the good agreement observed between lamps of the same type, though their lamps were 200 W (6.6A) models.

In developing an experimental procedure use was made of the suggestions by Parker (1962), (1966)*, (1968). The configuration used is illustrated in figure 4.2. It was found to be impractical to use the excitation geometry of the cell with the tungsten lamp radiation multi-passed between the excitation mirrors and to rely upon scattering from air molecules at

* Borresen and Parker (1966)
Figure 4.2. Configuration used in system calibration measurements with G.E.C. tungsten lamp.

Figure 4.3. Wavelength region of cut-off in PMT response.
atmospheric pressure to deflect the incoming light into the spectrometer
since the resultant light intensity seen by the PMT was too low.

The lamp was situated at a distance $D_1$ from the MgO* diffuse reflector
which was positioned at a distance $D_2$ from the sapphire window of the multi-
pass cell at an angle to give maximum throughput as measured by the PMT.
The angle was not critical, attesting to the effectiveness of the diffuse
reflector. Distances $D_1$ and $D_2$ could be varied to produce a uniform
distribution of approximately parallel light at the sapphire window and a
statistically significant count rate, though not so high as to induce non-
linearity effects in the PMT. Both distances were of the order 0.5-1 m.
The entrance window was shielded from direct rays from the lamp by placing
a light baffle near the lamp as illustrated. A 13 cm long brass cylinder
with a 25 mm circular aperture was placed over the Varian conflat flange
of the sapphire window to further confine the path and amount of light
entering the cell. Light from the lamp then passed (i) through the multi-
pass cell via the slits between the collection mirrors; (ii) through the
transfer lenses $L_1, L_2, L_3$; (iii) through the spectrometer and into the
9789QA EMI photomultiplier; (iv) via a focusing lens $L_4$ mounted on the
spectrometer exit slit; and (v) either a 2 mm thick Chance-Pilkington OX1
or a 3 mm thick Schott BG12 coloured glass filter in a specially constructed
chamber fixed to the front of the PMT housing. The PMT was cooled to
250 K in a Products for Research TE-102 photomultiplier tube housing.

* MgO screens were prepared by holding freshly cleaned aluminium sheets
in the vapour above burning magnesium ribbon till they were covered with
a uniform oxide layer about 1 mm thick. Fresh screens were prepared
from time to time though no visible deterioration in the coatings occurred
over a period of several months. No correction was made for the slight
change ($\sim 4\%$) in reflectivity of magnesium oxide over the range 300-500
nm [Parker, 1968].
Room lights were off for the duration of data collection though experiment showed that they made negligible contribution to the count rate at any wavelength setting under the conditions of the experiment. Background was recorded on completion of each scan at the extremes of the wavelength range for the scan, with the lamp on and the spectrometer slits closed. No wavelength dependence was observed for the background; it appeared to consist mainly of thermal noise (about 1.5 counts/6 sec). Before being processed, the counts recorded at each wavelength were corrected by subtracting the estimated background.

SVL fluorescence spectra are obtained using the 1 metre Spex spectrometer (grating 1200 g/nm blazed at 10,000 Å) in third order, so when calibrating the system, with the spectrometer operating in third order, it was necessary to avoid overlap from tungsten lamp light in the second and fourth orders by employing coloured glass filters (OX1, BG12). Fortunately, the 9789QA PMT with a bialkali photo-cathode has a peak response at about 370 nm and, as illustrated in figure 4.3*, is completely unresponsive to light of wavelengths above 675 nm.

Table 4.3 shows the estimated relative intensities $W(OX1 \lambda/3)$ etc. of light of various orders** impinging upon the PMT via the OX1 or BG12 filter after being diffracted into various orders by the spectrometer.

* The curve of figure 4.3 showing the cut-off in response of the PMT at higher wavelengths was obtained with a Kodak Wratten 8 cut-off filter in front of the PMT and with the G.E.C. lamp operated and data collected in the normal way. The Wratten 8 filter has a transmittance greater than 80% at wavelengths longer than 500 nm but less than 1% at wavelengths less than 460 nm so its use ensures that only light in the first order reaches the PMT when the Spex is scanned through the region 5000-8000 Å.

** For example, at a spectrometer setting of 9000 Å, light of wavelengths 9000 Å (1st order), 4500 Å (2nd order), 3000 Å (3rd order), 2250 Å (4th order), etc. can pass, with varying efficiencies, through a single grating spectrometer.
Table 4.2 Bandpasses ($\Delta$), OX1 and BG12 filter absorbances (A), and relative tungsten lamp intensities (W) at various orders ($\lambda/2$, etc.) at spectrometer setting $\lambda$.

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<th>A(BG12)</th>
<th>$W(\lambda/2)$</th>
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<th>$\Delta(\lambda/3)$</th>
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<th>A(BG12)</th>
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Table 4.3  Estimated relative tungsten lamp intensities in various orders with the BG12 or OX1 filter in the optical path

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</tbody>
</table>
grating (assuming for the calculations that the system has uniform sensitivity to light of all wavelengths), and why it is necessary to employ two different filters in the range 9300-12900 Å to isolate just tungsten lamp radiation in the third order (3100-4300 Å)*. For the fluorimeter calibration measurements, the OX1 filter was employed for spectrometer settings from 9300 Å to about 11250 Å (3100-3750 Å in the third order) and the BG12 filter for 10500-12900 Å (i.e. 3500-4300 Å in the third order) giving a wavelength region of overlap for OX1 and BG12 data. Data obtained with each filter were normalised to a value of 100 at 3600 Å enabling data from the two wavelength ranges to be combined (and compared in the region of overlap).

The G.E.C. tungsten lamp was powered by a Hewlett Packard 6286A Constant Voltage/Constant Current power supply operated at 8.3 A and 23.5 V as determined from a meter on the power supply. Data were collected by stepping the spectrometer in increments of 6 Å (i.e. 2 Å in the third order) with the slits set at 856 µ and full height. The PMT was operated in current mode, its output being fed to an Ortec 439 Digital Current Integrator at a $10^{-7}$ Coulombs/pulse setting. The digital output from the 439 module was counted for preset times, determined by an Ortec 719 timer.

* Data in table 4.3 were calculated from the data in table 4.2. In preparing table 4.2, the spectral distribution ($W(\lambda/2)$, $W(\lambda/3)$, $W(\lambda/4)$) of the tungsten lamp was assumed to be of the form for the Philips Type 7158 lamp whose calibration data are provided in figure 4.6. The relative bandpasses of the spectrometer (for a wavelength setting of $\lambda$) at the various orders ($\Delta(\lambda/2)$, $\Delta(\lambda/3)$, $\Delta(\lambda/4)$) were obtained from the spectrometer manual [Spex, 1973]. Absorbances $A$(OX1) and $A$(BG12) for the OX1 and BG12 filters were measured using a Cary 219 spectrophotometer at 1 nm bandpass. The values $W$(OX1$\lambda$), etc. of table 4.3 were obtained for various wavelengths by multiplying together the values of bandpass ($\Delta(\lambda/3)$, etc.), percentage transmission for the filter involved and the relative intensity of the lamp ($W(\lambda/3)$, etc.) at the corresponding wavelength ($\lambda/3$, etc.).
in an Ortec 770 Counter and the serial output from the 770 at the end of each counting interval was recorded on paper tape; thence the data were transferred to a central computer for processing. Full details concerning the electronics and the acquisition, manipulation and forms of presentation of the data are given in chapter 3.

Temperatures were measured with Leeds and Northrup 8627 and 8622-C optical pyrometers. Unfortunately, differences in temperature measurements of about 200 K were obtained for different parts of the filament and readings from the same part were irreproducible (±40 K) even when taken within intervals of five minutes. Most recordings were within the range 2933-3093 K and a value of 3000 K was assumed in calculating the spectral distribution of the lamp using equation (4.4). The emissivity, ε(λ), was considered constant in the range 310-430 nm.

Figures 4.1a and 4.1b illustrate the expected change with temperature in the shape of the spectral distribution curve for a tungsten lamp behaving like a blackbody radiator and table 4.4 exemplifies this quantitatively. According to table 4.4, if a temperature of 3100 K rather than an actual temperature of 2900 K was used in calculating the relative spectral distribution for the lamp, in the range 310-430 nm, errors of up to 30% would ensue.

Results obtained using the 200 W G.E.C. lamp are presented in tables 4.5 and 4.6 and figures 4.4 and 4.5. Table 4.5 gives an abridged listing of relative intensities measured in several separate scans after correction for the absorbance of the filters, computer smoothing (cf. chapter 3, 15 points used) and normalisation to a value of 100 at 360 nm. Considerable scatter in values obtained for the same wavelength is evident and there
Table 4.4 Relative intensities from a blackbody radiator at various temperatures and wavelengths

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Intensities(^a) relative to intensity at 360 nm</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(I(2900\text{ K}))</td>
<td>(I(3000\text{ K}))</td>
</tr>
<tr>
<td>310</td>
<td>0.20</td>
<td>0.21</td>
</tr>
<tr>
<td>360</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>430</td>
<td>4.63</td>
<td>4.29</td>
</tr>
</tbody>
</table>

\[^{b}\] \(\frac{I_{310}}{I_{430}}\)

\(^{a}\) In photon units.

\(^{b}\) Ratio of the relative intensities at 310 nm and 430 nm at various temperatures.

There is some disagreement between the OXl and BG12 results in the region of overlap. Figure 4.4 illustrates the relative spectral response of the fluorimeter system to the G.E.C. lamp (obtained by averaging the results of the several scans of table 4.5) compared with the expected spectral distribution of the G.E.C. lamp at 3000 K (calculated from equation 4.4), with both distributions normalised to 100 at 360 nm. This system response does not tally with what would be expected for the PMT-spectrometer-transfer optics combination involved since the highest sensitivity occurs at about 400 nm*.

The correction factors obtained by comparing the averaged results presented in figure 4.4 with the spectral distribution of a blackbody at 3000 K are given in figure 4.5 and in table 4.6. In preparing figure 4.5, results from the OXl scans were used in the range 310-360 nm and results from the BG12 scans from 360 nm to 430 nm. Details of how the correction factors were obtained and how they are applied to correct spectra are given in section 4.3.

* The maximum quantum efficiency of the 9789QA PMT is at 370 nm [EMI, 1975]; the spectrometer with a grating blazed at 10000 Å should give maximum throughput in first order at about 330 nm; the transfer optics were optimized at 334 nm (section 2.3).
Table 4.5  Relative intensities\(^a\) observed for G.E.C. 200 W tungsten quartz-halogen lamp in fluorimeter spectral response calibration

<table>
<thead>
<tr>
<th>Wavelength (^b) (nm)</th>
<th>OX1 filter (i)</th>
<th>(ii)</th>
<th>BG12 filter (iii)</th>
<th>(iv)</th>
<th>(v)</th>
</tr>
</thead>
<tbody>
<tr>
<td>320</td>
<td>19.3</td>
<td>17.4</td>
<td>68.6</td>
<td>67.8</td>
<td>69.0</td>
</tr>
<tr>
<td>330</td>
<td>26.1</td>
<td>22.1</td>
<td>79.8</td>
<td>83.4</td>
<td>81.3</td>
</tr>
<tr>
<td>340</td>
<td>38.1</td>
<td>34.7</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
</tr>
<tr>
<td>350</td>
<td>63.8</td>
<td>58.8</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
</tr>
<tr>
<td>355</td>
<td>77.4</td>
<td>89.4</td>
<td>124.4</td>
<td>121.2</td>
<td>124.2</td>
</tr>
<tr>
<td>360</td>
<td>100.0</td>
<td>100.0</td>
<td>146.3</td>
<td>147.2</td>
<td>151.6</td>
</tr>
<tr>
<td>365</td>
<td>126.4</td>
<td>127.6</td>
<td>202.6</td>
<td>205.4</td>
<td>228.1</td>
</tr>
<tr>
<td>370</td>
<td>161.1</td>
<td></td>
<td>305.7</td>
<td>284.6</td>
<td>318.4</td>
</tr>
<tr>
<td>380</td>
<td></td>
<td></td>
<td>408.9</td>
<td>377.0</td>
<td>421.5</td>
</tr>
<tr>
<td>390</td>
<td></td>
<td></td>
<td>455.4</td>
<td>462.2</td>
<td>489.2</td>
</tr>
<tr>
<td>400</td>
<td></td>
<td></td>
<td>512.1</td>
<td>486.5</td>
<td>541.5</td>
</tr>
<tr>
<td>410</td>
<td></td>
<td></td>
<td>474.3</td>
<td>492.2</td>
<td>545.5</td>
</tr>
</tbody>
</table>

\(^a\) Measured using PMT in charge integration mode and normalised to 100.0 at 360 nm.

\(^b\) Third order.

Table 4.6  Average correction factors obtained using a G.E.C. 200 W tungsten quartz-halogen lamp. Spectral distribution of lamp assumed to be that of a blackbody at 3000 K

<table>
<thead>
<tr>
<th>OX1 filter section</th>
<th>BG12 filter section</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength (nm)</td>
<td>Correction(^a) factor</td>
</tr>
<tr>
<td>---------------------</td>
<td>------------------------</td>
</tr>
<tr>
<td>311</td>
<td>1.24</td>
</tr>
<tr>
<td>315</td>
<td>1.27</td>
</tr>
<tr>
<td>320</td>
<td>1.31</td>
</tr>
<tr>
<td>325</td>
<td>1.39</td>
</tr>
<tr>
<td>330</td>
<td>1.48</td>
</tr>
<tr>
<td>335</td>
<td>1.46</td>
</tr>
<tr>
<td>340</td>
<td>1.41</td>
</tr>
<tr>
<td>345</td>
<td>1.28</td>
</tr>
<tr>
<td>350</td>
<td>1.18</td>
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<tr>
<td>355</td>
<td>1.08</td>
</tr>
<tr>
<td>360</td>
<td>1.00</td>
</tr>
<tr>
<td>365</td>
<td>0.92</td>
</tr>
</tbody>
</table>

\(^a\) Defined specifically in next section.
Figure 4.4. Spectral response of fluorimeter to G.E.C. lamp compared with the spectral distribution of a blackbody at 3000 K.

Figure 4.5. Correction curve for fluorimeter system obtained with G.E.C. lamp.
In view of the large uncertainty in the temperature measurements and hence in $dL_q/d\lambda$ of equation (4.3b), the scatter in the results (e.g. table 4.5) and the considerable difference between the observed and expected system response, it was decided to have a tungsten quartz-halogen lamp calibrated by the National Measurement Laboratory (NML), Sydney.

4.3 CALIBRATION WITH PHILIPS TYPE 7158 TUNGSTEN LAMPS *

A. LAMP "A"

A Philips Type 7158 24 V 150 W tungsten-halogen lamp with a type G 6.35-15 base was calibrated at the National Measurement Laboratory, Sydney**. This is a compact projector lamp comprising a single-coil tungsten filament, of approximate dimensions 6 mm x 3 mm, mounted in a cylindrical silica envelope and has an expected lifetime of 55 hours. The calibration was performed with the same leads and polarity and with the lamp, held in the same ceramic socket, at exactly the same orientation as employed in the fluorimeter calibration measurements. The lamp was operated from a regulated dc supply at a current of 6.255 A with a potential difference of 23.39 V across the soldered joints on the ceramic base. The relative spectral irradiance of the lamp was measured for radiation of 2 nm spectral bandwidth over the wavelength range 250-720 nm and provided in tabular form at wavelength intervals of 10 nm. The calibration data as supplied by NML, in units of power and normalised to unity at 500 nm, together with the corresponding values in units of photon/s normalised to 100 at 360 nm,

* The 200 W G.E.C. lamp was on loan. Dr P. Hannaford of CSIRO Division of Chemical Physics, Melbourne, and Mr J.E. Shaw of CSIRO Division of Applied Physics NML, Sydney, both suggested the Philips 7158 lamp as a suitable source for calibration.

** Thanks to Mr J.E. Shaw and the CSIRO who performed this calibration.
Table 4.7 Relative spectral irradiance of Philips 7158 tungsten quartz-halogen lamp A determined by the National Measurement Laboratory, Sydney

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Relative Irradiancea (power units)</th>
<th>Relative Irradianceb (photons/s units)</th>
<th>Percentage uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>0.0345</td>
<td>16.8</td>
<td>10</td>
</tr>
<tr>
<td>310</td>
<td>0.0480</td>
<td>24.2</td>
<td>9</td>
</tr>
<tr>
<td>320</td>
<td>0.0650</td>
<td>33.8</td>
<td>8</td>
</tr>
<tr>
<td>330</td>
<td>0.0850</td>
<td>45.6</td>
<td>7</td>
</tr>
<tr>
<td>340</td>
<td>0.1095</td>
<td>60.5</td>
<td>6</td>
</tr>
<tr>
<td>350</td>
<td>0.139</td>
<td>79.0</td>
<td>5</td>
</tr>
<tr>
<td>360</td>
<td>0.171</td>
<td>100.</td>
<td>4</td>
</tr>
<tr>
<td>370</td>
<td>0.207</td>
<td>124.</td>
<td>3</td>
</tr>
<tr>
<td>380</td>
<td>0.247</td>
<td>152.</td>
<td>2</td>
</tr>
<tr>
<td>390</td>
<td>0.290</td>
<td>184.</td>
<td>2</td>
</tr>
<tr>
<td>400</td>
<td>0.340</td>
<td>221.</td>
<td>1.5</td>
</tr>
<tr>
<td>410</td>
<td>0.396</td>
<td>264.</td>
<td>1.5</td>
</tr>
<tr>
<td>420</td>
<td>0.453</td>
<td>309.</td>
<td>1.5</td>
</tr>
<tr>
<td>430</td>
<td>0.513</td>
<td>358.</td>
<td>1.5</td>
</tr>
<tr>
<td>440</td>
<td>0.577</td>
<td>412.</td>
<td>1.5</td>
</tr>
<tr>
<td>450</td>
<td>0.642</td>
<td>469.</td>
<td>1.5</td>
</tr>
</tbody>
</table>

a Normalised to 1.000 at 500 nm

b Normalised to 100. at 360 nm

are given for the range 300-450 nm in table 4.7. Figure 4.6 presents the relative irradiance for the lamp in units of photon/s for the complete wavelength range of the calibration. The relative uncertainty in the measurements is 1.5% in the range 720-390 nm and increases linearly from 2% to 10% in the range 380-300 nm and from 20% to 60% in the range 290-250 nm.

Before the Philips 7158 lamp, lamp A, was sent for calibration, the response of the fluorimeter was measured using a procedure similar to that developed with the 200 W G.E.C. lamp. The configuration is illustrated in figure 4.7. To permit the count rate to be readily varied (e.g. to keep similar count rates for the 0X1 and BG12 scans), an additional aperture
Figure 4.6. Spectral distribution of Philips Type 7158 lamp (lamp A) in photon units and normalised to a value of 100 at 3600 Å. Calibration performed, at constant wavelength bandpass (2 nm), by National Measurement Laboratory, Sydney.
in the form of a 30 cm long brass cylinder with a 56 x 6 mm slit at one end was mounted on the 13 cm long brass cylinder. The overall length of the combination could be varied from 33 to 43 cm and the slit (offset to one side) was rotatable. The 7158 lamp A was operated from a Hewlett Packard 6286 A regulated power supply at 24.0 V* and 6.2-6.3 A according to the meter on the power supply; the 9789QA PMT was used in photon counting mode; the spectrometer slit widths were 856 µ corresponding to a collection bandpass of about 2.1 Å in third order; step sizes were 6 Å (2 Å in third order); the relative intensities were measured for 4 second time intervals by means of a single photon counting system identical to

* This corresponded to potential difference across the soldered joints at the base of 23.3 V. In the subsequent calibration, the lamp (lamp A) was operated at 23.39 V and 6.255 A.
that employed when collecting fluorescence spectra except that the Ortec 770 Counter was not gated (see section 3.3). Intensities were corrected for background.

It is appropriate here to discuss the application of equation 4.3 in greater detail. The calibration data for the tungsten lamp are provided in terms of energy* per unit wavelength interval (2 nm bandpass), \( dL_w/d\lambda \). To apply equation (4.3a) the calibration data must be converted to "photon units" per wavenumber (4.3a) or per wavelength (4.3b) interval, \( dL_q/d\nu \) or \( dL_q/d\lambda \) respectively. The change from energy to photon units is effected by dividing by the energy of the photon \((hc/\lambda)\) viz.:

\[
dL_q/d\lambda = (dL_w/d\lambda)\lambda/hc
\]

(4.5)

or, since the values are relative, merely by multiplying by \( \lambda \) and the conversion from a wavelength to a wavenumber scale by multiplying by \( \lambda^2 \) (equation 4.1). Thus

\[
dL_q/d\nu = (dL_w/d\lambda)\lambda^3/hc
\]

(4.6)

From equation (4.3a) it is evident that to obtain \( corr(\nu) \) it is necessary to convert the observed PMT response to the tungsten lamp, \( dP_q/d\lambda \), to \( dP_q/d\nu \) by multiplying by \( \lambda^2 \). Since spectra are recorded automatically in terms of a constant wavelength interval, however, this is not necessary and the reported correction factors are equivalent to \( \lambda^2 corr(\nu) \) since they are obtained without converting \( dP_q/d\lambda \) to \( dP_q/d\nu \) and are to be applied to spectra recorded directly on a wavelength scale \( dQ_{qobs}/d\lambda \). (In appendix A4 it is shown that the required corrected spectra \( dQ_q/d\nu \), results). The correction factors in terms of wavenumber \((\nu)\) as used

* The actual values are relative and have dimensions of power/length\(^3\).
Here are determined by the equation

\[
\text{correction factor} = \lambda^2 \text{corr}(\bar{\nu}) = \frac{(dL_w/d\lambda)}{(dP_q/d\lambda)} \frac{\lambda^3}{(hc)}
\]  

(4.7)

The wavelength correction factor, \(\text{corr}(\lambda)\), is given by

\[
\text{corr}(\lambda) = \frac{(dL_w/d\lambda)}{(dP_q/d\lambda)} \frac{\lambda}{hc}
\]

(4.8)

Table 4.8 gives the correction factors to be applied to spectral data (recorded directly in various "units") for graphical presentation (in various "units").

Table 4.8 Correction factors necessary for obtaining corrected plotted spectra in various units following direct recording of spectra

<table>
<thead>
<tr>
<th>Form of recorded spectrum</th>
<th>Form of corrected spectrum</th>
<th>Correction factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(dQ_{\text{obs}}/d\bar{\nu})</td>
<td>(dQ_q/d\bar{\nu})</td>
<td>((\lambda/hc)(dL_w/d\lambda)/(dP_q/d\lambda)) or ((\lambda^3/hc)(dL_w/d\lambda)/(dP_q/d\bar{\nu}))</td>
</tr>
<tr>
<td>(dQ_{\text{obs}}/d\lambda)</td>
<td>(dQ_q/d\lambda)</td>
<td>((\lambda/hc)(dL_w/d\lambda)/(dP_q/d\lambda))</td>
</tr>
<tr>
<td>(dQ_{\text{obs}}/d\lambda)</td>
<td>(dQ_q/d\bar{\nu})</td>
<td>((\lambda^3/hc)(dL_w/d\lambda)/(dP_q/d\lambda))</td>
</tr>
</tbody>
</table>

Computer processing yields spectral data in tabular form (printout) as well as graphical form to assist in accurately determining the wavenumber (or wavelength) of peaks and in integrating peak intensities. The tables list the intensity measured at each step of the spectrometer scan and consequently intensities apply to a constant wavelength bandpass. A cumulative intensity is kept to assist in evaluating peak intensities.
In determining peak areas for spectra plotted in terms of unit wavenumber intervals, the correction factors for the corresponding tabulated intensities must be \( \text{corr}(\lambda) \) since no \( \lambda^2 \) correction for the changing wavenumber bandpass is necessary here.*

Table 4.9 lists the relative intensities measured by the fluorimeter system for the Philips 7158 lamp A and table 4.10 the corresponding correction factors (equation (4.7)). Comparison of table 4.6 with table 4.10 shows there is reasonable quantitative agreement between the correction factors obtained with the G.E.C. 200 W lamp and with the Philips 7158 lamp A though the methods used in obtaining them were different. Table 4.9 shows there is still some disagreement in the results obtained in the region of overlap between the OX1 and BG12 scans. The differences in the results obtained with the BG12 filter, (scans (i) and (ii)), is the greatest difference observed for pairs of scans involving the same filter and may be due to the greater uncertainty in the 360 nm intensity value for scan (i) and/or the different optical configurations used.

Comparison with other results (e.g. table 4.14) shows the results of scan (i) agree much better with the results from other BG12 filter scans made using different Philips 7158 lamps. The experimental conditions of scan (i) differed from those of scan (ii) in that the lamp had not been

* The total intensity recorded between "points" in the spectrum must be the same whether these "points" are labeled as \( \lambda_1, \lambda_2 \) or \( \nu_1, \nu_2 \) and adding the intensities recorded in the table gives this total intensity. Spectra, being essentially histograms, require implicitly that each value of intensity plotted corresponds to the same bandpass if the area under the spectrum between \( \lambda_1 \) and \( \lambda_2 \) (or \( \nu_1 \) and \( \nu_2 \)) is to give the total intensity measured between these two points correctly.
Table 4.9  Relative intensities observed for Philips 7158 lamp A in the fluorimeter spectral response calibration. Numerals (i)-(iv) refer to figure 4.7

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>OX1 filter (iii)</th>
<th>OX1 filter (iv)</th>
<th>BG12 filter (i)</th>
<th>BG12 filter (ii)</th>
</tr>
</thead>
<tbody>
<tr>
<td>320</td>
<td>24.4</td>
<td>24.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>330</td>
<td>29.5</td>
<td>30.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>340</td>
<td>40.5</td>
<td>40.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>350</td>
<td>61.8</td>
<td>61.2</td>
<td>69.4</td>
<td>67.0</td>
</tr>
<tr>
<td>355</td>
<td>78.6</td>
<td>78.6</td>
<td>80.5</td>
<td>80.7</td>
</tr>
<tr>
<td>360</td>
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<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
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<tr>
<td>365</td>
<td>126.9</td>
<td>126.7</td>
<td>122.6</td>
<td>119.9</td>
</tr>
<tr>
<td>370</td>
<td>152.7</td>
<td></td>
<td>149.6</td>
<td>146.9</td>
</tr>
<tr>
<td>375</td>
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<td>420</td>
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<td></td>
<td>512</td>
<td>496</td>
</tr>
<tr>
<td>430</td>
<td></td>
<td></td>
<td>505</td>
<td>488</td>
</tr>
<tr>
<td>I (360)(^a)</td>
<td>10827</td>
<td>10172</td>
<td>958</td>
<td>3950</td>
</tr>
</tbody>
</table>

\(^a\) Intensities after background correction.

Table 4.10  Correction factors (equation 4.7) for fluorimeter system using lamp A. Identifiers (i), (ii), (iii), (iv) refer to figure 4.7.

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>OX1 filter (iii)</th>
<th>OX1 filter (iv)</th>
<th>BG12 filter (i)</th>
<th>BG12 filter (ii)</th>
</tr>
</thead>
<tbody>
<tr>
<td>320</td>
<td>1.09</td>
<td>1.07</td>
<td></td>
<td></td>
</tr>
<tr>
<td>330</td>
<td>1.30</td>
<td>1.27</td>
<td></td>
<td></td>
</tr>
<tr>
<td>340</td>
<td>1.33</td>
<td>1.32</td>
<td></td>
<td></td>
</tr>
<tr>
<td>350</td>
<td>1.21</td>
<td>1.22</td>
<td>1.08</td>
<td>1.12</td>
</tr>
<tr>
<td>355</td>
<td>1.11</td>
<td>1.11</td>
<td>1.08</td>
<td>1.08</td>
</tr>
<tr>
<td>360</td>
<td>1.00</td>
<td>1.00</td>
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<td>0.71</td>
<td>0.73</td>
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<td></td>
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<tr>
<td>430</td>
<td></td>
<td></td>
<td>1.01</td>
<td>1.05</td>
</tr>
</tbody>
</table>
used before scan (i) - it was "burnt in" for 20 minutes* prior to the
start of scan (i) - and in that for scan (i) the MgO screen was much
farther from the entrance window than it was in scans (ii), (iii), (iv)
of figure 4.7. Results from the OX1 filter (scans (iii) and (iv)) show
good agreement with the results from other OX1 filter scans (cf. table
4.13) adding to the puzzle. Furthermore, the trend in the correction
factors is (still) unexpected for the spectrometer-PMT-optics combination
employed. Further investigation of these problems had to be pursued
using other Philips 7158 lamps since the filament of the calibrated lamp,
Philips 7158 lamp A, broke in transit from NML.

B. LAMP "B"

A second Philips 7158 quartz-halogen lamp (lamp B)** was used to
test the spectral response of the following components of the fluorimeter
system (letters (a)-(e) refer to figure 4.8):

(a) and (e) total system
(b) spectrometer + lenses L₃, L₄
(c) spectrometer + lens L₄
(d) spectrometer alone

using single photon counting in the manner described for lamp A. The
operational details and optical configurations for experiments (a) to (e)

* Subsequently new lamps were "burnt in" at their operating voltages
and currents for at least 1½ hours before being used in calibrations.
Lamps already conditioned in this way were allowed to equilibrate for 30
minutes under operating conditions prior to use in calibration measurements.

** Four Philips Type 7158 projector lamps were purchased together from
the same source and were possibly from the same production run.
Figure 4.8. Optical configuration for Philips 7158 lamp B.

Table 4.11. Operational parameters for use of Philips 7158 lamp B. Scans identified as (a), (b), (c), (d), (e) in text. Positions X, I, M, N refer to figure 4.8.

<table>
<thead>
<tr>
<th>Scan</th>
<th>MgO $^a$</th>
<th>D $^b$</th>
<th>Lenses $^c$</th>
<th>Filter position</th>
<th>Slits $^d$</th>
<th>Time $^e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>M</td>
<td>110</td>
<td>L$_1$-L$_4$</td>
<td>OX1</td>
<td>I</td>
<td>650×25</td>
</tr>
<tr>
<td>(a)</td>
<td>M</td>
<td>110</td>
<td>L$_1$-L$_4$</td>
<td>BG12</td>
<td>I</td>
<td>400×25</td>
</tr>
<tr>
<td>(b)</td>
<td>N</td>
<td>115</td>
<td>L$_3$-L$_4$</td>
<td>OX1</td>
<td>I</td>
<td>100×5</td>
</tr>
<tr>
<td>(b)</td>
<td>N</td>
<td>115</td>
<td>L$_3$-L$_4$</td>
<td>BG12</td>
<td>I</td>
<td>100×2</td>
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<tr>
<td>(c)</td>
<td>N</td>
<td>125</td>
<td>L$_4$</td>
<td>BG12</td>
<td>I</td>
<td>140×2</td>
</tr>
<tr>
<td>(c)</td>
<td>N</td>
<td>125</td>
<td>L$_4$</td>
<td>BG12</td>
<td>X</td>
<td>140×2</td>
</tr>
<tr>
<td>(d)</td>
<td>N</td>
<td>125</td>
<td>-</td>
<td>OX1</td>
<td>X</td>
<td>140×2</td>
</tr>
<tr>
<td>(d)</td>
<td>N</td>
<td>125</td>
<td>-</td>
<td>BG12</td>
<td>X</td>
<td>140×2</td>
</tr>
<tr>
<td>(e)</td>
<td>M</td>
<td>110</td>
<td>L$_1$-L$_4$</td>
<td>OX1</td>
<td>X</td>
<td>600×25</td>
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<tr>
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<td>145</td>
<td>L$_1$-L$_4$</td>
<td>BG12</td>
<td>X</td>
<td>600×25</td>
</tr>
</tbody>
</table>

$^a$ Position of MgO diffuse reflector in figure 4.8  
$^b$ Distance D of figure 4.8(cm)  
$^c$ Lenses in optical path  
$^d$ Slit widths($\mu$) × slit heights(mm)  
$^e$ Collection time(s)
are given in figure 4.8 in conjunction with table 4.11. Different slit heights and widths were used to maintain reasonable count rates* (statistical accuracy) throughout the wavelength range of each scan while keeping the anode current (count rate) as low as possible at the longer wavelengths of each scan not only to avoid PMT saturation, pulse pile-up, etc. but also to keep the effects of PMT fatigue minimal [Coates, 1975]. Photon-counting reduces the effect of gain changes (all photomultiplier pulses with voltages greater than a set threshold are counted and treated identically irrespective of their heights) and hence PMT fatigue as Coates (1975) demonstrated. Experiment showed that optical differences such as different slit widths had no influence on the relative intensities if they were obtained under otherwise identical conditions (e.g. photon-counting with similar count rates).

The results for experiments (a) to (e) together with the relative spectral irradiance of the philips 7158 lamp A, curve w, are presented in figure 4.9. The curves of figure 4.9 reveal that when the multi-pass cell and lenses L₁-L₄ are excluded from the optical path the response of the spectrometer-PMT combination is indeed as expected with peak sensitivity in the region 340 to 360 nm ((d) cf. (w)). Inclusion of the focusing lens (L₄) at the exit slit does not change the spectral response of the system ((c) cf. (d)) whereas inclusion of lens 3 at the entrance slit does ((b) cf. (c)). The major influence on the response of the fluorimeter system is the multi-pass cell optics and/or lenses L₁ and L₂ ((a) cf. (b)).

* Greater than 1500 counts/interval at the shorter wavelength end of each scan which, with a background count of about 15 per interval, implies a Poisson error of 2.6% before computer averaging and smoothing which, for a 15 point moving average scheme, reduces the Poisson error ∼√15 times.
Figure 4.9. Spectral response of various components of the fluorimeter system and tungsten lamp spectral distribution (curve w). Curve (a) total fluorimeter system; curve (b) spectrometer + exit slit and entrance slit lenses L₃,L₄; curve (c) spectrometer + exit slit lens L₄; curve (d) spectrometer alone.
In conducting the above tests with lamp B another test was performed. Since spectra are collected without filters in front of PMT 9789QA, the response of the system with the BG12 filter mounted externally on the spectrometer entrance slit was compared with the response of the system with the BG12 filter mounted in front of the PMT for case (c) above. The results obtained were virtually identical (table 4.12) and, in subsequent calibration measurements, the filters OX1 and BG12 were placed in the optical path at the aperture of the brass cylinder on the entrance window of the multi-pass cell (figure 4.8).

Table 4.12 Response of fluorimeter system in configuration (c) of figure 4.8 with BG12 filter: (i) in front of PMT (position I), and (ii) at the entrance slit of the spectrometer (position X).

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Intensitya (i)</th>
<th>Intensitya (ii)</th>
<th>Wavelength (nm)</th>
<th>Intensity (i)</th>
<th>Intensity (ii)</th>
</tr>
</thead>
<tbody>
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<td>90</td>
<td>395</td>
<td>135</td>
<td>137</td>
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<tr>
<td>365</td>
<td>107</td>
<td>107</td>
<td>405</td>
<td>139</td>
<td>144</td>
</tr>
<tr>
<td>370</td>
<td>113</td>
<td>114</td>
<td>410</td>
<td>138</td>
<td>142</td>
</tr>
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<td>390</td>
<td>131</td>
<td>134</td>
<td>430</td>
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</tr>
<tr>
<td>I(360)b</td>
<td>7074</td>
<td>7310</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a Relative intensity after background and absorbance corrections, normalised to 100 at 360 nm.
b Intensity after background subtraction measured at 360 nm (i.e. without absorbance correction).

Because (a) the results obtained for the fluorimeter system calibration using the calibrated lamp contained inconsistencies (table 4.10), (b) the measurements were few in number and, less importantly, (c) the lamp was not operated exactly at the voltage of its calibration
(\(\sim 23.3 \text{ V}\) vs. 23.39 V), it was considered necessary to repeat the measurements with the lamp operated and monitored more precisely. Since there was not time for another lamp to be standardized after lamp A was returned broken**, it was decided to assume that similar lamps (Philips 7158 obtained from the same source) would have very similar spectral irradiance characteristics considering the uncertainty of the calibration measurements (± 1.5-8%) and the uncertainty in the measurements. The spectral irradiance data of Stair et al. (1963) for three tungsten lamps of the same type (reproduced in part in table 4.1), and the results for three Philips 7158 lamps lend support to this assumption.

Table 4.13 lists the relative intensities, obtained under slightly different optical configurations and lamp operating conditions, for four 150 W tungsten lamps, three Philips Type 7158 lamps*** and one Wotan Type 64640 lamp. In the results for the Philips lamps A, B and C, discrepancies only occur at wavelengths above 385 nm and the difficulty is with the lamp A values. These, as discussed before, show considerable disagreement between themselves which may reflect the less careful monitoring of voltage possible for lamp A. The results in the OXI wavelength range are all in excellent agreement. Since the greatest difference

* Estimated from the power supply meter and the ohmic drop in the connecting cables.

** Calibrations of this sort are only performed periodically at NML - calibration of lamp A "took" three months.

*** Philips 7158 tungsten lamps are not very robust and have a design life of 55 hours. It was necessary to use three separate lamps of this type in conducting the work described here, identified as lamps A (calibrated by NML), B and C. Lamp A was broken in transit from NML; lamp B fused.
in the results for the BG12 segment is only about 5%, the data of table 4.13 provide strong evidence that there are no significant differences in the irradiance characteristics of lamps A, B and C (cf. the difference in the results obtained in the BG12 section with one lamp in tables 4.14 and 4.17). The Wotan lamp was run at slightly lower voltages but exhibited very similar spectral irradiance characteristics to the Philips lamps.

The averaged results for the fluorimeter correction factors determined using Philips lamp B are given, in terms of wavenumber, in figure 4.10 and, in terms of wavelength, in figure 4.11. Results for the individual scans are listed in table 4.14. For these and all subsequent measurements the lamp operating voltage was set, (23.40 V at the solder joints on the lamps), and monitored using a Fluke 8012A Digital Multimeter and the current by the meter on the HP power supply for the lamp. Constant time intervals (better than 0.02%) were ensured by counting a pre-determined number of pulses derived from the quartz crystal clock of a microprocessor system* (Henderson, 1978) with the 719 Timer operating as a pre-set scaler.

The Philips 7158 lamp B results are in good accord with those of the G.E.C. lamp and the Philips 7158 lamp A, and there is a reasonably smooth transition from OX1 to BG12 values at 360 nm. The small discrepancies between OX1 and BG12 results in the overlap region are perhaps due more to "fatigue" effects in the PMT induced by the different average anode

* Thanks to C.N. Henderson. This may seem to be unnecessary refinement but the Timer was not performing correctly as a timer and the microprocessor system was a convenient alternative source of variable frequency pulses.
Figure 4.10. Fluorimeter calibration curve (in terms of wavenumber) determined using Philips 7158 lamp B.

Figure 4.11. Fluorimeter calibration curve (in terms of wavelength) determined using Philips 7158 lamp B.
Table 4.13 Relative spectral intensities measured with the fluorimeter system for the MgO reflector external to the multi-pass cell of four 150 W tungsten lamps

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Philips 7158 Lamp A&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Philips 7158 Lamp B&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Philips 7158 Lamp C&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Wotan 64640&lt;sup&gt;d&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>OX1</td>
<td>BG12</td>
<td>OX1</td>
<td>BG12</td>
</tr>
<tr>
<td>315</td>
<td>23.2</td>
<td>24.7</td>
<td>24.8</td>
<td>22.0</td>
</tr>
<tr>
<td>320</td>
<td>24.9</td>
<td>27.0</td>
<td>26.8</td>
<td>24.0</td>
</tr>
<tr>
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<td>28.7</td>
</tr>
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<td>509</td>
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<td>3950</td>
<td>958</td>
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</tr>
</tbody>
</table>

<sup>a</sup> From table 4.9; OX1 average of (iii) and (iv) of table 4.9.
<sup>b</sup> Average of (a) and (e) of table 4.11.
<sup>c</sup> From scans 1 and 2 of table 4.16.
<sup>d</sup> Configuration as in figure 4.2 with $D_1 = 82$, $D_2 = 51$, LA = 54 cm; 27.7 V, 6.25 A.
<sup>e</sup> Intensity at 360 nm (after background subtraction only).
Table 4.14  Correction factors (equation 4.7) at 5 nm intervals obtained for the fluorimeter using lamp B. References (a) and (e) refer to figure 4.8 and its associated table 4.11.

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>(a)</th>
<th>(e)</th>
</tr>
</thead>
<tbody>
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<td>1.27</td>
</tr>
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<tr>
<td></td>
<td>10945</td>
<td>3080</td>
</tr>
</tbody>
</table>

^a Intensity after background subtraction (about 20) in counts/6 second interval.

Currents that prevail in the OX1 and BG12 scans around 360 nm rather than to a real optical effect. It is necessary to employ slightly different optics (e.g. slit widths) between OX1 and BG12 scans to maintain similar, reasonable anode currents for both scans. (For example, in case (e) of table 4.14, if count rates for the OX1 and BG12 scans were similar at 360 nm, then the count rate at 430 nm in the BG12 scan would be >13000/sec cf. a count rate of 300/sec at 315 nm in the OX1 scan so a compromise is necessary). At the count rates employed (250-3700/sec), application of
equation 25 or 28 of Harris and Selinger (1979) for determining the extent of instrumental pile-up shows that for an instrumental dead time of 10 ns pile-up is completely insignificant (<0.004%). For the 9789QA PMT used it is desirable to keep the average anode current well below 0.2 mA and for best gain stability it should be one hundred times lower or less [EMI, 1972]. The average charge corresponding to single photon pulses at the anode for this PMT is greater than $10^{-9}$ C (chapter 3) so these count rates correspond to anode currents of 0.003 to 0.04 mA which are in the range where gain instability effects are expected to become operative.

As an independent check of the correction factors for the fluorimeter system in the region around 360 nm, a Carl Zeiss Jena 365 nm interference filter with absorbance characteristics as shown in figure 4.12, was used in place of the OX1 and BG12 filters to obtain a calibration for the fluorimeter. The operating conditions are given in table 4.16 and the results in table 4.15 where they are compared with results of OX1 and BG12 scans. The 365IF results are considerably different from the OX1 and BG12 results and the differences increase as the 365IF absorbance increases. A similar trend is observed (table 4.17) with OX1 and BG12 data, with discrepancies increasing at wavelengths where the absorbance of one of the filters starts to increase markedly. It is also worth noting (figure 4.12) that the absorbance of the 365IF filter is higher than the absorbance of the OX1 and BG12 filters throughout the wavelength range 335-400 nm and that the absorbance of the BG12 filter is higher than that of the OX1 filter below 380 nm. It might be expected that there is a greater uncertainty associated with the higher absorbance values; the fact that the absorbance value can affect the results so markedly
Figure 4.12. Absorbance of OX1, BG12 and 365IF filters.

caused us to question the applicability of the Cary 219 absorbance measurements in these experiments*.

* The absorbance of some filters can change depending on the intensity of light (e.g. bleaching), some filters show "inhomogeneous" absorbance characteristics due to small occluded bubbles, some show instability with time of exposure, age, etc., and some fluoresce. OX1 and BG12 filters are very stable (absorbance unchanged in three months), do not fluoresce and, though OX1 filters can contain scattered small bubbles, both filters showed uniform absorbance over their areas (Chance-Pilkington Optical Works, 1962).
Table 4.15 Correction factors (equation 4.7) obtained with Philips lamp C and filters OX1, BG12 and 365IF. Scan identifiers (1), (2), (3) refer to table 4.16

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>OX1 (1)</th>
<th>BG12 (2)</th>
<th>365IF (3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>320</td>
<td>1.00</td>
<td></td>
<td>0.89</td>
</tr>
<tr>
<td>325</td>
<td>1.12</td>
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<td>1.16</td>
</tr>
<tr>
<td>340</td>
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</tr>
<tr>
<td>355</td>
<td>1.18</td>
<td>1.08</td>
<td>1.10</td>
</tr>
<tr>
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<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
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<td>365</td>
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<td>0.93</td>
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<td>0.85</td>
<td>0.91</td>
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</tr>
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<td>375</td>
<td>0.84</td>
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<td>0.75</td>
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<td>380</td>
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<td>0.65</td>
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<td>390</td>
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</tr>
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<td>400</td>
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<td>0.67</td>
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<td>410</td>
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<td>0.70</td>
<td>0.70</td>
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<td>420</td>
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<td>0.81</td>
<td>0.81</td>
</tr>
<tr>
<td>430</td>
<td></td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>I(360)</td>
<td>9081</td>
<td>3130</td>
<td>3614</td>
</tr>
</tbody>
</table>

The 365IF results give no clear indication as to which of the two sets of data (BG12 or OX1) are "better" in the overlap region (350-370 nm) since in this region the 365IF results are an average of the two. If "worse" results are obtained with higher absorbance data then, in obtaining a composite correction curve for the fluorimeter, perhaps the OX1 results should be used up to 380 nm. Table 4.3 indicates there are no problems with overlapping orders to prevent this. Outside the 355-370 nm region, the 365IF values are generally about 0.1 units below the corresponding OX1 or BG12 values. Unfortunately, the 365IF values do not extend very far into the region where the BG12 filter is used. The 365IF data, however, do exhibit the same trend as the OX1-BG12 data, lending some support to the validity of the OX1-BG12 results.
C. LAMP "C"

It was considered that the experimental conditions for the collection of fluorescence spectra could be simulated more closely if the MgO screen was placed within the multi-pass cell and light scattered from a spot in the region of highest concentration of laser excitation light. To this end, the top observation window of the cell was removed and a MgO diffuse reflector suspended in the cell so that the spot formed on the reflector by the tungsten light beam was on the line joining the slots between the collection mirrors*. The operating conditions are given in table 4.16. Two circular apertures (diameters 1.6 mm and 0.08 mm) were deployed alternatively in front of the OX1 or BG12 filter to vary the count rate/spot size on the MgO screen and the sapphire window at E was removed to eliminate any wavelength dependent effects it might introduce**.

Results obtained with the MgO diffuser located within the cell ("MgO internal" results) for six scans are given in table 4.17 and, in composite form, in figure 4.14. The measurements were conducted with a third Philips 7158 lamp, lamp C. This lamp exhibited similar spectral irradiance characteristics to lamps A and B when operated under similar conditions (table 4.13). Table 4.13 indicates that any discrepancy in the irradiance characteristics of lamps A and C was no greater than that between lamps A and B and, in calculating the correction curve using

* It was impossible to locate the spot at the geometric centre of the internal optics of the cell.

** The transmission of the UV grade sapphire of these viewing ports varies linearly in the wavelength range 320-430 nm from about 84% to 87% (Varian Vacuum Division). The window can also act as a lens. All previous calibrations were performed with the cell evacuated.
Figure 4.13. Configuration for use of Philips 7158 lamp C.

Table 4.16. Parameters for use of Philips lamp C. Scans identified as 1, 2, 3 etc. Position of MgO diffuse reflector refers to figure 4.13.

<table>
<thead>
<tr>
<th>Scan</th>
<th>MgO</th>
<th>D</th>
<th>Aperture</th>
<th>Filter</th>
<th>Slits</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>M</td>
<td>206</td>
<td>-</td>
<td>OX1</td>
<td>856x25</td>
<td>27.2</td>
</tr>
<tr>
<td>2</td>
<td>M</td>
<td>206</td>
<td>-</td>
<td>BG12</td>
<td>856x25</td>
<td>16.4</td>
</tr>
<tr>
<td>3</td>
<td>M</td>
<td>132</td>
<td>-</td>
<td>365IF</td>
<td>856x25</td>
<td>22.0</td>
</tr>
<tr>
<td>4</td>
<td>C</td>
<td>135</td>
<td>A₁</td>
<td>OX1</td>
<td>600x25</td>
<td>15.3</td>
</tr>
<tr>
<td>5</td>
<td>C</td>
<td>135</td>
<td>A₁</td>
<td>BG12</td>
<td>600x25</td>
<td>8.5</td>
</tr>
<tr>
<td>6</td>
<td>C</td>
<td>135</td>
<td>A₂</td>
<td>OX1</td>
<td>856x25</td>
<td>15.3</td>
</tr>
<tr>
<td>7</td>
<td>C</td>
<td>135</td>
<td>A₂</td>
<td>BG12</td>
<td>600x25</td>
<td>8.5</td>
</tr>
<tr>
<td>8</td>
<td>C</td>
<td>135</td>
<td>A₁</td>
<td>OX1</td>
<td>856x25</td>
<td>15.3</td>
</tr>
<tr>
<td>9</td>
<td>C</td>
<td>135</td>
<td>A₂</td>
<td>BG12</td>
<td>856x25</td>
<td>15.3</td>
</tr>
</tbody>
</table>

a Position of MgO diffuse reflector
b Distance D of figure 4.13(cm)
c Apertures A₁: 1.6 mm diameter; A₂: 0.8 mm diameter
d Slit widths(µ) x slit heights(mm)
e Collection time(s)
Figure 4.14. Correction curve (in terms of wavenumber) for fluorimeter system obtained with MgO reflector in cell and with lamp C.

Figure 4.15. Correction curve (in terms of wavelength) for fluorimeter system obtained with MgO reflector in cell and with lamp C.
data obtained with lamp C, the calibration data obtained by NML for lamp A were used without adjustment.

Table 4.17 Correction factors for fluorimeter (equation 4.7) obtained with Philips lamp C and the MgO diffuse reflector inside the multi-pass cell. Scan identifiers refer to table 4.16

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>OX1 Scan 4</th>
<th>OX1 Scan 6</th>
<th>OX1 Scan 8</th>
<th>BG12 Scan 5</th>
<th>BG12 Scan 7</th>
<th>BG12 Scan 9</th>
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<td>0.93</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>320</td>
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<td>1.06</td>
<td>1.05</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>325</td>
<td>1.28</td>
<td>1.21</td>
<td>1.17</td>
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<td></td>
</tr>
<tr>
<td>330</td>
<td>1.37</td>
<td>1.31</td>
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<tr>
<td>335</td>
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<td>1.40</td>
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</tr>
<tr>
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<td>0.99</td>
<td>1.01</td>
</tr>
<tr>
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<td>1.22</td>
<td>1.11</td>
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<td>1.12</td>
</tr>
<tr>
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<td>1.14</td>
<td>1.13</td>
<td>1.08</td>
<td>1.09</td>
<td>1.11</td>
</tr>
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<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>365</td>
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<td>0.92</td>
<td>0.94</td>
<td>0.93</td>
<td>0.97</td>
</tr>
<tr>
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<td>0.84</td>
<td>0.86</td>
<td>0.87</td>
<td>0.88</td>
</tr>
<tr>
<td>375</td>
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<td>0.79</td>
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<tr>
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<td>0.75</td>
<td>0.75</td>
<td>0.75</td>
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<tr>
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<td>0.69</td>
<td>0.69</td>
<td>0.70</td>
</tr>
<tr>
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<td>0.60</td>
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<td>0.66</td>
<td>0.66</td>
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<td>0.64</td>
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<td>0.64</td>
<td>0.64</td>
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<td>0.65</td>
<td>0.68</td>
<td>0.69</td>
<td>0.68</td>
</tr>
<tr>
<td>415</td>
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<td>0.68</td>
<td>0.73</td>
<td>0.73</td>
<td>0.73</td>
</tr>
<tr>
<td>420</td>
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<td>0.73</td>
<td>0.89</td>
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<td>0.80</td>
</tr>
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<td>0.89</td>
<td>0.88</td>
<td>0.88</td>
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<tr>
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<td>0.88</td>
<td>0.89</td>
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<td></td>
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<tr>
<td>I(360)</td>
<td>10263</td>
<td>5280</td>
<td>19374</td>
<td>3040</td>
<td>806</td>
<td>3221</td>
</tr>
</tbody>
</table>

The "MgO internal" results differ significantly from the results obtained with the MgO reflector outside the cell. This difference can perhaps be attributed to variations in the transmission and refractive index of the sapphire window with wavelength, the operation of different chromatic aberration effects, particularly with lens L1, and the absence
of reflections between mirrors in the "MgO internal" measurements. Different chromatic aberration effects could apply for the different locations of the MgO reflector. With the MgO screen outside the cell, the tungsten lamp light passing through the cell is restricted to a narrow beam passing through the centre of lens \( L_1 \) and chromatic (and other) aberration effects, especially in lens \( L_1 \), are reduced; with the MgO screen inside the cell the tungsten lamp light radiates out from a point and chromatic aberration effects may be more significant. It has already been demonstrated, (figure 4.9), that chromatic aberration effects in lenses of the fluorimeter system have a pronounced effect on the spectral response of the system. Multiple reflections between the pairs of Welsh collection mirrors are possible for the experiments performed with the MgO screen located outside the cell and this may contribute a wavelength dependent factor. (Reflectivity data for the mirrors are not available). This factor could also cause some irreproducibility between scans since the magnitude of the effect would depend critically on the direction of the light beam through the cell. Use of a chemical standard as standard source would obviate this difficulty. For the corrected spectra reported in this work, the correction curve obtained with lamp C and with the MgO reflector inside the cell, figure 4.14, was used. The corresponding correction curve for spectra plotted on a wavelength scale, \( \text{corr}(\lambda) \) (equation 4.8), is given in figure 4.15.

4.4 VALIDATION OF METHOD

Since there was some doubt as to the applicability of the absorbance values obtained with the Cary 219 spectrometer to the calibration, "system-derived" absorbances in the range 310-430 nm were obtained for the OX1 and BG12 filters by using the fluorimeter with the scanning Spex
spectrometer used in first order. Relative intensities obtained with and without the filters in the optical path were compared using the configuration of figure 4.13 with the MgO reflector in the cell (position C). If the intensity of the tungsten lamp light source at wavelength $\lambda$ is represented by $T(\lambda)$, the relative intensity measured by the fluorimeter system by $\text{FLS}(\lambda)$ when either the OX1 or BG12 filter is inserted in the optical path and by $\text{SYS}(\lambda)$ in the absence of filters then

$$T(\lambda) = a\text{SYS}(\lambda) = \beta 10^{\text{A}(\lambda) \text{FLS}(\lambda)}$$  \hspace{1cm} (4.9)

where $a$ and $\beta$ are constants and $\text{A}(\lambda)$ is the absorbance at wavelength $\lambda$. Constants $a$ and $\beta$ depend in a sense on the geometry of the system, i.e. on how much of the tungsten lamp radiation is captured by the fluorimeter, are independent of wavelength but differ from one scan to the next. To obtain a measure of $\text{A}$ using the fluorimeter it is necessary to set the absorbance of the filter at some wavelength ($\lambda'$) in the wavelength range to obtain $a/\beta$ viz:

$$a/\beta = 10^{\text{A}(\lambda') \text{FLS}(\lambda')/\text{SYS}(\lambda')}$$

The "system-derived" value for the absorbance of the filter at wavelength $\lambda$ relative to its value at $\lambda'$ is then

$$\text{A}(\lambda) = \log_{10}(a/\beta)[\text{SYS}(\lambda)/\text{FLS}(\lambda)]$$  \hspace{1cm} (4.10)

Two series of scans were performed (table 4.18) giving four possible sets of "system-derived" absorbance values for the OX1 and BG12 filters. The absorbances of the OX1 and BG12 filters as determined by the fluorimeter system are presented in tables 4.19 and 4.20 where they are compared with the Cary 219 values. Results for all the scans are reproduced here to
show the magnitude of the discrepancies observed between different though essentially identical* runs. These discrepancies may be taken as indicative of the variability to be expected in correction factors (and other results) obtained from different scans due to uncontrollable effects such as fluctuations in tungsten lamp irradiance and in the PMT gain.

Table 4.18 Operating conditions for determination of relative absorbances of OX1 and BG12 filters using Philips 7158 lamp C. MgO reflector in cell, D = 135 cm (figure 4.13).

<table>
<thead>
<tr>
<th>Scan</th>
<th>Aperture(^a)</th>
<th>Filter</th>
<th>Slits(^b)</th>
<th>Time(^c)</th>
</tr>
</thead>
<tbody>
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<td>(i)</td>
<td>A(_1)</td>
<td>None</td>
<td>856 x 25</td>
<td>15.3</td>
</tr>
<tr>
<td>(ii)</td>
<td>A(_1)</td>
<td>OX1</td>
<td>856 x 25</td>
<td>15.3</td>
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<tr>
<td>(iii)</td>
<td>A(_1)</td>
<td>BG12</td>
<td>856 x 25</td>
<td>15.3</td>
</tr>
<tr>
<td>(iv)</td>
<td>A(_2)</td>
<td>None</td>
<td>856 x 25</td>
<td>15.3</td>
</tr>
<tr>
<td>(v)</td>
<td>A(_2)</td>
<td>OX1</td>
<td>856 x 25</td>
<td>29.1</td>
</tr>
<tr>
<td>(vi)</td>
<td>A(_2)</td>
<td>BG12</td>
<td>856 x 25</td>
<td>29.1</td>
</tr>
</tbody>
</table>

\(^a\) Apertures A\(_1\): 1.6 mm diameter; A\(_2\): 0.8 mm diameter.

\(^b\) Slit widths (µ) x slit heights (mm).

\(^c\) Collection time (s).

The excellent agreement between Cary 219 and system-derived absorbance values even at high absorbance values evident from tables 4.19 and 4.20 indicate that the use of the Cary 219 values is quite valid in computing fluorimeter calibration factors and confirm the validity of

* The only differences between runs, (apart from presumably slightly different parts of the filters and the MgO screen being irradiated), are the apertures (table 4.18).
### Table 4.19
Correlation of fluorimeter system-derived and Cary 219-determined absorbance values for OX1 filter. "Combination" refers to Table 4.18.

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Cary 219</th>
<th>Combination (iv) &amp; (ii)</th>
<th>Combination (i) &amp; (ii)</th>
<th>Combination (iv) &amp; (v)</th>
<th>Combination (i) &amp; (v)</th>
</tr>
</thead>
<tbody>
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<td>0.47</td>
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</tr>
<tr>
<td>315</td>
<td>0.28</td>
<td>0.32</td>
<td>0.37</td>
<td>0.38</td>
<td>0.43</td>
</tr>
<tr>
<td>320</td>
<td>0.23</td>
<td>0.28</td>
<td>0.31</td>
<td>0.32</td>
<td>0.35</td>
</tr>
<tr>
<td>325</td>
<td>0.20</td>
<td>0.21</td>
<td>0.24</td>
<td>0.26</td>
<td>0.29</td>
</tr>
<tr>
<td>330</td>
<td>0.17</td>
<td>0.19</td>
<td>0.22</td>
<td>0.21</td>
<td>0.24</td>
</tr>
<tr>
<td>335</td>
<td>0.16</td>
<td>0.16</td>
<td>0.19</td>
<td>0.17</td>
<td>0.20</td>
</tr>
<tr>
<td>340</td>
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<td>0.17</td>
<td>0.17</td>
<td>0.18</td>
</tr>
<tr>
<td>345</td>
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<td>0.14</td>
<td>0.15</td>
<td>0.15</td>
<td>0.16</td>
</tr>
<tr>
<td>350</td>
<td>0.13</td>
<td>0.13</td>
<td>0.13</td>
<td>0.12</td>
<td>0.12</td>
</tr>
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<td>0.13</td>
<td>0.13</td>
<td>0.13</td>
</tr>
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<td>0.12</td>
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</tr>
<tr>
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<td>0.12</td>
<td>0.13</td>
</tr>
<tr>
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<td>0.14</td>
<td>0.13</td>
<td>0.14</td>
</tr>
<tr>
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<td>0.23</td>
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<td>0.21</td>
</tr>
<tr>
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<td>0.35</td>
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<td>0.34</td>
</tr>
<tr>
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<tr>
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### Table 4.20
Correlation of fluorimeter system-derived and Cary 219-determined absorbance values for BG12 filter. "Combination" refers to Table 4.18.

<table>
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<tr>
<th>Wavelength (nm)</th>
<th>Cary 219</th>
<th>Combination (i) &amp; (iii)</th>
<th>Combination (iv) &amp; (iii)</th>
<th>Combination (iv) &amp; (vi)</th>
<th>Combination (i) &amp; (vi)</th>
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<td>0.17</td>
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<td>0.22</td>
<td>0.17</td>
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<td>0.14</td>
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<td>0.18</td>
<td>0.14</td>
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<td>0.24</td>
<td>0.20</td>
<td>0.17</td>
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<tr>
<td>430</td>
<td>0.23</td>
<td>0.23</td>
<td>0.27</td>
<td>0.22</td>
<td>0.18</td>
</tr>
</tbody>
</table>
the method adopted for obtaining the calibration factors. Discrepancies that occur are at wavelengths where the tungsten lamp intensity and count rates are lower and not necessarily where absorbance of the filter employed is relatively high. That the extent of agreement between the Cary 219 and system-derived absorbance values varies markedly at some wavelengths illustrates the occurrence of fluctuations in the system. It has already been stressed that the average anode current of the PMT and recent usage of the PMT can influence its gain significantly (though photon counting reduces this effect (Coates, 1975)). Lamp instabilities, changes in beam position on the MgO screen, etc. may also contribute to the variability in the absorbance results determined from different runs.

Differences in fluorimeter correction factors, obtained in different runs but under essentially identical conditions, may also be due to the same fluctuations in the system, the most important of which are probably fluctuations in PMT gain induced by different prevailing and/or preceding anode currents. The greater fluctuations (between different runs and within a single run) in results obtained using photocurrent measurement (table 4.5) than in results obtained using photon counting is evidence that fluctuations in PMT gain contribute to variations in results obtained from different runs (and different lamps) and to the discrepancies observed between OX1 and BG12 results in the wavelength region of overlap.

4.5 APPLICATION OF FLUORIMETER CALIBRATION TO SVL SPECTRA

Table 4.21 presents a summary of the fluorimeter correction factors (with estimated uncertainties) obtained with Philips 7158 lamps A, B and C. The major contribution to the uncertainty comes from the relative
spectral irradiance data for the tungsten lamps*. The other sources of uncertainty included in the estimation are the Poisson error in the "counts" recorded** and the uncertainty in the absorbance measurement. The scatter in the results used to form the average values of table 4.21 was used as an estimate of the uncertainty where it exceeded the Poisson error. It should be remembered that the correction factors were obtained by normalising measured lamp intensities to a value of 100 at 360 nm so that OX1 and BG12 data could be combined*** and that differences of up to 6% were observed between individual OX1 and BG12 results in the overlap region (lamp A: 335-365 nm, 5%; lamp B: 355-365 nm, 3%; lamp C: 355-380 nm, 6%).

Table 4.21 also gives the maximum percentage deviation between correction factors obtained with the MgO reflector inside and outside the cell. Differences of +7% at 320 nm and -15% at 430 nm mean that the correction curves obtained differ by as much as 22%. As explained, the values obtained with the MgO reflector inside the cell are considered to be more nearly correct. That such considerable discrepancies are observed in the results obtained by the two methods demonstrates (a) the necessity of carrying out calibrations of this sort in such a way as to simulate the conditions of fluorescence spectra collection as closely as possible.

* The data used strictly only applied to lamp A but differences in the spectral distribution of the lamps was less than 3% (table 4.13).

** Estimated without taking account of computer smoothing; see footnote p. 152

*** Since the intensity measured at 360 nm was lower for BG12 data, normalisation to the value at 360 nm gave a greater contribution to the uncertainty in BG12 values (~ +3%) than with OX1 values (+1%).
possible* and (b) the desirability of having a vapour phase chemical standard.

Table 4.21 Summary of the fluorimeter correction factors** (equation 4.7) obtained with three Philips Type 7158 tungsten filament quartz-halogen lamps: A, B, C. Percentage uncertainty in parentheses.

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>MgO &quot;external&quot;***</th>
<th>MgO &quot;internal&quot;</th>
<th>Deviation(^e) (percentage)</th>
</tr>
</thead>
<tbody>
<tr>
<td>320</td>
<td>1.08(14)</td>
<td>1.04(14)</td>
<td>1.00(12)</td>
</tr>
<tr>
<td>330</td>
<td>1.28(13)</td>
<td>1.26(11)</td>
<td>1.24(11)</td>
</tr>
<tr>
<td>340</td>
<td>1.32(11)</td>
<td>1.31(9)</td>
<td>1.28(10)</td>
</tr>
<tr>
<td>350</td>
<td>1.21(8)</td>
<td>1.20(7)</td>
<td>1.19(8)</td>
</tr>
<tr>
<td>360</td>
<td>1.00(6)</td>
<td>1.00(6)</td>
<td>1.00(6)</td>
</tr>
<tr>
<td>370</td>
<td>0.88(9)</td>
<td>0.87(7)</td>
<td>0.91(7)</td>
</tr>
<tr>
<td>380</td>
<td>0.78(8)</td>
<td>0.77(6)</td>
<td>0.80(6)</td>
</tr>
<tr>
<td>390</td>
<td>0.68(7)</td>
<td>0.69(5)</td>
<td>0.69(6)</td>
</tr>
<tr>
<td>400</td>
<td>0.66(7)</td>
<td>0.67(5)</td>
<td>0.67(6)</td>
</tr>
<tr>
<td>410</td>
<td>0.71(6)</td>
<td>0.70(4)</td>
<td>0.71(5)</td>
</tr>
<tr>
<td>420</td>
<td>0.82(6)</td>
<td>0.82(4)</td>
<td>0.81(5)</td>
</tr>
<tr>
<td>430</td>
<td>1.01(6)</td>
<td>1.02(5)</td>
<td>1.00(5)</td>
</tr>
</tbody>
</table>

** OX1 values 320-360 nm; BG12 values 360-430 nm.
*** i.e. results obtained with the MgO diffuse reflector outside vs. inside (MgO "internal") the multi-pass cell.
\(a\) From table 4.10 ((i), (iii), (iv).
\(b\) From table 4.14
\(c\) From data in table 4.13
\(d\) From table 4.17

Figures 4.16-4.23 demonstrate the effect of correcting spectra for the response of the fluorimeter. These spectra will be referred to in chapter 6 when considering Franck-Condon factors. Table 4.22 explains the nature of the correction applied in each of these figures. In table 4.22, spectrum \(0^0\) is from the \(0^0\) level of pyrimidine-d\(_4\) at 0.017 torr and spectrum \(12^1\) is from the \(12^1\) level of pyrimidine-d\(_4\) at 0.067 torr. The fluorescence excitation and collection bandpasses were 0.4 cm\(^{-1}\) and 13-20 cm\(^{-1}\) respectively for both spectra.

* Use of a fluorescent solution or solid as reference will not suffice for example.
Figure 4.16. Fluorescence from the $0^0$ level of pyrimidine-$d_4$ at 0.017 torr. No correction (see table 4.22).
Figure 4.17. Fluorescence from the $0^0$ level of pyrimidine-$d_4$ at 0.017 torr. Partly corrected (see table 4.22).
Figure 4.18. Fluorescence from the $0^0$ level of pyrimidine-\textsubscript{d\textsubscript{4}} at 0.017 torr. Corrected (see table 4.22).
Figure 4.19. Fluorescence from the $0^0$ level of pyrimidine-$d_4$ at 0.017 torr. No correction (see table 4.22).
Figure 4.20. Fluorescence from the \( 0^0 \) level of pyrimidine-\( d_4 \) at 0.017 torr. Corrected (see table 4.22).
Figure 4.21. Fluorescence from the $12^1$ level of pyrimidine-$d_4$ at 0.067 torr. No correction (see table 4.22).
Figure 4.22. Fluorescence from the $12^1$ level of pyrimidine-$d_4$ at 0.067 torr. Partly corrected (see table 4.22).
Figure 4.23. Fluorescence from the $12^1$ level of pyrimidine-$d_4$ at 0.067 torr. Corrected (see table 4.22).
Table 4.22 Corrections applied in obtaining the spectra of pyrimidine-d₄ in figures 4.16-4.23

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>NSMᵃ</th>
<th>Abscissaᵇ</th>
<th>Correctionᶜ</th>
<th>Figure</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-0</td>
<td>3</td>
<td>(\bar{\nu})</td>
<td>None</td>
<td>4.16</td>
</tr>
<tr>
<td>0-0</td>
<td>3</td>
<td>(\bar{\nu})</td>
<td>(\lambda^2)</td>
<td>4.17</td>
</tr>
<tr>
<td>0-0</td>
<td>3</td>
<td>(\bar{\nu})</td>
<td>corr((\bar{\nu}))(\lambda^2)</td>
<td>4.18</td>
</tr>
<tr>
<td>0-0</td>
<td>3</td>
<td>(\lambda)</td>
<td>None</td>
<td>4.19</td>
</tr>
<tr>
<td>0-0</td>
<td>3</td>
<td>(\lambda)</td>
<td>corr((\lambda))</td>
<td>4.20</td>
</tr>
<tr>
<td>12¹</td>
<td>3</td>
<td>(\bar{\nu})</td>
<td>None</td>
<td>4.21</td>
</tr>
<tr>
<td>12¹</td>
<td>3</td>
<td>(\bar{\nu})</td>
<td>(\lambda^2)</td>
<td>4.22</td>
</tr>
<tr>
<td>12¹</td>
<td>3</td>
<td>(\bar{\nu})</td>
<td>corr((\bar{\nu}))(\lambda^2)</td>
<td>4.23</td>
</tr>
</tbody>
</table>

ᵃ Number of points in moving point averaging scheme.
ᵇ Intensity/unit wavelength (\(\lambda\)) or wavenumber (\(\bar{\nu}\)).
ᶜ \(\lambda^2\) implies a spectrum recorded directly as dQ/d\(\lambda\), corrected for the changing bandpass in terms of wavenumber and plotted as dQ/d\(\bar{\nu}\); corr(\(\bar{\nu}\))\(\lambda^2\) implies a completely corrected dQ/d\(\bar{\nu}\) spectrum; corr(\(\lambda\)) implies a corrected dQ/d\(\lambda\) spectrum.

4.6 CONCLUDING REMARKS

The extensive detail of this chapter has stemmed from the need to account for the difference between the obtained and the expected spectral response of the fluorimeter, the need to come to terms with discrepancies in results obtained under slightly different experimental conditions and the necessary use of several lamps which had not been calibrated directly. The results have been verified to some extent by (i) showing that the difference between the obtained and expected calibration curves can be attributed to individual optical components of the system, (ii) showing that similar results are obtained when a different filter is used to shield the PMT from overlapping second and fourth order light, and (iii) by showing that excellent values for the relative absorbance of two filters employed in the experiments could be obtained using the same methods as used in arriving at the calibration curves.
Several general results arise from the investigation. A number of these were expected but had to be confirmed for the system nevertheless. Consistent with the finding that PMT gain stability could only be ensured by maintaining a low and relatively constant anode current was the observation that results obtained using photon counting displayed fewer fluctuations than those obtained by photocurrent measurement. It was shown that, apart from having too short a lifetime, cheap projector lamps can serve as satisfactory irradiance standards and that similar lamps show very similar spectral irradiance characteristics. The extent to which it is necessary to simulate the conditions of fluorescence collection in fluorimeter calibration was examined; chromatic aberration effects of lenses were found to markedly influence the spectral response of the fluorimeter; and the desirability of using a chemical standard for effecting fluorimeter calibrations was indicated. Associated with the use of tungsten lamps for this type of calibration is the inconvenience of overlapping orders of light with grating instruments and the difficulty of maintaining similar anode currents to avoid fluctuations in PMT gain throughout the wavelength range of calibration. Though the spectral irradiance of the 150 W lamps used increases by a factor of about eleven between 320 and 430 nm, when coupled with the spectral response of the system this amounted to a twenty-one-fold increase in count rate between 320 and 430 nm. Since the collection time (15.3 s dwell time) required for the data of a single calibration (i.e. one OX1 scan plus one BG12 scan) curve is about five hours for the calibrations described herein, use of much lower count rates to ensure suitably low anode currents is not very feasible (6 Å is the maximum step size available). The use of more robust lamps than the Philips 7158 lamp is certainly recommended (e.g. coiled-coil type having a design life of 500
hours) and perhaps use of lamps more powerful than 150 W, to enhance the output in the ultraviolet, should be considered. The 250 W Philips 7748 projector lamp would provide higher ultraviolet output but, like the Philips 7158 lamp, has an average life of only 50 hours. A 200 W 8.33 A G.E.C. lamp with a much higher design life is recommended.
CHAPTER 5

INTERPRETATION AND APPLICATIONS OF SVL FLUORESCENCE SPECTRAL MEASUREMENTS

The term "SVL fluorescence" as used in this thesis is defined and the molecular properties necessary for a SVL fluorescence study are considered. Applications of SVL fluorescence spectral measurements in elucidating details of the electronic spectroscopy of polyatomic molecules and in probing excited state nonradiative processes are surveyed. The principles for interpreting the vibrational structure and intensity distribution in SVL fluorescence spectra are considered, especially those required in the analysis of the SVL fluorescence spectra of pyrimidine.
5.1 INTRODUCTION

Though single vibronic level (SVL) fluorescence experiments are a direct probe of excited state photophysical processes intrinsic to a molecule, they have only become feasible in the past decade with the resolution of formidable experimental difficulties, principally the quantitative detection of low intensity fluorescence generated by small concentrations of excited state molecules. Experimental facilities have been improved since about 1970 with the introduction of tunable lasers and improvements in detectors and electronics to the extent that now selected rotational levels may be populated and probed, further advances being restricted to some extent by the overlap of rotational bands, a molecular property. Molecular beam studies perhaps may circumvent this difficulty.

Interest in SVL fluorescence studies was stimulated not so much by spectroscopists as by those interested in radiationless transitions in excited electronic states and their desire to establish that such processes could occur in the isolated molecule. (Even the basic association of internal conversion (IC) and intersystem crossing (ISC) with isolated molecule behaviour occurred only since about 1965). Information on the properties of excited electronic states had to be derived from condensed phase or "high" pressure gas phase systems where close interactions of the probed molecule and its environment bring about a superposition of intramolecular and environmental (intermolecular) effects which are difficult, if not impossible, to separate. In these systems, emission occurs from molecules that have been brought into "thermal" equilibrium and information about higher vibronic levels is lost. The low pressure gas phase alone provides a medium for observing properties intrinsic to the isolated molecule, for examining strictly intramolecular contributions to excited
state relaxation and for obtaining emission from higher vibronic levels. Because of the rapidity of non-radiative processes in electronic states higher than the first excited singlet state ($S_1$), fluorescence can generally be used to monitor these processes only in $S_1$.

The study of radiative decay following excitation of SVL's in $S_1$ takes three basic forms. (i) Fluorescence lifetimes can be measured very accurately and, in combination with less reliable quantum yield measurements (ii), provide absolute rate constants for radiative and non-radiative decay in the isolated molecule for different vibronic levels. Monitoring the changes in the yields and lifetimes as gas pressure increases provides a means of studying collision induced relaxation. (iii) The vibrational structure of the fluorescence spectrum can be recorded and information derived from this structure. For convenience, this will be referred to as SVL fluorescence spectral studies. Monitoring changes in the structure with increasing gas pressure gives information on nonradiative relaxation processes. This and the following two chapters will be concerned with selected vibronic level spectral measurements in pyrimidine-$h_4$ and $-d_4$.

5.2 REQUIREMENTS FOR A SVL FLUORESCENCE EXPERIMENT

Strictly applied, the term single vibronic level fluorescence implies emission from molecules isolated from all environmental perturbations between the time of their excitation to a specific vibronic level and the time of their radiative decay from the initially prepared level. The term tends to be applied rather liberally in the case of polyatomics. Intra-molecular vibrational relaxation and radiationless transitions between different electronic states is possible for some molecules even under
isolated molecule conditions; useful data are obtained, and even sought, following the onset of collisional interactions; exclusive population of a single vibronic level can be impossible because of congestion in the absorption spectrum of the probed molecule; in all three cases the term is applied.

Interactions with other gaseous molecules are the environmental perturbations that need to be reduced to an insignificant level for the time that the molecule is in the excited state before it fluoresces if true isolated molecule behaviour is to be observed. The pressures at which these perturbations are effectively eliminated depend on the lifetime of the excited vibronic state and the effective collision cross section for various relaxation processes induced by intermolecular interactions. Radiationless transitions induced in this way can have very large cross sections since only very small perturbations may be necessary to couple near-resonant vibronic levels of different electronic states (e.g. $S_1$ and $S_0$, $S_1$ and $T$). It is vibrational rearrangement, however, which changes the vibrational structure of the fluorescence spectrum and even for this process effective collision cross sections can be larger than gas kinetic. To avoid any of these quenching or rearrangement processes, intermolecular perturbations must be reduced to a level equivalent to less than the average matrix element for intramolecular coupling processes. For benzene, it has been estimated [Robinson, 1967] that pressures of less than $10^{-3}$ torr, corresponding to average collisional interaction energies of $10^{-5}$ cm$^{-1}$, are required; it is found that benzene quantum yields are constant only below pressures of $10^{-2}$ torr [Parmenter and White, 1969]. From a practical viewpoint, a molecule should not have too long a lifetime so that isolated molecule fluorescence studies can be done at reasonable pressures. There is still considerable conjecture as to when a molecule
is truly isolated and the subject has been discussed in chapter 2.

Exclusive excitation of single vibronic levels is impossible if the absorption spectrum does not contain discrete vibrational structure. The most complicated vibrational features arise from sequence bands. Sequence bands are usually formed by low-frequency modes and several members of a sequence often appear attached to the main progression bands. The number of modes involved in sequences increases rapidly with molecular size (e.g. benzene:1, naphthalene:8 [Blondeau and Stockburger, 1971b]). The rotational profiles of different sequence bands then overlap to form a background beneath the sharp structure. Byrne and Ross (1965, 1971) have considered sequence congestion in absorption spectra and the occurrence of sharp absorption structure. Only transitions to the lowest excited singlet state ($S_1$) are found to give rise to sharp absorption spectra, if any sharp structure is observed at all. Stockburger (1973) considered the implications for fluorescence spectra of complicated vibrational structure and sequence background in the absorption spectrum and suggested a classification of molecules into three groups according to the properties of the $S_1$ absorption spectrum.

For benzene, only one mode is active in forming sequence bands of appreciable intensity and parent and sequence bands can be pumped without mutual interference. If a "discrete" band which is superimposed on a sequence background is irradiated, however, not only the vibronic level corresponding to the discrete band is excited but, due to the background, many other levels related to higher overlapping members of different sequences are also excited. The fluorescence will then exhibit "sharp" structure correlated with the discrete component of the absorption band and a diffuse background arising from the background on which the discrete
absorption is built. This behaviour would not change no matter how narrow
the excitation bandwidth and thus molecules of this kind, though
exhibiting structured fluorescence spectra, cannot exhibit pure SVL
fluorescence as strictly defined. Illustrative of these molecules are
the xylenes with the intensity of the background in fluorescence spectra
proportional to the background fraction of the absorption band [Blondeau
and Stockburger, 1971].

The density of vibrational levels in an electronic state of a "large"
polyatomic molecule increases almost exponentially with energy [Byrne and
Ross, 1971]; therefore even molecules of medium size such as naphthalene
and aniline manifest the sequence congestion of higher $S_1$ absorption bands
in increased background in fluorescence spectra originating from higher
vibronic levels, while displaying discrete fluorescence structure devoid
of significant background when excited to vibronic levels near the origin
[Blondeau and Stockburger, 1971; Quack and Stockburger, 1972].

From calculations of the density of sequence bands [Byrne and Ross,
1965], molecules of the size of tetracene are expected to show irresolvably
crowded absorption spectra while molecules of the size of anthracene and
phenanthrene should show sequence structure in absorption and hence
structured fluorescence when excited near the origin. This has been con-
firmed in the case of anthracene, fluorescence bands superimposed on a
diffuse background being observed as long ago as 1938 when the 0-0 band
was excited with a Cd line source [Pringsheim, 1938]. Thus, only a limited
number of organic molecules which do not exceed a certain size will
produce structured fluorescence spectra and still fewer are suitable for
SVL fluorescence studies. While sharp structure in absorption is necessary
for the observation of sharp features in fluorescence, it does not guarantee
it. In molecules like phenanthrene, apart from the sequence congestion inherent at room temperature, their low vapour pressure necessitates the use of high temperatures to obtain adequate pressure which creates additional sequence congestion by intensifying higher sequence members so that structure may be washed out entirely. For example, vibrational structure in the absorption spectrum of naphthalene is completely eliminated at 480 K [Byrne and Ross, 1971].

For absorption bands of molecules such as benzene where sequence congestion is not a problem, the exclusive excitation of single vibronic levels may still be impossible if the rotational substructure of neighbouring vibronic bands overlap. Because the rotational constants of aromatic hydrocarbons and related molecules are so small (\( \sim 0.1 \text{ cm}^{-1} \)), individual rotational lines are crowded together to the point of being more closely spaced than their own Doppler determined line widths (\( \sim 0.02 \text{ cm}^{-1} \)) and therefore individual lines cannot be resolved [Ross, 1971]. Every vibrational band, however, has a well defined rotational contour of width and shape dependent on such factors as the polarization of the band, the change in the rotational constants upon excitation and the principal moments of inertia of the molecule. In general, these contours have peaks or band termini of widths of the order of 1 cm\(^{-1}\) but extend over some tens of cm\(^{-1}\) [McHugh and Ross, 1970; Ross, 1971]. For example, in the \(^1B_{2u} - ^1A_{1g}\) absorption spectrum of benzene vapour, the unresolved rotational structure associated with each vibrational band extends with steadily decreasing intensity for about 60 cm\(^{-1}\) to the red from a sharp band edge and these rotational tails overlap each other throughout the entire spectrum [Parmenter et al., 1976]. Though excitation into such regions does not conform to a literal definition of a SVL fluorescence...
experiment, it has been demonstrated that much useful information is obtained even when less than 50% of the exciting radiation populates a particular SVL [Atkinson et al., 1974].

There are other desirable properties of a molecule for a SVL fluorescence spectral study apart from the necessity of having a discrete absorption spectrum. It assists if the absorption spectrum of the molecule is sufficiently well assigned for the precise vibrational content of the terminating level to be known. A complete assignment is not essential and indeed this has only been achieved for a few large polyatomic molecules with the assistance of SVL fluorescence spectroscopy [Ross, 1971 and, for example, Knight, Parmenter and Schuyler, 1975a,b; Atkinson and Parmenter, 1978a,b,c]. The extinction coefficient of the band excited should be large enough for adequate absorption to occur at reasonable pressures (≈0.1 torr), within an absorption path length of reasonable dimensions. The fluorescence lifetime of the isolated molecule should be sufficiently short so that isolated molecule behaviour is approached at reasonable pressure. The vapour pressure of the molecule should be sufficiently high to enable spectra to be measured and self quenching behaviour to be monitored without heating the sample. Ideally, the molecule should have a high quantum yield (≥0.1) so that fluorescence can be detected at low pressures. Finally, the molecule should have theoretical accessibility by reason of symmetry or small size so that data obtained are useful in guiding theory. Several authors have identified most of the requirements for SVL fluorescence spectra listed in the preceding paragraphs [e.g., Parmenter, 1972a,b].

The benzene molecule fulfils the above requirements to a large extent and has been the molecule most intensively scrutinized by the SVL
fluorescence technique. Since the Parmenter and Stockburger groups demonstrated the feasibility of SVL fluorescence spectral studies, interest in the field has broadened. Almost every suitable molecule has received attention and the topic has been the subject of several reviews [Parmenter, 1972a,b; Stockburger, 1973; Atkinson, Parmenter and Schuyler, 1974]. Recently SVL fluorescence spectral work has been used to probe more detailed aspects of spectroscopy and photophysics such as the operation of Franck-Condon factors in large molecules [Parmenter, Tang and Ware, 1976], vibronic coupling in molecules such as isoquinoline [Fischer and Knight, 1976], the pattern of vibrational energy flow in $S_1$ [Atkinson, Parmenter and Tang, 1979], and rotational relaxation in large polyatomic molecules [Coveleskie and Parmenter, 1978]. Improved technology, particularly that of lasers, has made this possible.

5.3 APPLICATIONS OF SVL FLUORESCENCE SPECTRAL MEASUREMENTS

There are two basic motives for the study of SVL fluorescence spectra:

(I) to elucidate the electronic spectroscopy of polyatomic molecules, and

(II) to probe excited state nonradiative processes either intrinsic to the molecule or induced as an increase in pressure takes the molecule out of isolation.

I. SVL fluorescence spectral studies can lead to an improved understanding of the $S_1-S_0$ spectroscopy of a molecule because the structure of SVL fluorescence spectra is generally simpler than that of the corresponding absorption spectrum and because fluorescence can be generated from different upper state ($S_1$) vibronic levels by exciting in different absorption bands. In SVL fluorescence, as in absorption, transition
probabilities are governed by symmetry selection rules and intensities within progressions by the Franck-Condon principle. Unlike absorption, SVL fluorescence originates from an optically prepared single vibronic level and not from a Boltzmann distribution of levels. Consequently, SVL fluorescence spectra have a relatively sparse vibrational structure. Since transitions in SVL fluorescence terminate in vibrational levels of the ground state, the displacements, measured in cm\(^{-1}\), from the excitation line correspond to ground state fundamentals, overtones and combinations. These are usually well established from infrared and Raman spectroscopy and so the assignment of an SVL fluorescence spectrum is usually straightforward [Parmenter and Schuyler, 1969]. Though SVL fluorescence spectra from different vibronic levels are characterised by common displacements, the intensity distributions within progressions give each spectrum a uniqueness, [e.g. Knight et al., 1975a] which, combined with the ability to excite different upper state vibronic levels, gives SVL fluorescence spectra their diagnostic value. Studies of SVL fluorescence spectra can thus provide information on absorption assignments, ground and upper state vibrational frequencies, the activity of vibrations in the \(S_1\)-\(S_0\) transition, vibronic coupling and ground and excited state anharmonic perturbations.

A series of works on benzene illustrates the use of SVL fluorescence spectra in refining absorption spectrum assignments [Parmenter and Schuyler, 1970a; Atkinson, Parmenter and Schuyler, 1971, 1974; Parmenter, 1972a; Knight, Parmenter and Schuyler, 1975a,b]. By examining intensity patterns within progressions and the activity of the various vibrational modes in the two types of spectra, one can check whether the SVL fluorescence spectra are consistent with the originating levels proposed by the absorption spectrum assignments. SVL fluorescence spectra give
more information about energy levels in the ground state than does the absorption spectrum where observation of absorption bands from higher ground state vibrational levels (hot bands) is severely limited by small Boltzmann factors. In addition, if excitation occurs to an electronic state of very different geometry from the ground state, fluorescence may subsequently occur to highly excited levels of the ground electronic state [e.g. in NO₂, Hardwick, 1977], providing information about those levels which would be inaccessible by ordinary infrared or Raman techniques [Hardwick and Till, 1979]. For benzene, Knight et al. (1975b) have used the selection rules and relative intensities gleaned from the analyses of SVL fluorescence spectra from securely assigned levels to clarify the identity of the emitting level in SVL fluorescence spectra resulting from excitation in less securely assigned bands. In this way, 28 transitions in the weaker vibrational structure of the 1B₂u - 1A₁g spectrum were confirmed or newly established and four previously unknown upper state frequencies were obtained bringing the number of secure 1B₂u fundamentals to eleven. Despite the extensive study of the 260 nm absorption spectrum of benzene, many less intense absorption bands remained unassigned even after the 1975 investigation. The SVL fluorescence spectral studies of benzene paved the way for a detailed re-examination of the 260 nm absorption system by Atkinson and Parmenter (1978a,b,c) which led to revised or new values for nine fundamentals in the 1B₂u state and two in the 1A₁g state. Now over 90% of the absorption intensity is securely assigned.

Atkinson, Malstrom and McIlwain (1979a,b) have examined the 1A_u - 1A_g transition in glyoxal in a similar fashion to the treatment of the benzene 1B₂u - 1A₁g transition by Knight et al. (1975a,b). From the
vibronic selection rules and general vibronic activity revealed in the time-resolved SVL fluorescence spectra of the major absorption transitions, absorption and fluorescence activity in less active modes was identified and a value for a $^1A_u$ fundamental established.

Two of the more unusual SVL fluorescence spectral studies directed towards checking absorption assignments and/or providing additional data for ground state vibrational levels are (i) a study of 25 SVL fluorescence spectra of aniline and deuterated anilines from which absorption transitions involving the strongly anharmonic inversion vibration were assigned more securely and an improved value for the barrier height of the double minimum potential for this vibration in the ground state was derived [Quack and Stockburger, 1972]; and (ii) a two-photon excited SVL fluorescence spectral study of benzene which confirmed the assignments of the dominant two-photon absorption progression and the identity of the principal inducing mode [Knight and Parmenter, 1976c]. Implied in every SVL fluorescence spectral study is a confirmation of absorption assignments and further examples of this use of SVL fluorescence spectra are to be found in references cited throughout the remainder of this section.

SVL fluorescence spectra have proven to be very useful in probing ground and excited state anharmonic mixing of vibrational levels. In pyrimidine-$h_4$, Fermi resonances in the ground state between levels $6a_1$ and $16b_2$, proposed from an analysis of hot bands in the $^1B_1 - ^1A_1$ absorption spectrum, [Innes et al., 1969] appear clearly in the SVL fluorescence spectra as multiplet structure ($6a_2...16b_2$ diad; $6a_2...6a_1$; $16b_4$ triad; etc.) [Knight, Lawburgh and Parmenter, 1975]. Fermi resonances in the $^1B_1$ state are confirmed by distorted intensity distributions in SVL fluorescence spectra from many higher levels.
(1^1, 9a^1, 6a^1) which can be explained if the originating levels are of mixed character. In particular, the fluorescence structure generated from exciting each of the two members of the proposed 6a^1...6b^2 Fermi resonance diad could be analysed as a weighted mixture of the vibrational structure predicted from each of the upper state levels in the absence of Fermi resonance [Knight, Lawburgh and Parmenter, 1975]. Innes, Tincher and Pearson (1970) have proposed that a similar anharmonic mixing occurs in pyridazine-\textsubscript{h}_4. The SVL fluorescence spectrum from the more intense component of the proposed 6a^1...16b^2 Fermi diad, however, shows no evidence of being of mixed character with the progression in J\textsubscript{1a} showing the same intensity distribution as in the zero point fluorescence spectrum [Jordan and Parmenter, 1972]. Part of the aim of our SVL fluorescence spectral study of pyrimidine-\textsubscript{d}_4 was an investigation of the Fermi resonances proposed from its absorption spectrum.

In polyatomic molecules, orbitally forbidden electronic transitions can occur by borrowing intensity from an allowed transition via a vibronic coupling mechanism and SVL fluorescence spectral studies can provide a more comprehensive experimental view of this coupling. Herzberg and Teller (1933) recognized two mechanisms of vibronic coupling in their original treatment which was concerned mainly with the vibrational structure of induced spectra. The mechanism based on the breakdown of the Born-Oppenheimer approximation (separability of electronic and nuclear motion), and subsequently termed Born-Oppenheimer (BO) coupling, was considered negligible in quantitative work until a more comprehensive approach was suggested by Orlandi and Siebrand (1972, 1973). The other mechanism arises from deviations from the assumption that the electronic transition dipole is independent of the nuclear coordinates (Condon approximation) and is termed Herzberg-Teller (HT) coupling. Both mechanisms
give rise to the same induced bands in the spectra but, when only one
inducing mode is involved, it should be possible to distinguish between
the two contributions experimentally from absorption-emission asymmetry
and the isotope effect [Orlandi and Siebrand, 1972, 1973]. The relative
importance of the two contributions may be gleaned from examination of
the vibronic intensity distribution in analogous absorption and emission
spectra because the BO matrix element changes sign on going from
absorption to emission but the HT matrix elements do not [Orlandi and
Siebrand, 1972, 1973].

Stockburger, Gattermann and Klusman (1975) have examined the relative
ccontributions of the two mechanisms in naphthalene from SVL fluorescence
spectral studies. Their results suggest that the two contributions
interfere as suggested in the more comprehensive theory of Orlandi and
Siebrand, with the conventional HT mechanism making the dominant contribu-
tion. A striking asymmetry observed between fluorescence and absorption
transitions involving a totally symmetric vibration (band pair $8\frac{1}{2}$ and $8\frac{3}{2}$)
was interpreted by Stockburger et al. (1975) in terms of vibronic
coupling induced by a totally symmetric vibration in which constructive
and destructive interference effects between the orbitally allowed (FC)
component and the vibronically induced (HT) component can lead to absorption-
emission asymmetry [Craig and Small, 1969; Small, 1971].

The $^1B_{2u} - ^1A_{1g}$ radiative transition in benzene has long been
considered a classic example of a vibronically induced transition. The
successful structural analyses of numerous SVL fluorescence spectra of
benzene in terms of first and second order conventional HT theory have been
cited in qualitative support of this theory [e.g. Knight, et al., 1975a,b].
One of the few quantitative tests of vibronic coupling theory in benzene
is the study by Parmenter, Tang and Ware (1976) of band intensities in SVL fluorescence from benzene. The tests derive from comparison of experimental and calculated intensity ratios for transition pairs such as $6\gamma/6\delta$. The authors find that neither vibronic coupling mechanism gives a satisfactory account of intensity ratios unless long-range normal mode mixing of the type described by Fischer, Sharf and Parmenter (1975) is introduced. It is shown that modest anharmonic interactions between levels separated by 121 cm$^{-1}$ and 223 cm$^{-1}$ can produce detectable intensity perturbations when the interactions occur between inducing modes and progression forming modes.

SVL fluorescence spectra have been used to extend the view of the vibronically tangled 3100 Å absorption system of isoquinoline [Fischer and Knight, 1976]. Fischer and Naaman (1976) found that the transition energies and intensities of the 0,0 band group of isoquinoline could be understood in terms of near resonance interactions between two near degenerate electronic states (about 1000 cm$^{-1}$ apart) and that off-resonance contributions could be safely ignored. In contrast to the complex absorption spectrum, Fischer and Knight (1976) found that the SVL fluorescence spectra exhibit discrete, open vibrational structure which can be assigned readily but which shows pronounced deviations from conventional Franck-Condon behaviour. The abnormal intensities provide a basis for development of a more complete view of the interaction spectrum; when a certain number of off-resonance interactions are included in the Fischer-Naaman (1976) model, all the spectral data of the isoquinoline 3100 Å system can be satisfactorily interpreted. The SVL fluorescence spectra also serve to identify the major off-resonance contributions.
The SVL fluorescence spectrum from the $6^1$ level of the $S_1$ state ($1E''$) of $\sigma$-triazine has been used in an investigation of the excited state spectroscopy of $\sigma$-triazine. Because the first excited singlet state of $\sigma$-triazine is orbitally degenerate there is the possibility that Jahn-Teller coupling and vibronic coupling may occur simultaneously. The SVL fluorescence spectrum is found to be relatively simple in contrast to the absorption spectrum which is still largely unassigned; the bulk of the fluorescence vibronic structure can be assigned as first order or second order Herzberg-Teller allowed transitions. Minor structure in the $6^1$ fluorescence spectrum and structure in the fluorescence from other levels, however, cannot be reconciled solely in terms of Herzberg-Teller coupling, suggesting that other mechanisms may be important [Knight and Parmenter, 1979].

SVL fluorescence spectra from different excited states can provide a more extensive view of Franck-Condon factors in a polyatomic molecule than offered by the absorption spectrum. The uniqueness of SVL fluorescence spectra from different vibronic levels results primarily from the operation of the Franck-Condon principle. The key to a description of the vibrational structure is given by applying the Born-Oppenheimer approximation in combination with the harmonic approximation (vibrational motion is resolved into a product of one-dimensional oscillators).* Concepts from diatomic molecular spectroscopy can then be applied in the treatment of the vibrational structure of electronic spectra of polyatomic molecules [Herzberg, 1950, p. 193].

Franck-Condon factors are a function of the change in frequency and in the equilibrium position (displacement) of the normal coordinate between

* The appearance of "forbidden" transitions induced by vibronic coupling of different electronic states and the observation of anharmonicities in the vibrational structure such as Fermi resonances are manifestations of the breakdown of the approximations.
the two electronic states. Henderson et al. (1964a,b), using harmonic oscillator wavefunctions, have tabulated Franck-Condon overlap integrals for various displacements and frequency ratios.

In all spectra, Franck-Condon factors are best examined in progressions where the relative intensities of various members of a progression are governed by the Franck-Condon factors for the totally symmetric progression forming mode. In absorption spectra, progressions in some vibration, X, can generally be observed only from $v''_X = 0$ because the Boltzmann factors are very often too small for hot band transitions from $v''_X = 1, 2, \ldots$ to be seen. In SVL fluorescence spectra, however, various progressions $X_0^n, X_1^n, X_2^n, \ldots$ can be generated by simply tuning to successive progression members, $X_0^n$, in excitation and much of the diagnostic value of SVL fluorescence spectra derives from an analysis of the Franck-Condon factors they provide. The parameters $D(\alpha$ normal coordinate displacement) and $\delta(\alpha(v''/v'))^{1/2}$ obtained by fitting progression envelopes, observed in, say, zero-point fluorescence, to Henderson's tables can be used to predict Franck-Condon factors for progressions developed upon excitation of other levels. Thus analyses of Franck-Condon factors are useful in testing vibronic coupling theories and in identifying vibrational anharmonicities.

For example, the Herzberg-Teller theory prediction that Franck-Condon factors are independent of the inducing mode (e.g. in benzene $6^0_1 1^0_1, 6^1_0 1^0_1, 6^1_2 1^0_2$) for vibronically induced transitions can only be tested in detail in SVL fluorescence spectra [Atkinson et al., 1974; Parmenter et al., 1976]. Inconsistencies in the relative intensities of members of the same progression (e.g. $X_0^n Y_0^n$ vs. $X_0^n Z_1^n$ where $Y_0^n$ and $Z_1^n$ are progression origins) or deviations from the relative intensities predicted for other progressions are often indicative of the operation of anharmonic or
previously unidentified vibronic couplings. For example, anomalous relative intensities in SVL spectra of benzene [Parmenter, Tang and Ware, 1976] and pyrimidine [Knight, Lawburgh and Parmenter, 1975] have been reconciled in terms of anharmonic couplings while deviations from conventional Franck-Condon behaviour in isoquinoline [Fischer and Knight, 1976] led to a more detailed view of vibronic coupling in that molecule.

Parmenter et al. [e.g. Parmenter and Schuyler, 1970a; Knight, Parmenter and Schuyler, 1975a], have given numerous illustrations of the more complete picture of Franck-Condon factors in benzene provided by SVL fluorescence spectra. They have demonstrated that the change in relative intensities of progression members changes dramatically for the series \( 1_0^i, i = 0,1,2 \ldots \) in benzene, with minima appearing in the envelopes \( i > 1 \) and intensities being more widely distributed as \( i \) increases; this is in qualitative agreement with theory. These authors also demonstrate how a knowledge of Franck-Condon factors (e.g. distinctive profile of the above progression types) can be applied in fluorescence analysis, especially where measurements of band positions are not sufficiently precise to allow assignments on the basis of frequency values alone or when the contributions of coincident or nearly coincident bands need to be evaluated quantitatively [e.g. Atkinson, Parmenter and Schuyler, 1971].

From the Franck-Condon principle, a long progression can only occur if the normal coordinate has quite different equilibrium values in the ground and first excited singlet states. Consequently, the intensity distribution within such a progression can yield information on the geometry of the molecule in the excited state. From a Franck-Condon analysis of the \( 1_0^n \) progression in the benzene absorption spectrum, Craig (1950) derived a value of 0.036-0.037 Å for the C-C bond lengthening, \( \Delta r(C-C) \),
upon excitation of the $^1B_{2u}$ state of benzene. Parmenter, Tang and Ware (1976) were able to carry out a much more extensive Franck-Condon analysis from the relative band intensities measured in 13 strong progressions found in seven SVL fluorescence spectra of benzene. These yielded three sets of Franck-Condon factors: $|\langle 1^0|1_n^1 \rangle|^2$, $|\langle 1^1|1_n^1 \rangle|^2$, $|\langle 1^2|1_n^1 \rangle|^2$ for benzene. Once anharmonic contributions to progression intensities were taken into account, the Franck-Condon fits to the $v_1$ fluorescence progressions gave $\Delta r(C-C) = 0.034 \pm 0.001 \text{ Å}$ in exact agreement with the value obtained from a refined band contour analysis and line broadening study (Callomon, 1976).

SVL fluorescence spectra from various excited state vibronic levels provide a library of spectra which assist in interpreting emission spectra obtained at higher pressures and in the condensed phase and in monitoring environment-induced structure changes in such spectra. Where the absorption spectrum is sufficiently spread out so that, with narrow-band sources, single or just a few individual rovibronic levels can be excited, $S_1$ fluorescence studies can be extended down to single rotational levels as in studies of formaldehyde [Hardwick and Till, 1979] and glyoxal [Parmenter and Rordorf, 1978].

Environmental influences can have dramatic effects on the fluorescence emission. In the high pressure gas phase and in condensed phases, the rapid redistribution of energy which often washes out fluorescence from higher $S_1$ levels also distorts the fluorescence spectrum obtained from excitation into the $S_1$ zero-point level, so that the true zero-point fluorescence spectrum can only be obtained from a low pressure of gas. For example, fluorescence from benzene at a pressure of 8 torr and in the presence of 92 torr of isopentane, when excited to the zero-point level of
S\textsubscript{1}, contains transitions from levels up to 1234 cm\textsuperscript{-1} above the zero-point level and only about 18\% of the emission occurs from the originally excited level. This was established by comparison of the "equilibrated" spectrum with the zero-point SVL fluorescence spectrum [Parmenter and Schuyler, 1970b]. Similarly, comparison of the zero-point fluorescence spectrum obtained by the method of matrix isolation, (10\textsuperscript{-3} M benzene in solid cyclohexane at 77 K), confirms that the additional symmetry-forbidden progression of the latter spectrum is probably entirely induced by site interactions of benzene with its host [Parmenter and Schuyler, 1970b].

II. SVL fluorescence spectra can provide information on the relaxation pathways accessible to an excited molecule, either isolated or subject to environmental perturbations ("collisions"). The power of the technique arises from its direct reflection of excited state vibronic populations: following the absorption act, a network of relaxation channels compete to redistribute the excitation energy possibly among other excited state SVL's; fluorescence occurs from SVL's in the excited state and, if sufficiently discretely structured and well analysed, its various vibronic origins can be recognized; relaxation processes which bring the molecule into nonradiative states will be evident from reduced fluorescence intensity (\(\Phi_F<1\)). Thus fluorescence spectra directly monitor excited state populations and serve as a sensitive probe of relaxation processes with which fluorescence emission competes. Relaxation processes which affect fluorescence structure can generally be identified and monitored more accurately and precisely than those which do not (e.g. electronic relaxation).
Intramolecular electronic relaxation* is reflected in fluorescence quantum yields ($\phi_F$) for isolated molecules of less than unity (e.g. $\phi_F = 0.22$ for the zero point level of $^1B_{2u}$ benzene [Parmenter and Schuyler, 1970a], there being no discernible effect on the structure of the fluorescence spectra from $S_1$). Higher vibrational levels of an electronic state merge into a virtual continuum and the vibrational levels of different electronic states often overlap each other. Generally, a weak coupling exists between different electronic states which becomes more effective the more nearly degenerate are the states involved. Electronic relaxation refers to processes in which the $S_1$ vibronic level selected in absorption is coupled to vibronic levels in other electronic states and relaxation into this dissipative array of states destroys the initially prepared state. SVL fluorescence measurements from $S_1$ are much more sensitive in detecting this effect than $S_1$ absorption measurements where the effect is usually invisible. Radiative lifetimes are never less than about $10^{-9}$ s for which the uncertainty broadening** would be less than $3 \times 10^{-3}$ cm$^{-1}$ which is two orders of magnitude less than Doppler broadening [Byrne and Ross, 1971]. Byrne and Ross (1971) have reviewed the effects of electronic relaxation on diffuseness of absorption spectra. For example, about 75% of collision-free relaxation from the $6^1$ level in the $^1B_{2u}$ state of benzene is by ISC to the $3^1B_u$ state but a high resolution examination of $S_1 \leftrightarrow S_0$ absorption reveals no trace of the coupling; bands are sharp with no evidence of dissipative broadening. Similarly electronic relaxation from the $S_1$ state is not detectable by observable line broadening of fluorescence bands.

* Internal conversion or intersystem crossing, often referred to by the more general term radiationless transitions.

** $\Delta t, \Delta \nu \gg 1/4\pi c$. 
Only broadening of the order of 1 cm$^{-1}$ could be observed which would require the mean lifetime of the state with respect to electronic relaxation to be less than $3 \times 10^{-12}$ s; any radiative process ($\sim 10^{-9}$ s) would be overwhelmed by such a process and the emission would be too weak for high resolution work ($\phi_F < 10^{-3}$), [Byrne and Ross, 1971]. Rapid electronic relaxation (e.g. IC $S_2 - S_1$) dominates the decay when a molecule is excited to higher singlet states than $S_1$ and is detectable from the structure of isolated molecule fluorescence (most of the observed fluorescence is red-shifted with respect to the excitation energy with the maximum nearly coincident with that of normal $S_1 - S_0$ fluorescence [Stockburger, 1973]) and the diffuseness of higher absorption systems compared with the generally observed sharp first system [Byrne and Ross, 1971].

Intramolecular redistribution of vibrational energy within the $S_1$ state can occur if the optically selected level is coupled to a set of levels within the same electronic state. If this energy redistribution occurs on a time scale competitive with radiative decay, fluorescence will be effectively from the many levels mixed by the coupling and so will be poorly structured and congested, giving the appearance of diffuseness. The effect is expected to increase with the complexity of the molecule and as higher vibronic levels of $S_1$ are probed. Unfortunately, observation of diffuseness in SVL fluorescence spectra does not provide unequivocal evidence of intramolecular vibrational coupling since diffuse fluorescence structure can (and often does), arise from the trivial mechanism of exciting many upper state vibronic levels directly in absorption. This trivial mechanism of congestion is also expected to become more significant as higher levels in $S_1$ are excited because the absorption spectrum
increases in complexity towards shorter wavelengths. For example, Parmenter (1972b) considered the trivial mechanism to be responsible for the underlying congestion observed in the fluorescence spectrum of anthracene when the 0,0 band is pumped [Pringsheim, 1938], and the increased diffuseness observed in the fluorescence spectra as higher vibronic levels in aniline and the xylenes are pumped has been interpreted similarly [Blondeau and Stockburger, 1971]. A more recent SVL fluorescence spectral study of 15 vibronic levels of aniline [Chernoff and Rice, 1979a] in which lifetime information was also obtained, confirms this for aniline. For example, emission observed at different wavelengths in the congested 131 fluorescence spectrum of aniline was found to have the same rise time though slightly different decay times. The equal rise times were taken to indicate that all of the emission is directly excited by the laser and the different lifetimes were attributed to the effect of many vibronic levels being excited because of the underlying continuum in the absorption band. Furthermore, an examination of the fluorescence from 6a1, 11 and 121 and of the fluorescence excitation spectrum revealed that the increasing relative intensity of continuous emission corresponded to the increase in the relative intensity of the background in the absorption transition. On the other hand, the diffuseness observed in the fluorescence spectrum of toluene, excited at 0,0 + 932 cm⁻¹, was considered excessive when compared with the diffuseness observed in the fluorescence spectrum resulting from excitation at either side of this band and with the diffuseness in the fluorescence spectrum of aniline pumped to a similar excited state level and was attributed partly to intramolecular vibrational energy transfer [Blondeau and Stockburger, 1971]. Parmenter (1972b), however, considered that vibrational redistribution could not make any contribution to the observed congestion since he
regarded the density of states at +932 cm\(^{-1}\) (21 vibronic states between +900 and +964 cm\(^{-1}\)) as being too low to establish an opportunity for dissipative coupling. Where intramolecular electronic relaxation causes fluorescence spectra to be diffuse, many more states quasi-degenerate with the excited level are available. For example, the fluorescence spectrum obtained upon excitation of the \(S_2 \rightarrow S_1\) 0,0 band of naphthalene is very diffuse [Blondeau and Stockburger, 1971b] which is consistent with rapid \(S_2 \rightarrow S_1\) IC. The density of \(S_1\) states quasi-degenerate with the initially excited level has been estimated to be \(10^5\) per cm\(^{-1}\) [Watts and Strickler, 1966].

The diffuseness observed in fluorescence spectra obtained by probing higher energy absorption features of the 3100 Å interaction system of isoquinoline has been attributed to widespread vibronic mixing and anharmonic mixing among the higher vibrational levels of the near-degenerate \(^1\pi\pi^*\) and \(^1\pi\pi^*\) states [Fischer and Knight, 1976]. The proposal that accelerated intramolecular electronic relaxation was responsible for diffuseness observed in the absorption spectrum beyond \(\sim 0,0 + 750\) cm\(^{-1}\) [Fischer and Naaman, 1976], was discounted because the increased congestion in the fluorescence spectra was not accompanied by any appreciable diminution in the fluorescence quantum yield. The congestion observed in the fluorescence spectra from several levels of the first excited singlet state of pyrimidine-h\(_4\) under isolated molecule conditions [Knight, Lawburgh and Parmenter, 1975] is also attributable to anharmonic coupling in the excited and ground state [Fischer, O'Brien, Selinger, 1980]. Though intramolecular vibrational redistribution in benzene is neither expected nor observed [Parmenter (1972a)], vibrational rearrangement can be induced by collisions [Parmenter and Tang (1978)].
All of the previously discussed uses of SVL fluorescence spectra require that the molecule be kept isolated from environmental perturbation for the duration of its excited state relaxation (except perhaps phosphorescence). SVL fluorescence is also a sensitive probe of relaxation processes that occur as the fluorescing molecule becomes increasingly less isolated. Couplings between various states of the molecule can then be induced by environmental perturbations. As a corollary, these experiments provide a means of studying the mechanisms by which such inducements occur.

By measuring fluorescence spectra of a molecule, M, excited to various SVL's, as a function of the pressure of various collision partners (ground state M molecules or other gases with non-interfering spectroscopy), general kinetic data can be obtained by a Stern-Volmer method. For example, relaxation in glyoxal [Anderson, Parmenter and Poland, 1973; Beyer and Lineberger, 1975] and pyrimidine [Jones, 1973] has been studied in this way. These are effectively relative $\Phi_F$ measurements. More accurate quenching data are generally obtained by measuring fluorescence lifetimes as a function of collision gas pressure [Beyer, Zittel and Lineberger, 1975; Nott and Selinger, 1978a,b], particularly self quenching data [Knight and Parmenter, 1976a]. SVL fluorescence spectral studies are a necessary adjunct of fluorescence lifetime measurements since they assist in the identification of the quenching process. Quenching studies conducted with a range of collision partners can be used to develop theories as to the nature of the quenching process [e.g. Thayer and Yardley, 1972; Jones, 1973; Lin et al., 1979]. If the

* In which case the term SVL fluorescence does not strictly apply.
structure of fluorescence spectra is unchanged as pressure is increased because collision-induced electronic relaxation dominates the quenching process as in pyrimidine [Knight et al., 1975] and a-triazine [Knight and Parmenter, 1979], a single band may be monitored in the relative $\phi_F$ measurements [e.g. Jones, 1973].

If information on relaxation processes other than electronic relaxation is sought, the ability of SVL fluorescence spectra to identify and quantify excited state populations is utilised. For these studies, the SVL fluorescence structure must be discrete and well analysed so that the origin of bands that appear can be identified. (a) Mode-to-mode vibrational energy flow, (b) intermolecular electronic energy transfer, and (c) rotational relaxation have been studied in this way; the effective collision cross sections for these various processes and for various collision partners are found to vary quite markedly [Coveleskie and Parmenter, 1978].

(a) Parmenter and coworkers studied collision-induced mode-to-mode vibrational energy flow within the $S_1$ state of benzene by using fluorescence spectra to monitor the populations of $S_1$ vibronic levels as a function of added gas pressure [Parmenter and Tang, 1977, 1978; Atkinson, Parmenter and Tang, 1979]. They found that the partitioning of vibrational energy among many levels in the vicinity of the initially excited level is governed by strong propensity rules which account for the energy dispersal pattern even when the collision partner has a near-resonant bending vibration. Vibrational relaxation in the excited state (cross sections $\sim 0.1$ gas kinetic) was found to be much more efficient than in the ground state where a similar set of propensity rules seems to describe vibrational energy flow.
Chernoff and Rice (1979b) have made similar use of SVL fluorescence spectroscopy to trace collision-induced vibrational energy transfer from 8 vibronic levels of $S_1$ aniline with argon as collision partner. They used intensity versus time measurements to complement the steady state measurements; each wavelength emitted by the same state must have the same time behaviour. Energy transfer cross sections were found to be of the order of magnitude of gas kinetic collision cross sections and the pathways of decay were found to follow strong propensity rules which agreed qualitatively with the rules describing vibrational relaxation in benzene. The vibrational relaxation behaviour showed some striking similarities with that of benzene but quantitative agreement with the propensity rules inferred from the study of benzene was not observed; for example, though the rate of the two quantum change $0^0 \rightarrow T^2$ was less than that of the one quantum change $0^0 \rightarrow T^1$ (observed ratio 0.25), the values were not nearly as disparate as suggested by application of the propensity rules for benzene (calculated ratio 0.073). The most important finding in the aniline study was that vibrational levels of aniline are grouped into sets, with collision induced energy transfer being much more efficient between levels of the same group than between levels of different groups; this was taken to indicate that details of intramolecular coupling of the vibrational modes are at least as important in determining the pattern of energy flow as parameters such as the energy gap and the vibrational overlap integrals.

Beyer, Zittel and Lineberger (1975) combined SVL fluorescence spectral and lifetime measurements in studying relaxation in $S_1$ glyoxal. They present evidence for very rapid vibrational (and rotational) energy transfer. By monitoring an entire fluorescence vibronic band as a
function of total glyoxal pressure, single vibronic level loss rate constants were obtained for 26 vibronic levels. These were found to be dominated by vibrational relaxation and to range from gas kinetic to 7 times gas kinetic.

(b) Using a 45 cm⁻¹ excitation bandpass to pump the zero-point level (0-level) of S₁, C₆D₆, Parmenter, Setzer and Tang (1977) studied the collisional transfer of energy from the level excited to specific levels in S₁, C₆H₆, by monitoring the resolved fluorescence from various C₆H₆ and C₆D₆ gas mixtures. Fluorescence spectra from the isotopic gas mixtures are necessary for distinguishing ordinary vibrational relaxation in S₁ from electronic energy transfer between S₁ and S₀ molecules in which vibrational energy is not transferred. It was found that the most favourable energy transfer process was the population of the C₆H₆ 0-level (ΔE = 203 cm⁻¹) despite there being a near resonance (ΔE = +37 cm⁻¹) of a C₆H₆ fundamental with the initially excited C₆D₆ level. The large cross sections (as large as gas kinetic) observed for the electronic energy exchanges were taken to indicate that energy transfer by the long range Förster mechanism was not important. It was concluded from the estimated efficiency of electronic energy transfer between S₁ and S₀ benzene that electronic energy transfer contributes substantially to apparently vibrational relaxation within S₁ for benzene.

The emission of glyoxal vapour following SVL excitation under isolated molecule conditions is anomalous. It is a superposition of resonance emission from the initially selected level and non-resonance fluorescence from the 0-level and levels 7¹ and 7² (Eᵥib = 232 and 463 cm⁻¹), the non-resonance fluorescence originating from intermediate
levels being of extremely low intensity [Frad and Tramer, 1973; Anderson et al., 1971, 1973]. Furthermore, the transfer of the total available vibrational energy between two colliding similar molecules, rather than an equipartitioning of the vibrational energy between them, is improbable. The problems have been solved in a study of fluorescence spectra obtained, after SVL excitation, from mixtures of glyoxal-h$_2$ and glyoxal-d$_2$ [Frad and Tramer, 1973]. It was found that long range electronic energy transfer was the main contributor to the apparently $S_1$ vibrational relaxation and that electronic energy transfer accompanied by vibrational relaxation was the dominant electronic energy transfer process. Because of the strong self quenching of glyoxal it was concluded that relaxation processes due to long range interactions were accentuated in glyoxal; "hard" collisions necessary for ordinary relaxation processes only quench the fluorescence.

Using SVL excitation of benzene (bandwidth 75 cm$^{-1}$), Lardeux and Tramer (1976) observed electronic energy transfer from benzene to aniline by monitoring the resultant fluorescence from various benzene-aniline gas mixtures. They took advantage of the different fluorescence lifetimes of benzene (> 70 ns) and aniline (< 2.15 ns) to confirm the presence of induced aniline fluorescence by time-resolved excitation spectra, observed at 330 nm where the intensity of benzene emission is negligibly small. The fluorescence quenching by aniline was found to be almost entirely due to electronic energy transfer. From results obtained with different initially excited benzene SVL's it was tentatively concluded that electronic energy transfer between aromatic molecules in the gas phase necessitates relatively close collisions and that long-range-interaction models (e.g. Förster model) do not apply.
(c) Rotational relaxation from initial nonequilibrium rotational distributions in excited state vibronic levels has been studied in several molecules by monitoring the rotational contours of fluorescence vibronic bands as a function of pressure. Narrow-band excitation (e.g. 0.1-0.3 cm\(^{-1}\)) is required to create the initial nonequilibrium distribution. Coveleskie and Parmenter (1978) found that the rate constant (or cross section) for rotational relaxation in \(S_1\) benzene is 8-10 times gas kinetic with \(S_0\) benzene as collision partner (though direct electronic energy transfer in collisions between \(S_1\) and rotationally equilibrated benzene makes a substantial contribution to the relaxation) and 1.5-3.5 times gas kinetic with argon as collision partner, the two values given in each case corresponding to different positions of excitation within the \(6_1^0\) absorption band. Rordorf, Knight and Parmenter (1978) found the rate constant for rotational relaxation in glyoxal to be about 4.5 times gas kinetic with \(S_0\) glyoxal and other molecules as collision partners. Much of the rotational energy transfer in glyoxal was found to occur with large changes in the \(K'\) and \(J'\) quantum numbers. No strong selection rules for rotational state changes were observed. For aniline, the rate of rotational relaxation was observed to be at least as large as gas kinetic and the lifetimes and fluorescence yields of different initial rotational ensembles were found to be identical within experimental error [Chernoff and Rice, 1979b].

5.4 PRINCIPLES OF INTERPRETATION OF SVL FLUORESCENCE SPECTRA*

The vibrational structure of electronic spectra of polyatomic molecules is usually rather complicated even for molecules of high symmetry. In

* Emphasis is on aspects relevant to the electronic spectroscopy of pyrimidine. Only non-degenerate electronic and vibrational states are considered.
order to facilitate vibrational analyses, the structure can be simplified
by studying absorption at low temperature or emission under conditions
where only one vibrational level of the excited state is excited, i.e. SVL
fluorescence. The same principles established for the analysis of
absorption spectra [e.g. Herzberg, 1966] apply for SVL fluorescence
spectral analyses.

It has been established that the $^{1}B_{1} - ^{1}A_{1}$ electronic transition of
pyrimidine-$h_{4}$, -$d_{4}$ is electric dipole allowed and that vibronically
induced intensity "stealing" from electronic transitions of higher oscilla­
tor strength is negligible. Consequently, the interpretations of the SVL
fluorescence spectra of pyrimidine-$h_{4}$ [KLP] and pyrimidine-$d_{4}$ (vide infra)
are found to be relatively easy, with transitions occurring between
totally symmetric vibrational levels in both the excited and the ground
state, totally symmetric modes contributing to the bulk of the intensity.

A. Allowed transitions

For an electric dipole transition, the emission intensity $I_{u1}^{em}$ is rela­
ted to the transition moment $R_{u1}$

$$I_{u1}^{em} \sim \overline{v}_{u1}^{4} | R_{u1} |^{2}$$  

where $\overline{v}_{u1}$ is the wavenumber of the emission. $R_{u1}$ is, ignoring the effects
of electron spin [Herzberg, 1966, p. 14,131]; given by

$$R_{u1} = \int \Psi^{*} \cdot P \cdot \Psi_{1} \, d\tau$$  

where $\Psi_{u}$ and $\Psi_{1}$ are rovibronic eigenfunctions of the upper and lower states
respectively and $P$ is the electric dipole moment vector of the system of
nuclei and electrons. A general group theoretical argument shows that
$R_{u1}$ can be different from zero only if the integrand is totally symmetric
for at least one orientation of \( P \), i.e. if \( \Psi_u \Psi_1 \) belongs to the same species as one of the components of \( P \). This exact selection rule, however, is of no great practical benefit because it allows a large number of transitions, many of which are weak.

Disregarding rotation [Herzberg, 1966, pp. 129-131]* and introducing the Born-Oppenheimer approximation, the vibronic eigenfunction can be factored into an electronic part \( \Phi(q,Q) \) depending parametrically on the nuclear coordinates \( Q \) and a vibrational part \( \Lambda(Q) \), viz.:

\[
\Psi(q,Q) = \Phi(q,Q) \Lambda(Q)
\]  

(5.3)

where \( q \) represents the electronic coordinates. This approximation neglects the interaction (or coupling) of electronic and nuclear motion. The transition moment connecting vibronic states \( \Psi_{iv} \) and \( \Psi_{jw} \) where \( i,j \) are electronic and \( v,w \) vibrational quantum numbers then reduces to, in bra-ket notation,

\[
R_{iv,jw} = \langle \Lambda_v^{(i)}(Q) | \Phi_i(q,Q) | p^{(e)}(q,Q) | \Phi_j(q,Q) | \Lambda_w^{(j)}(Q) \rangle
\]  

(5.4)

\[
= \langle \Lambda_v^{(i)}(Q) | p^{(e)}(Q) | \Lambda_w^{(j)}(Q) \rangle
\]  

(5.5)

where \( p^{(e)} \) is the component of \( P \) due to the electrons and the parametric dependence of the electronic transition dipole moment \( p_{ij}^{(e)}(Q) \) on the nuclear coordinates arises from the dependence of the electronic wavefunctions on \( Q \). Under the additional (Condon) approximation that this latter dependence is slight, \( p_{ij}^{(e)}(Q) \) can be replaced by its value at the equilibrium positions of the nuclei in one of the two electronic states,

* Interaction of rotation and electronic motion is in general very weak.
\( p_{ij}^{(e)}(Q_0) \), and the expression for \( R_{iv,\text{vw}} \) can be factored to give

\[
R_{iv,\text{vw}} = p_{ij}^{(e)}(Q_0) \langle \Lambda_v^{(i)}(Q) | \Lambda_w^{(j)}(Q) \rangle
\]

(5.6)

Transitions for which the electronic transition dipole moment does not vanish by symmetry are said to be (orbitally) allowed. In this degree of approximation therefore, the strength of the vibronic transition is determined by the vibrational overlap integral since the electronic transition dipole moment has been considered independent of vibrational motion.* That is, to the symmetry selection rule that the direct product of the symmetry species of \( \Phi_i \) and \( \Phi_j \) belongs to same symmetry species as one of the components of the electric dipole moment** is added the requirement that the symmetry of vibrational state \( \Lambda_v^{(i)} \) be the same as that of \( \Lambda_w^{(j)} \). Equation 5.6 applies to normal electronic-vibration spectra such as those of pyrimidine.

B. Franck-Condon principle

In the Harmonic-Oscillator approximation the vibrational motion is considered as a superposition of the motion of independent non-coupled oscillators and the vibrational eigenfunction can be resolved into a product of \( 3N-6(5) \) normal mode functions*** viz.:

* \( p_{ij}^{(e)}(Q) \) is very nearly the same for all vibrational transitions of a given electronic transition [Herzberg, 1966, p. 149].

** The components of the electric dipole moment operator transform just like the translations \( x, y \) and \( z \).

*** Normal vibrations are characterised by each nucleus moving in simple harmonic motion of the same frequency and phase. Energy levels are equally spaced (separation \( hv \)).
\[ \Lambda(Q) = x_1(Q_1)x_2(Q_2) \cdots x_{3N-6}(Q_{3N-6}) \]  
\[ \langle \Lambda_v^{(i)}(Q)|\Lambda_w^{(f)}(Q)\rangle = \prod_{h=1}^{3N-6} \langle x_v^{(i,v)}(Q_h)|x_w^{(f,w)}(Q_h)\rangle \]  

the total vibrational energy being the sum of the energies of the individual oscillators [e.g. Wilson, Decius and Cross, 1955, pp. 34-39]. If the molecule has the same symmetry in the two combining states [e.g. pyrimidine, Herzberg, 1966, p. 661], the normal coordinates of the two states may be related to each other. The overlap integral may then be expressed as a product of one-dimensional oscillator functions and concepts from diatomic molecular spectroscopy may be applied in the analysis of the vibronic band systems. In particular, the potential energy curve for individual vibrations may be pictured as in figure 5.1 with the normal coordinate forming the abscissa in place of the internuclear distance of diatomic molecules.

The intensity distribution of symmetry allowed vibrational transitions is interpreted in terms of the Franck-Condon principle [Herzberg, 1950, pp. 193-203; Herzberg, 1966, pp. 148-157; Sponer and Teller, 1941]. According to this principle, the relative positions and velocities of the nuclei do not change during the electron "jump" because it occurs so rapidly, i.e. the most intense vibrational bands correspond to vertical transitions between the curves in the potential energy diagram. The wave-mechanical formulation of the principle is that the probability of the transition depends on the degree of overlap of the two vibrational eigenfunctions.

If the symmetry of the molecule is the same in both electronic states, only vibrational changes which preserve the symmetry of the
Wave-functions (dashed) and probability distributions (solid) for a harmonic oscillator (after Herzberg (1950) p.77)

Most probable transitions in emission from levels $v=0$ and $v=1$ according to the Franck-Condon principle

$\Delta Q = \text{Displacement of normal coordinate in the electronic transition}$

Figure 5.1. Representation of potential energy curves in the ground and first excited electronic states for a harmonic normal mode of vibration in a polyatomic molecule.
molecule can occur in the vibronic transition. Thus the equilibrium configurations for non-totally symmetric vibrations must be the same in the initial and final states, the potential energy surfaces having their minima above one another (i.e. vibrational change occurs with zero displacement of the normal coordinate). When the "equilibrium positions" of the normal mode in the two combining states are alike, the Franck-Condon principle suggests that the most probable transitions for symmetrical and for non-totally symmetrical vibrations will be 0-0, 1-1, ..., v-v, involving zero changes in the vibrational quantum number \( (v_i - v_f = \Delta v = 0) \). Transitions involving vibrational quantum number changes of ±1 (forbidden by symmetry for non-totally symmetrical modes), ±2, ... are always very much weaker than \( \Delta v = 0 \) transitions, becoming more so as \( |\Delta v| \) increases.

When \( v_i \approx 1 \), there is the possibility of transitions from either side of the potential energy well (and from intervening positions if overlap of maxima or minima of the eigenfunctions occurs) but when there is zero displacement of the normal coordinate these transitions tend to occur to the same final level. Even where the frequency is quite different in the two electronic states, if the equilibrium position of the normal coordinate

---

* If the potential functions for the normal mode of vibration in the two electronic states are nearly alike (i.e. vibrational frequencies are also nearly the same), then the vibrational eigenfunctions with different vibrational quantum numbers in the initial and final state are nearly orthogonal so the overlap integral will vanish unless the vibrational quantum number does not change.

** Calculations performed with purely harmonic vibrations show that even if the frequency changes by a factor of two, 94% of the intensity of 0-v transitions is concentrated in the 0-0 band if the minima of the potential energy curves overlap. For members of the \( \Delta v = 0 \) sequence of such a vibration, the overlap integral does not vary greatly with \( v_i \) whereas for \( \Delta v \neq 0 \) sequences, which are always very weak compared with \( \Delta v = 0 \) sequences, there is a strong dependence on \( v_i \). For example, for \( |\Delta v| = 2 \) sequences in non-totally symmetric vibrations, the intensity increases as \( (v + 1)^2 \) while for \( |\Delta v| = 4 \) sequences the intensity increases as \( (v + 1)^4 \) [Sponer and Teller, 1941; Herzberg, 1966, p. 155].
remains nearly the same in the electronic transition, the intensity distribution is heavily biased towards the 0-0 band though this bias towards $\Delta v = 0$ diminishes as $v_1$ increases. The consequences for SVL fluorescence spectra are that (unmixed) non totalement symmetric modes can only be weakly excited, will be involved in primarily $\Delta v = 0$ transitions, $\Delta v = 2, 4, \ldots$ transitions being progressively much weaker, and will not form progressions. A SVL fluorescence spectrum generated by exciting a sequence band* will replicate the spectrum obtained by pumping the parent band since transition probabilities are heavily biased towards zero vibrational quantum number changes ($\Delta v = 0$) according to the Franck-Condon principle. In benzene, for example, $v_{16}$ forms sequences and the displacements and relative intensities of fluorescence bands in parent spectra are replicated in sequence fluorescence (e.g. $6^1_{16}$ and $6^1_{16} 16^1$ spectra) [Knight, Parmenter and Schuyler, 1975a]. In pyrimidine-$h_4$, $v_{16}$ can form sequences and the fluorescence spectrum observed upon excitation in the $16^1_1$ absorption band is identical in structure and intensity pattern to the $0^0$ fluorescence spectrum [KLP]**. The same principle applies when sequence bands are irresolvably attached to main absorption bands. For example, the appearance of SVL fluorescence spectra obtained from pyridazine [Jordan and Parmenter, 1972] and naphthalene [Stockburger et al., 1975] excited with radiation of sufficiently broad bandpass for sequence bands attached to absorption bands to be simultaneously excited, shows no evidence of the participation of the sequences in the absorption when the fluorescence bandpass is of similar magnitude.

* Low ground state frequency and usually non totalement symmetric in aromatic and azaaromatic molecules.

** KLP = Knight, Lawburgh and Parmenter, 1975.
If the equilibrium position of the nuclei differ significantly in the two electronic states, only activity in totally-symmetric vibrational modes should be observed if the equilibrium symmetry of the molecule is to be preserved, activity being highest for those modes which most closely replicate the change in geometry that accompanies the electronic transition. This often corresponds to a superposition of two or more normal modes of vibration. With the positions of the minima of the two potential energy curves of a normal vibration displaced with respect to each other, overlap of several final state vibrational eigenfunctions with the initial state vibrational eigenfunction can be significant and a progression in the final state vibration is formed. The intensity distribution within such progressions is determined by the extent of the change in the equilibrium position, the shapes of the potential energy curves and the vibrational level of the initial state \( v_i \). The overlap integral will have a maximum value when maxima (or minima) of the two eigenfunctions overlap. The eigenfunction for the vibrational zero-point level is a bell-shaped curve whereas eigenfunctions for higher vibrational levels have broad maxima or minima near the classical turning points of motion, between which are smaller and narrower maxima and minima. If \( v_i = 0 \), one maximum in the intensity distribution of the progression will be observed, at a \( v_f \) value \( (v_{fm}) \) depending on the normal coordinate displacement involved in the transition. If the change in the equilibrium position is significant, \( v_{fm} \) will differ from zero, the intensity decreasing for larger and smaller values of \( v_f \). Progressions for which \( v_i \neq 0 \) may display two principal intensity maxima corresponding to transitions from near the classical turning points, intensity being distributed over a larger number of progression members as \( v_i \) increases. Multiple maxima (up to \( v_i + 1 \)) may be observed since additional maxima corresponding to the
constructive interference between the two vibrational eigenfunctions in
regions between the two turning points may occur. Such intensity patterns
have been observed in SVL fluorescence spectra. Three maxima have been
observed in the $l^2_n$ progression of benzene fluorescence spectra and,
whereas in the $l^0_n$ progressions fluorescence intensity is essentially
limited to the first five members, in the $l^2_n$ progressions the intensity
distribution extends over eight members [Knight, Parmenter and Schuyler,
1975a]. Fischer (1974) observed multiple maxima, again in accord with
predicted Franck-Condon envelopes, in hot band progressions of NSF and
Hardwick (1977) has observed multiple maxima in fluorescence progressions
in mode $\nu''_2$ of NO$_2$ which were in reasonable agreement with the Franck-Condon
factors calculated using zero-order vibrational eigenfunctions of the
upper and lower electronic states determined by numerical solution of a
vibration-rotation Schrödinger equation developed in terms of a modified
"rigid bender" Hamiltonian. Conversely, minima occur in the intensity
distributions of vibrational progressions, the minimum at the member $l^1_{1}$
of absorption ($l^0_{1}$) and fluorescence ($l^1_{1}$) progressions in benzene in accord
with the calculations of Smith (1968) being the most celebrated example
in polyatomic molecular spectroscopy [e.g. Smith, 1968; Parmenter, Tang
and Ware, 1976]. In SVL fluorescence spectra therefore, long progressions
in ground state totally-symmetric vibrational modes can occur when the
$S_1 - S_0$ electronic transition involves substantial displacement in the
equilibrium positions of the nuclei, the extent of the progressions
reflecting the extent of the displacement. Absence of long progressions,
however, does not necessarily imply little change in the equilibrium
positions of the nuclei in the $S_1 - S_0$ transition. In aniline, the
$^1B_2 - ^1A_1$ transition involves a large change in the equilibrium geometry
of the molecule, but this change does not parallel the motion of any
particular normal modes and probably has components along several of the
totally symmetric normal coordinates. Therefore, while several totally
symmetric modes are active in the transition, none of them forms long
progressions [Chernoff and Rice, 1979a].

While many investigators have calculated theoretical Franck-Condon
factors (vibrational overlap integral squared) for diatomic molecules
(e.g. review by Nichols, 1961), relatively few quantitative calculations
of Franck-Condon factors have been reported for polyatomic molecules
1980] and the converse problem of deducing geometry changes from observed
Franck-Condon factors has received less attention [Craig, 1950; McCoy
and Ross, 1962]. The most useful calculations of Franck-Condon factors
for analyses of SVL fluorescence spectra have been those reported by
Henderson et al. (1964a). In these evaluations, the displacement of the
normal coordinate between the two electronic states (related to parameter
D) and the relative vibrational frequencies (parameter $\delta$) were taken into
account and the overlap integrals were tabulated in terms of $D$ and $\delta$
[Henderson et al., 1964b]. Intensities observed in progressions of one
normal mode (e.g. $x^0_n$) can be matched to the intensity profiles of the
tables to obtain estimates of $D$ and the tables can then be used to calculate
relative intensities for different progressions in the same normal mode
(e.g. $x^1_n$) using the values determined for $\delta$ and $D$. Significant deviations
between observed and predicted intensity distributions may be due to
anharmonic mixing of the normal modes (e.g. in pyrimidine-h$_4$ [KLP]) or
vibronic interactions (e.g. in isoquinoline [Fischer and Knight, 1976])
both of which are neglected at this level of approximation. Corrections
for anharmonic mixing have been incorporated into such calculations of
predicted intensity [KLP; Fischer, Sharf and Parmenter, 1975; Parmenter, Tang and Ware, 1976]. The approach in this thesis will be to obtain predicted intensities from tables of overlap integrals identical to those of Henderson et al. (1964a) in the manner indicated above. Ohno (1978, 1980) has adopted a composite approach, involving semi-empirical MO calculations of geometry changes upon electronic excitation and normal coordinate analyses, to calculate Franck-Condon intensity distributions for several aromatic hydrocarbons which are in good agreement with the vibrational structures observed in high resolution spectra.

C. Vibronically induced transitions

If the types of interaction of vibrational and electronic motion neglected in the assumptions used to obtain equations (5.3) and (5.6) are not negligible then transitions, forbidden by selection rules arising from equation (5.6) but permitted by the general selection rules derived from equation (5.2), may occur. The classic article of Herzberg and Teller (1933) forms the basis of interpretations of "forbidden" vibrational bands in polyatomic electronic spectra; only relatively recently have more rigorous extensions of their approach been developed [Geldof, Rettschnick and Hoytink, 1971; Orlandi and Siebrand, 1972, 1973]. As better approximations are adopted, eventually all the transitions predicted by the general selection rule would be permitted but with varying intensity. By going to better approximations in stages, the restrictions on the more weakly forbidden transitions should be lifted first and the usefulness of selection rules for predicting the occurrence of transitions of at least moderate intensity is retained.

Interaction of vibrational and electronic motion induces mixing of electronic states (\( ^1\phi_1 \) and \( ^1\phi_2 \), say) and so intensity for a vibronic
transition \( |^1\psi_1 \rightarrow |^1\psi_0 \rangle \) can be in effect stolen from a strongly allowed transition \( |^1\psi_2 \rightarrow |^1\psi_0 \rangle \) because \(^1\psi_1 \) has some \(^1\psi_2 \) character.* Inducing vibrational modes need to be of the appropriate symmetry for the mixing vibronic states to be of the same symmetry.** If the inducing mode is totally symmetric it may be both progression forming and active in intensity stealing.

The separability of the wavefunction \( \psi \) resulting from the Born and Oppenheimer treatment (1927) rests on the neglect of certain mixing terms brought about by the nuclear kinetic energy operator \( T_N \)*** [Herzberg, 1966, p.9] while in the Condon approximation, the dependence of the

* In estimating the effect of the vibronic coupling of electronic states neglected in the BO and Condon approximations, matrix elements of the transition dipole moment for a transition \( i,j \) contain terms of the sort [Orlandi and Siebrand, 1972]:

\[
<\phi_i | p(e) | \phi_k \rangle <\phi_k | \partial / \partial Q_1 | \phi_j \rangle
\]

where the first factor is the electric dipole moment for the electronic transition \( i \rightarrow k \) and the second factor defines the symmetry requirements of the inducing vibrational mode, the operator \( \partial / \partial Q_1 \) having the same symmetry as \( Q_1 \) [e.g. Hochstrasser, 1966, p. 233].

** The vibronic species can always be obtained from the direct product \( \Gamma_x \times \Gamma_y \) even when the product resolution \( \psi = \phi x \) is only a very rough approximation [Herzberg, 1966, pp.22, 138].

*** Operator \( T_N \) leads to integrals of the form

\[
<\psi_{ku} | T_N | \psi_{jw} > <\psi_{iv} | p(e) | \psi_{ku} >
\]

and

\[
<\psi_{iv} | T_N | \psi_{ku} > <\psi_{jw} | p(e) | \psi_{jw} >
\]

which lead to integrals of the form

\[
[<\phi_k | \partial / \partial Q_1 | \phi_j > + <\phi_m | \partial^2 / \partial Q_1^2 | \phi_j >] <\phi_i | p(e) | \phi_k > <\phi_i | p(e) | \phi_k >
\]

in the expression for the transition dipole moment between \( \psi_{iv} \) and \( \psi_{jw} \); in typical polyatomic molecules there will always be modes \( Q_1 \) causing nonvanishing coupling between \( \phi_k \) and \( \phi_j \) and between \( \phi_m \) and \( \phi_k \) thus in such molecules there is always first order mixing of BO states [Orlandi and Siebrand, 1973].
electronic part of the adiabatic HO wavefunction, \( \phi(q,Q) \), on the nuclear coordinates \( Q \) is neglected. In estimations of the relative importance of neglecting these two effects, the conventional approach [e.g. Albrecht, 1960] has been to assume that the ground electronic state does not mix with higher electronic states to any appreciable extent under vibronic perturbation*. This led to the belief that generally the contribution to the intensity of "forbidden" transitions resulting from failure of the Condon approximation, referred to as Herzberg-Teller (HT) coupling, was dominant except when the states involved in the transition are not too widely separated in energy from other states**. Both mechanisms of vibronically inducing "forbidden" transitions (HT and vibronic coupling due to the breakdown of the BO approximation) yield the same vibrational structure (selection rules) to first order. Orlandi and Siebrand (1972, 1973) have indicated the deficiencies of this conventional approach and the weakness of the experimental evidence cited in its support, the theory

* The justification given for this is that the energy gap between the ground electronic state \( \phi_0 \) and a higher electronic state with which \( \phi_0 \) could mix, \( \phi_m \) say, is larger than the gap between the second state of the transition \( \phi_0 \rightarrow \phi_f \) (i.e. \( \phi_f \)) and a higher electronic state with which \( \phi_f \) could mix, \( \phi_h \) say. Thus the assumption allows intensity stealing from the transition \( \phi_0 \rightarrow \phi_h \) but not from the transition \( \phi_f \rightarrow \phi_m \).

** The ratio of the contributions from the BO and HT mechanisms of vibronic coupling to the transition dipole moment is estimated, in the conventional treatment, to be

\[
\left| \frac{R_{iv,fw}^{BO}}{R_{iv,fw}^{HT}} \right| = \frac{\hbar \omega}{|E_f - E_k|}
\]

where \( \hbar \omega \) is the energy of the inducing vibrational mode and \( |E_f - E_k| \) is the energy gap between the mixing states [Orlandi and Siebrand, 1973]. Herzberg and Teller (1933) considered from their estimation that the vibronic perturbation could become considerable for energy gaps of 0.5-0.1 eV by the BO mechanism and 1 eV for the HT mechanism which was generally accepted till recently [e.g. Herzberg, 1966, p. 140] even though vibronically induced intensities calculated by the conventional approach grossly exceeded observed intensities [e.g. Albrecht, 1960]. 1 eV \( \equiv 8.0657 \times 10^3 \) cm\(^{-1}\).
being inadequate in explaining quantitative aspects of the induced spectra even in the classic examples of benzene* and pyrazine [Herzberg (1966) p. 140; Innes, Simmons and Tilford, 1963]. Orlandi and Siebrand indicate sensitive experimental tests for determining the relative importance of the two mechanisms (isotope effect, absorption-emission asymmetry) and conclude that, in general, while the conventional HT approach yields a satisfactory interpretation of induced vibrational structure, it is inadequate for quantitative work because it neglects vibronic coupling involving the ground state and the BO component of the induced transition dipole moment. At the time they also lamented the scarcity of quantitative intensity data through which the theory might be tested more rigorously. The electronic spectra of several molecules have been examined in terms of the extended theoretical approach. The SVL fluorescence spectral study of naphthalene-\( \text{H}_4 \) and -\( \text{D}_8 \) by Stockburger et al. (1975) has already been cited. Fischer, Jakobson and Scharf (1976) re-examined the absorption spectra of pyrazine-\( \text{H}_4 \) and -\( \text{D}_4 \) and found that, while the HT mechanism is predominant in inducing vibronic intensity, the BO mechanism provides a measurable contribution, particularly in the emission spectrum.

The consequences for SVL fluorescence spectra are that, in addition to the already discussed fully allowed transitions for which electronic transition dipole moment \( p(e)_{ij}(Q_0) \) does not vanish and neither state involved in the transition mixes with higher electronic states, three

* For example, intensities calculated using the conventional theory are invariably too high by about an order of magnitude [e.g. Murrell and Pople, 1956; Albrecht, 1960]. When vibronic perturbation involving the ground state is taken into account, complete cancellation of the dominant HT terms is expected, the calculated intensity being reduced as required to get agreement with experiment [Orlandi and Siebrand, 1973].
cases of vibronically induced transitions can occur. (i) Electronic transitions for which all components of $p_{ij}(Q)$ vanish can become allowed in at least one component because of vibronic coupling usually involving the upper state of the transition as in the $^1B_{2u} - ^1A_{1g}$ transition of benzene. (ii) Forbidden components of allowed electronic transitions can be induced by vibronic coupling. The vibronically induced forbidden $p_{ij}(e)$ component is ten times stronger than the allowed $p_{ij}(e)$ component in the 3200 Å absorption system of naphthalene [Craig, Hollas, Redies and Wait, 1961] and consistent with this Stockburger et al. (1975) found that the allowed origin $0^0_0$ is ten times weaker than the vibronic origin $8b^0_1$ in fluorescence from the $0^0_1$ level. In cases (i) and (ii) the perturbing vibration is non-totally symmetric. Case (iii) is the same as case (ii) except that the perturbing vibration is totally symmetric as in phenanthrene [Hochstrasser and Small, 1966; Craig and Small, 1969]. Vibronically induced transitions of cases (i) and (ii) can be recognized by the occurrence of so called false or vibronic origins (formed by non-totally symmetric vibrations) which are of different polarization and perhaps have observably different rotational contour than the electronic origin. Vibronically induced transitions of case (iii), however, cannot be recognized by such distinguishing characteristics. When there is an upper electronic state of the same symmetry as one of the two states involved in the electronic transition, deviations from expected Franck-Condon intensities may indicate intensity stealing induced by totally symmetric vibrations. (Deviations from expected vibrational intensity patterns may also arise from anharmonic mixing of vibrational modes). "If a relatively strong totally symmetric fundamental derives most of its intensity vibronically, the intensity of its overtones depends on their own vibrational perturbation effectiveness. The effectiveness for the first overtone is expected to be considerably
less than that of the fundamental. Thus "the absence of overtones of relatively strong (harmonic) vibrations in an allowed electronic band system" is a strong indication of vibronic mixing through totally-symmetric vibrations [Hochstrasser and Small, 1966].

For pyrimidine-d$_4$ with C$_{2v}$ symmetry, electronic transitions between the ground state and excited singlet states are all allowed with polarizations: A$_1$ - A$_1$(z); A$_1$ - B$_1$(x); A$_1$ - B$_2$(y). The closest lying singlet to the first excited singlet is of B$_2$ symmetry and 8237 cm$^{-1}$ higher in energy. Vibronically induced transitions requiring the mixing of states as far apart as this are expected to be weak compared with fully allowed transitions [Herzberg, 1966, p. 140]. The inducing mode would be of b$_2$ symmetry.

Innes et al. (1969) suggest that some of the intensity of the totally symmetric 930 cm$^{-1}$ ground state mode is derived from another $^1$B$_1$ - $^1$A$_1$ transition. Reference to figure 6.1 shows that there are higher $^1$B$_1$ and $^1$A$_1$ states which are however very remote in energy from the states involved in the S$_0$ - S$_1$ transition. The transition from the ground state to the higher $^1$A$_1$ state is very strong, however, and the two upper $^1$B$_1$ and $^1$A$_1$ states are close in energy and of the same orbital type as the states involved in the S$_0$ - S$_1$ transition.

D. Anharmonicity of vibrations

Breakdown of the third approximation (harmonic oscillator) used in the interpretation of electronic spectra is manifested in the mixing of vibrational modes of the same symmetry, the contraction (usually) of the spacing between higher overtone vibrational levels and in the appearance of Fermi resonances.
By applying the HO approximation, the Schrödinger equation for the nuclear motion of a molecule in terms of the normal coordinates can be separated into mutually independent terms, each of which is the equation of a simple harmonic oscillator*. In particular, the nuclear potential energy is separable into a sum of independent terms involving only quadratic terms, viz.:

\[ V = \frac{1}{2}(\lambda_1 Q_1^2 + \lambda_2 Q_2^2 + \ldots + \lambda_{3N} Q_{3N}^2) \]  

(5.8)

[e.g. Wilson, Decius and Cross, 1955, pp. 14-20]. The frequencies (in cm\(^{-1}\)) for a vibronic transition then take the form

\[ \nu = \nu_0 + \sum_{i} (\omega_i' \nu_i' - \omega_i'' \nu_i'') \]  

(5.9)

where \(\nu_0\) is the wavenumber of the 0-0 band and \(\omega_i\) the frequency and \(\nu_i\) the vibrational quantum number of the \(i\)th normal mode.

Breakdown of the HO approximation means that the nuclear potential energy also involves cubic and higher cross terms in the normal coordinates, i.e.

\[ V = \frac{1}{2} \lambda_1 Q_1^2 + \sum \sum \lambda_{ijk} Q_i Q_j Q_k + \ldots \]  

(5.10)

and the resolution of the vibrational motion into a number of normal vibrations is no longer rigorously possible. The vibrational motion

* Since the total energy, kinetic plus potential, is separable into a sum of 3N (including nuclear translational and rotational motion) mutually independent terms. Solution of the resulting secular equation for the nuclear motion, using the symmetry of the molecule to simplify the problem as much as possible [e.g. Wilson, Decius and Cross, 1955], gives the normal frequencies of vibration (cf. observed vibrational frequencies) and the normal coordinates. Such normal coordinate analyses involve extensive computation and the cursory reference they are given here is not meant to imply that they are "simple and straightforward".
is anharmonic and a mixing of the normal modes of vibration is said to occur. This departure from harmonic oscillator conditions can be treated quantum mechanically by using the normal mode eigenfunctions, obtained using the HO approximation, as zero order eigenfunctions and the mixing terms in the potential energy expression as the perturbation in a perturbation calculation of the anharmonic vibrational wavefunctions and energies. Referring the vibrational energies to the zero-point level in each state, the wave numbers of all possible vibronic transitions of a given electronic transition are represented by [Herzberg, 1966, pp. 20-21, 142-143; Herzberg, 1945, pp. 206-209]

\[ \nu = \nu_0 + \sum_i \omega_i^0 v_i + \sum_{i k} \sum_j x_{ik}^j v_i v_j + \ldots \]

\[ - \left( \sum_i \omega_i^0 v_i + \sum_{i k} \sum_j x_{ik}^j v_i v_j + \ldots \right) \]  (5.11)

where

\[ \omega_i^0 = \omega_i + x_{ii} + 1/2 \sum_{i \neq k} x_{ik} \]  (5.12)

\( \omega_i \) are the frequencies (in cm\(^{-1}\)) for infinitesimal amplitudes of the normal vibrations (where the HO approximation is valid) and \( x_{ik} \) are anharmonicity constants.

If two vibrational levels (fundamentals and/or combinations of fundamentals) of the same symmetry are nearly degenerate in the zero order approximation of harmonic vibrations, the anharmonic terms of the potential energy are sufficient for substantial mixing of the eigenfunctions of the two states involved to occur and for the near resonance to be lifted, the zero-order energy levels repelling each other and deviating from formula 5.11. The smaller the zero approximation energy difference the stronger the mixing and the greater the mutual repulsion. The magnitude
of the perturbation also depends on the magnitude of the anharmonic terms in the potential energy which act as the perturbation function $W$. These vibrational perturbations are referred to as Fermi resonance and are a sort of vibrational analogue of vibronic coupling. If the resonance between two vibrational levels $n,m$ is fairly close, the magnitude of the shift according to first-order perturbation theory is

$$E = \frac{1}{2}(E_n + E_m) \pm \frac{1}{2}(4|W_{nm}|^2 + \delta^2)^{\frac{1}{2}} \quad (5.13)$$

where $E_n$ and $E_m$ are the energies of the two levels before the perturbation, $W_{nm}$ is the matrix element of the perturbation function $W$ for the two interacting vibrations and is given by

$$W_{nm} = \langle \psi_n | W | \psi_m \rangle = \langle \chi_n | W | \chi_m \rangle$$

$\chi_n, \chi_m$ being the zero approximation vibrational eigenfunctions of the two levels perturbing each other and $\delta$ is the separation of the two levels before perturbation $W$. The eigenfunctions of the two resulting mixed states are

$$\psi_1 = a\psi_n - b\psi_m \quad (5.14)$$

$$\psi_2 = b\psi_n + a\psi_m \quad (5.15)$$

where $a, b = \left[ \frac{(4|W_{nm}|^2 + \delta^2)^{\frac{1}{2}} \pm \delta}{2(4|W_{nm}|^2 + \delta^2)^{\frac{1}{2}}} \right]^{\frac{1}{2}} \quad (5.16)$


In SVL fluorescence spectra, Fermi resonances involving ground state vibrational levels are evident from the vibrational structure [e.g. in
pyrimidine-$h_4$ (KLP)]. A more subtle manifestation of the anharmonic mixing of vibrational motion occurs when the vibronic level excited is of mixed character. Intensity distributions are then determined by composite Franck-Condon factors for the modes making up the mixed state and can be quite anomalous when compared with normal Franck-Condon intensity patterns as demonstrated by KLP for pyrimidine-$h_4$ and Fischer et al. (1975) and Parmenter et al. (1976) for benzene.

While the occurrence of Fermi resonance must be common in the electronic spectra of polyatomic molecules because of the congestion of vibrational levels, Cotton (1963, p. 333) has deplored the tendency to invoke Fermi resonance to explain features which are difficult to assign; this must apply especially to "hot" bands of electronic absorption spectra. SVL fluorescence spectra provide a means to check such assignments.

E. Concluding remarks

Harris and Bertolucci (1978, p. 411), in concluding their book "Symmetry and Spectroscopy", say:

we are nowhere near the stage of being able to predict the appearance of molecular spectra from first principles ... while we seem to be able to adequately ... rationalize the appearance of electronic and vibrational spectra, assignments are often less than satisfying. When we lack the number of bands we expect we can say that some are too weak to see or are buried beneath stronger bands. When we find too many bands we can invoke any of a dozen or so reasons (Jahn-Teller distortion, ... Fermi resonance) why the bands appear.

Often it becomes a matter of interpreting what is observed in terms of the breakdown in some approximate theory. In such cases it must be remembered that what is real is an inexplicable line in a spectrum and that concepts such as normal modes of vibration are "products of imagination". That concepts such as Fermi resonance/anharmonicity and vibronic coupling often appear to be invoked on an ad hoc basis as universal remedies in the
solution of difficult assignment problems, reflects to a certain extent the inadequacy of current descriptions of molecular structure and spectra, based as they are on sometimes gross approximations.

The principles of assignment of SVL fluorescence spectra have been discussed, for example, by Parmenter and coworkers [e.g. Knight, Parmenter and Schuyler, 1975a,b, and references therein].
CHAPTER 6

Fluorescence spectra of selected vibronic levels in the $^1B_1 (S_1)$ state of pyrimidine-$d_4$

Fluorescence spectra from several SVL's of the first excited singlet state of pyrimidine-$d_4$ are presented and analysed. Assignments and Franck-Condon factors for fluorescence spectra of levels $0^1$, $12^1$ and the Fermi resonance pair $6a^1 ... 6b^2$ are treated in detail. The proposed Fermi resonance between $v_{6a}$ and $2v_{16b}$ for pyrimidine-$d_4$ and pyrimidine-$h_4$ and the effect on fluorescence intensity distributions of anharmonic coupling involving the vibrational level excited are examined. Fluorescence spectra of levels $8a^1$ and $8a^112^1$ were found to be too diffuse for detailed analysis. The effect of exciting in different regions of the pyrimidine-$d_4$ 0-0 absorption band on the rotational contours of fluorescence bands is illustrated.
6.1 MOTIVES FOR SVL FLUORESCENCE SPECTRAL STUDY OF PYRIMIDINE-d$_4$

In bringing the SVL fluorimeter into operation initially, use of a fluorescent molecule presenting few experimental difficulties and with well established electronic spectroscopy was desirable. Pyrimidine-d$_4$ is expected to have similar excited state photophysical properties to pyrimidine-h$_4$ which has a fluorescence quantum yield ($\Phi_F$) approaching unity at zero pressure [Knight and Parmenter, 1976a], allowing SVL fluorescence spectra to be obtained with relative ease at low enough pressure \textit{(vide infra)} [Yamazaki, Uchida and Baba, 1974; Knight, Lawburgh and Parmenter, 1975 = KLP]. Pyrimidine-h$_4$ (and presumably pyrimidine-d$_4$) does display excited state behaviour unsuitable for SVL fluorescence spectral studies. Lifetime and quantum yield studies have shown that fluorescence from low lying $S_1$ levels of pyrimidine-h$_4$ consists of a fast component (lifetime $\sim 1$ ns) and a slow component (zero pressure lifetime $\sim 1$ µs) at low pressures and that the slow component is very efficiently self-quenched, rate constants for self-quenching being several times the gas kinetic collision rate.* However, the fluorescence quenching is not accompanied by any change in the vibrational structure of $S_1$ fluorescence at pressures less than one torr [Logan and Ross, 1968; KLP]. Electronic relaxation is the major and perhaps exclusive consequence of collisional perturbation and $\Phi_F$ is still greater than 0.1 at 0.02 torr. Thus pressures of 0.02-0.07 torr should be satisfactory for obtaining SVL fluorescence spectra of pyrimidine-d$_4$.

* On average, a pyrimidine molecule would undergo 1 hard sphere collision ($d = 5.7$ Å) with other pyrimidine molecules in a time of 1 µs at 295 K and a pressure of 0.05 torr. The observed lifetime of the long component of pyrimidine fluorescence decreases markedly as pressure increases.
Furthermore, the $S_1 - S_0$ transition of pyrimidine-$d_4$ is orbitally allowed, and contains no significant vibronically induced contributions [Innes et al., 1967; Hochstrasser and Marzzacco, 1972] and by analogy with the results for pyrimidine-$h_4^*$, no interference from phosphorescence is expected for the vapour phase fluorescence. Therefore, the SVL fluorescence spectra of pyrimidine-$d_4$ should be readily interpreted.

SVL fluorescence spectra provide a means of investigating the extensive Fermi resonances documented for the ground and the $S_1$ state of pyrimidine-$d_4$ [Innes et al., 1969] and of checking some $S_1$ state vibrational assignments which are uncertain (e.g. $3^1$ or $12^1$ for the 32190.8 cm$^{-1}$ band [Innes et al., 1969]).

The SVL fluorescence spectra of pyrimidine-$d_4$ provide a basis for the study of its excited state decay behaviour. From changes in the vibrational structure and intensity of the fluorescence spectra as the molecule is brought out of isolated molecule conditions, rotational, vibrational and electronic relaxation can be investigated. The six azabenzenes display a range of radiationless decay behaviour and so can serve as model compounds in the development of the theory of radiationless transitions between electronic states in vapours of polyatomic compounds [Knight and Parmenter, 1976a,b]. One criterion applied in the classification of the $S_1$ excited state decay behaviour of a molecule is the sensitivity of its radiationless decay rates to collisional perturbations. Among the azabenzenes, pyrimidine-$h_4$ shows the highest sensitivity to collisions in its excited state decay behaviour, so information on the collisional quenching of the fluorescence

* Phosphorescence from pyrimidine-$h_4$ vapour has only been detected recently: it commences at 28530 cm$^{-1}$ and has a quantum yield in the pressure range 1 - 160 torr of $\sim 10^{-4}$ [Takemura et al., 1980] which is more than 100 times lower than the fluorescence quantum yield at 0.05 torr [Uchida et al., 1978]. If the $S_1 - T_1$ energy gaps in pyrimidine-$h_4$ and -$d_4$ are similar, the vapour phase phosphorescence for pyrimidine-$d_4$ is expected to commence at $\sim 28650$ cm$^{-1}$. 
from pyrimidine-\(d_4\), provided by the pressure dependence of its SVL fluorescence spectra, may be important in characterising the nature of the collisional interaction for pyrimidine and for polyatomic vapours in general.

One of the major reasons for the SVL fluorescence spectral study of pyrimidine-\(d_4\) was to establish, with the corresponding pyrimidine-\(h_4\) spectra [KLP], a library of spectra to which spectra from mixtures of the pyrimidine-\(d_4\) and pyrimidine-\(h_4\) vapours could be referenced in a study of intermolecular electronic energy transfer such as that performed with benzene-\(d_6\) and -\(h_6\) by Parmenter, Setzer and Tang (1977).

For the purpose of discussion, the SVL fluorescence spectral study of pyrimidine-\(d_4\) has been divided into two parts (i) presentation and analysis of SVL fluorescence spectra (this chapter) and (ii) fluorescence quenching and energy transfer studies (chapter 7).

6.2 ELECTRONIC SPECTROSCOPY OF PYRIMIDINE-\(d_4\)

(The photophysics of pyrimidine-\(d_4\) parallels that of pyrimidine-\(h_4\) in many respects so where specific information on pyrimidine-\(d_4\) is unavailable, reasonably accurate data can be obtained from the more complete description available for pyrimidine-\(h_4\)).

As analogues of benzene and because they exhibit a range of radiative and non-radiative behaviour, the azabenzenes have been extensively investigated in respect of their electronic and vibrational states (reviewed by Innes, Byrne and Ross, 1967) and their radiative and non-radiative behaviour (reviewed by Knight and Parmenter, 1976a,b). The significance of environmental perturbations in influencing excited state decay behaviour is demonstrated in the azabenzenes. Kasha (1960) had
proposed, mainly on the basis of condensed phase data, that the azabenzines were nonfluorescent in the vapour phase. Logan and Ross (1965, 1968) dispelled this impression with the observation of weak fluorescence following mercury line excitation of pyrazine and pyrimidine vapours. Subsequently, as experimental facilities for the detection of weak emission were improved, vapour fluorescence has been generated from pyridazine [Jordan and Parmenter, 1972], pyrimidine-\textsubscript{h\textsubscript{4}} [KLP], pyrazine [Frad, Lahmani, Tramer and Tric, 1974; Udagawa, Ito and Suzuka, 1980], \textit{s}-triazine [Nott and Selinger, 1975, 1978b; Knight and Parmenter, 1979], \textit{s}-tetrazine [Vemulapalli and Cassen, 1972] and pyridine [Yamazaki and Baba, 1977; Mochizuki, Kaya and Ito, 1978, 1980; Yamazaki, Sushida and Baba, 1979]. Before Yamazaki and Baba (1977) observed vapour phase fluorescence (\(\phi_F \approx 6 \times 10^{-5}\)) from pyridine following relatively broad bandpass (2 nm) excitation, emission from pyridine in any phase had escaped detection.

The positions of the known electronic states of pyrimidine-\textsubscript{d\textsubscript{4}} are summarized in figure 6.1. Though there is evidence from theoretical considerations [El-Sayed and Robinson, 1961a,b,c] and low temperature absorption and emission studies [El-Sayed and Robinson, 1961b; Li and Lim, 1971] of an excited singlet state lower in energy than the \(1\text{B}_1 (\text{n\textsubscript{n}\text{*}})\) state in pyrimidine, the high resolution study of the absorption spectra of pyrimidine-\textsubscript{h\textsubscript{4}} and -\textsubscript{d\textsubscript{4}} vapours by Innes \textit{et al.} (1969) and a more recent low temperature (4.2 K) investigation of pyrimidine-\textsubscript{h\textsubscript{4}} and -\textsubscript{d\textsubscript{4}} singlet-triplet absorption, fluorescence and phosphorescence spectra establish fairly conclusively that \(1\text{B}_1 (\text{n\textsubscript{n}\text{*}})\) is the lowest singlet excited state and that there is no evidence of interelectronic state perturbations [Hochstrasser and Marzzacco, 1972].

For pyrimidine -\textsubscript{h\textsubscript{4}} and -\textsubscript{d\textsubscript{4}} Innes \textit{et al.} (1969) tentatively proposed that a pair of bands they assigned as \(12^0_1\) and \(12^1_0\) may owe part or all of
Figure 6.1. Electronic states of pyrimidine-\textsubscript{d\textsubscript{4}}. [From Innes \textit{et al.}, 1967, Hochstrasser and Marzzacco, 1972 and Takemura \textit{et al.}, 1980].

* Estimated from assumed \textit{S\textsubscript{1} - T\textsubscript{1}} energy gap of 2543 cm\textsuperscript{-1}.\textit{S\textsubscript{1} - T\textsubscript{1}} energy gaps for pyrimidine-\textit{h\textsubscript{4}} (P-\textit{h\textsubscript{4}}) in the vapour, P-\textit{h\textsubscript{4}} and P-\textit{d\textsubscript{4}} in mixed crystals with benzene are 2543, 2454 and 2453 cm\textsuperscript{-1} respectively.

Figure 6.2. Geometry change for the \textit{S\textsubscript{1} - S\textsubscript{0}} transition. The bond lengths (\textdegree) and angles (degrees) are for the ground state, with the estimated changes in bond lengths in parentheses. Bond angles are little affected. [after Innes \textit{et al.}, 1969].
their intensity to mixing with another $B_1 - A_1$ transition since the absence of $\Delta v = \pm 2$ bands was in accord with the Herzberg-Teller selection rule $\Delta v = \pm 1$. SVL fluorescence spectra of pyrimidine-$h_4$ do not support this view. Band $12^1_{0}$ of Innes et al. (1969) was reassigned as $1^1_{0}$ and progressions $1^1_{n}$, $1^0_{n}$, $12^0_{n}$, and $12^1_{n}$ were observed indicating that no $\Delta v = \pm 1$ restriction applies. Anomalous intensity distributions in the fluorescence spectrum from level $1^1$ were attributed to anharmonic mixing of $v'_1$ and $v'_{12}$ [KLP]. Virtually identical vibrational structure and relative intensities in the fluorescence and phosphorescence spectra of both pyrimidine-$h_4$ and -$d_4$ in the solid phase [Hochstrasser and Marzzacco, 1972] further support the view that vibronically induced intensity borrowing is insignificant in the $1B_1 - 1A_1$ electronic transition of pyrimidine-$h_4$ and -$d_4$. The "most important conclusion" of the analysis by Innes et al. (1969) of the 2600-3500 Å absorption system of pyrimidine-$h_4$ and -$d_4$ was that "the strongest bands all arise from only one electronic transition". It was pointed out in section 5.40 that vibronically induced transitions for the 2600-3500 Å absorption system of pyrimidine-$d_4$ are unlikely in view of the separation between the electronic states which would need to mix.

From their analysis of the high resolution absorption spectra of pyrimidine-$h_4$ and -$d_4$, Innes et al. (1969) found that all of the 800 or so measured bands exhibited a sharp edge of a type C band and inferred from this that the electronic transition moment is parallel to the top axis and perpendicular to the aromatic ring. They found that the most active modes in forming progressions in absorption are ring elongation vibrations, one of which, with a frequency of about 1000 cm$^{-1}$, accounts for the extension of the spectrum over 6000 cm$^{-1}$. From a qualitative application of the
Franck-Condon principle and the change in the inertial constants derived from the rotational analysis, Innes et al. (1969) estimated the geometry change for the electronic transition illustrated in figure 6.2. It is relatively large, with some bond lengths in the aromatic ring changing by 5-10% and accounts for the absorption maximum occurring 2500 cm\(^{-1}\) above the origin band. They identified extensive Fermi resonances involving \(v_{6a}\) in each electronic state and found the strongest sequence bands of the absorption system for pyrimidine-\(d_4\) at distances of \(-137.4\) (\(16a_{1}^{1}\)) and \(+65.4\) cm\(^{-1}\) from the origin band and other strong bands.

Knight, Lawburgh and Parmenter (1975) confirmed or established many excited state fundamentals in their SVL fluorescence spectral study of pyrimidine-\(h_4\). They found that the intensity distributions in fluorescence from higher levels than 0,0 deviated from the Franck-Condon intensity patterns predicted from an analysis of the 0,0 spectrum. The deviations were attributed to strong anharmonic coupling in the excited state, every totally symmetric fundamental being involved. The fluorescence quantum yield was found to decrease appreciably with increasing energy of excitation, and there was no evidence of phosphorescence. There were no indications of vibrational redistribution in their spectra (measured at pressures of less than 0.1 torr). Upward vibrational relaxation (from the 0,0 level) competes very poorly with collision-induced \(S_1 \rightarrow T\) ISC, the only evidence of its occurrence in the presence of 100 torr of added isopentane gas being the "hesitant appearance" of transitions \(16a_{1}^{1}\) and \(6a_{1}^{0}16a_{1}^{1}\) [Lawburgh, 1974] and no significant transfer of intensity occurs from one region of the 0,0 fluorescence spectrum to another for 0.1 torr of pyrimidine in the presence of 0.25 torr of isopentane [Jones, 1973]. Downward vibrational relaxation after pumping levels higher than the 0,0 level is sufficiently fast to compete with \(S_1 \rightarrow T\) crossing [Knight and Parmenter, 1976a]. Phosphorescence was not observed from pyrimidine-\(h_4\) vapour even where
addition of 150 torr of isopentane gas to 0.1 torr of pyrimidine-h4 gas quenched 0.0 fluorescence completely [Jones, 1973] until a recent study by Takemura et al. (1980) in which time-delayed detection was employed to enhance any phosphorescence intensity relative to that of the much more intense fluorescence; the phosphorescence lifetime was found to be 53 µs.

Collisional quenching of pyrimidine-h4 is extremely efficient [Nott and Selinger, 1978a; Knight and Parmenter, 1976; Uchida, Yamazaki and Baba, 1976, 1978; Spears and El-Manguch, 1977] and sensitized biacetyl phosphorescence studies show that \( S_1 - T_{ISC} \) is the dominant collisional decay channel for pyrimidine-h4 in the vapour phase, with triplet yields ranging from 0.8 to 1.0 in the \( S_1 \) state [Jones, 1973, Knight and Parmenter, 1976a,b]. This behaviour is characteristic of a so called small molecule [Robinson, 1967] and the low \( S_1 - T_1 \) zero point energy gap (\( \nu 2560 \text{ cm}^{-1} \)), which ensures a low density of triplet states in the region of the \( S_1 \) excited state, encouraged the belief that the \( S_1 \) photophysics of pyrimidine was in the small molecule limit. As discussed in chapter 7, it has since been established that the \( S_1 \) decay behaviour of pyrimidine conforms more closely to the "intermediate case" than to the "small molecule" classification of radiationless transitions.

6.3 GROUND STATE FUNDAMENTAL FREQUENCIES OF PYRIMIDINE

In labelling the normal vibrational modes of the azabenzenes, two notations have been used: (i) that of Herzberg (1945, Ch.2) in which the vibrations are arranged in order of decreasing symmetry, the order within each symmetry species being of decreasing frequency, and numbered sequentially; and (ii) that of Lord, Marston and Miller (1957), which is based on Wilson's [Wilson, Decius and Cross, 1955] normal mode numbering of benzene, with letters a and b distinguishing vibrations which are doubly degenerate in benzene. Since the normal vibrational modes of all the azabenzenes are closely related, there is an advantage in using Lord's notation in which similar mode types for different azabenzenes are correlated.
[Innes, Byrne and Ross, 1967]. There can be difficulties in correlating the azine frequencies with particular benzene frequencies since it is not always evident which of the benzene modes most nearly approximates the motion in the azine. As indicated below, there can also be difficulties in correlating modes of isotopically substituted molecules.

The vibrational spectrum of pyrimidine has been studied by several authors. A vibrational assignment was first proposed by Ito et al. (1956) and then by Lord et al. (1957) who investigated the vibrational spectra of the three diazines. From a vibrational analysis of the ultraviolet "hot" absorption bands, Simmons and Innes (1964) reassigned $v_{6a}$. They also measured the Raman and infrared spectra of pyrimidine-d$_4$. Sbrana, Adembi and Califano (1966) = SAC found that, with the assignments of Lord et al. (1957) and Simmons and Innes (1964), there was poor agreement between observed frequencies and frequencies obtained from a normal coordinate analysis so they measured the infrared spectra of pyrimidine-h$_4$ and pyrimidine-d$_4$ in gas, liquid and solid phases. Where analysis of the rotational band envelopes of the high resolution vapour spectrum was not sufficient for a definite assignment, useful information was obtained from analysis of crystal spectra in polarized light. It was found that bands which were indistinguishable in the vapour spectrum were well separated and clearly characterizable from their polarization since symmetry and envelope type could be correlated with polarization character. Six fundamentals were reassigned, with all but three fundamentals in pyrimidine-d$_4$ ($v_4$, $v_{11}$ and $v_{14}$) being "identified with certitude". The assignments of Innes et al. (1969), who studied the ultraviolet absorption spectra of pyrimidine-h$_4$ and -d$_4$ under high resolution and the Raman spectrum of liquid pyrimidine-d$_4$, agreed with those of SAC. On the basis of normal coordinate analyses of pyrimidine-h$_4$, -d$_4$ and 2-chloropyrimidine (in which only the 17 in-plane vibrations were calculated), Sarma (1974) interchanged
SAC's $v_{9a}$ and $v_1$ in pyrimidine-$d_4$. Otherwise Sarma's results confirmed the assignments of SAC though the calculated bending frequencies $v_3$, $v_{15}$, and $v_{18b}$ did not agree very well with those observed by SAC. Milani-Nejad and Stidham (M-NS) (1975) reported liquid phase Raman and liquid and vapour phase infrared spectra of pyrimidine-$h_4$, -$d_4$ and other $C_{2v}$ deuterium substituted pyrimidines and made tentative band assignments consistent with frequency sum and product rules and non-crossing. This necessitated the alteration of some of the frequency assignments of pyrimidine-$d_4$ made by previous authors. Sarma (1978) extended his earlier normal coordinate analysis [Sarma (1974)] to other deuterium substituted pyrimidines with $C_{2v}$ symmetry. His calculations suggested that some of the assignments made by M-NS for these molecules, in particular the reassignments for pyrimidine-$d_4$, needed revision.

Table 6.1 presents the assignments, descriptions of mode type and observed frequencies for the fundamental vibrations of pyrimidine-$h_4$ and -$d_4$. Two sets of observed data are presented for each molecule. For pyrimidine-$h_4$, the observed frequencies are: (i) those found to be consistent with the SVL fluorescence spectral study [KLP] and derived from SAC's vapour phase results where available except as noted; and (ii) those obtained from the study by M-NS which were based on liquid phase infrared and Raman spectral results. The assignments for pyrimidine-$d_4$ (i) and (ii) are based on the assignments of SAC and the normal coordinate studies of Sarma (1974, 1978). For pyrimidine-$d_4$, the observed frequencies are: (i) those of SAC (vapour phase i.r. results except where noted); and (ii) those of M-NS (liquid phase i.r. and Raman spectral results). There are considerable discrepancies between the two sets of observed frequencies for pyrimidine-$d_4$. Some of these may arise from the different phases for which the data are
Table 6.1 Ground state vibrational assignments in pyrimidine-h₂ and -d₂

<table>
<thead>
<tr>
<th>Species</th>
<th>No.</th>
<th>Description</th>
<th>Pyrimidine-h₂</th>
<th>Pyrimidine-d₂</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>(i)</td>
<td>(ii)</td>
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<tr>
<td>A₁</td>
<td>20a</td>
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<td>3074</td>
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<td>2053</td>
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</tr>
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<td>1323&lt;sup&gt;x&lt;/sup&gt;</td>
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<td>344</td>
<td>304&lt;sup&gt;i&lt;/sup&gt;</td>
</tr>
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c Values used in assigning SVL fluorescence spectra of pyrimidine-d₂. SAC's original assignments and SAC's observed data combined with that of M-NS and Innes et al. (1969) where appropriate.

Notes: Pyrimidine-h₂: x - SAC crystal i.r.; u - vapour u.v. absorption from Innes et al., 1969; f - SVL fluorescence spectrum from Knight, Lawburgh and Parmenter, 1975; F - Fermi resonance estimate; I - from Innes, Byrne and Ross, 1967; I - SAC liquid i.r.; n - M-NS vapour i.r. value 804 cm⁻¹; v - M-NS vapour i.r.

Pyrimidine-d₂: x, w, F, I, v as for pyrimidine-h₂.

ey - SAC data given in text and their tables 4 and 5 are inconsistent for modes 20a, 2, 13 and 7b. Values given here are from the SAC text and are consistent with SAC's summary of data table 5 for 20a, 2 and 13 but not 7b. For 7b a value 2290 cm⁻¹ appears only in table 5 of SAC.
d - value from SAC force constant calculation; p - calculated by SAC from the product rule; m - M-NS vapour i.r. value same as that of SAC; e - M-NS give values of 1114, 985, 930, 907 cm⁻¹ for modes 16, 3, 15, 18b respectively but these assignments are not consistent with normal coordinate analyses [Sarma, 1974, 1978].
reported*. But this is not the sole reason since the frequencies reported from various studies conducted in the same phase also contain differences**.

The SVL fluorescence spectral assignments of pyrimidine-d₄ are based on the composite set of fundamental frequencies in column (iii) of table 6.1. The assignments are those of SAC and differ from those of sets (i) and (ii) of table 6.1 in the interchange of υ₉α and υ₁. M-NS interchanged υ₁₂, υ₉α and υ₁ but the assignments given in (i) and (ii) of table 6.1 for υ₁₂, υ₉α and υ₁ are unquestionable. υ₉α is primarily an in-plane C-H bending mode whereas υ₁₂ is a ring breathing mode. On deuteration, the C-H bending mode is expected to shift while the ring mode remains almost unaffected. Normal coordinate calculations by Sarma (1974) suggest υ₉α should be shifted from 1138 cm⁻¹ in pyrimidine to ~830 cm⁻¹ in the perdeuterated compound. Furthermore, the geometry change in the ¹B₁ → ¹A₁ electronic transition more closely resembles the motion of mode υ₁₂ than the motion of mode υ₉α so the frequency corresponding to υ₁₂ should be more active in forming progressions. As will be seen below, frequency 1048 cm⁻¹ is the second most active in forming progressions in the SVL fluorescence spectra of pyrimidine-d₄. This confirms the assignment of 1048 cm⁻¹ to mode υ₁₂. Strong activity in mode υ₁₂ is also observed in the SVL fluorescence spectra of α-triazine [Knight

* For example, for mode υ₆α of pyrimidine-d₄, SAC observed i.r. peaks at 650, 659 and 669 in the vapour, 656 in the liquid and 653 in the crystal whereas M-NS observed i.r. peaks at 651, 659 and 669 in the vapour, and 655 in the liquid and a liquid phase Raman peak at 657 (cm⁻¹ throughout) and both sets of data agree within the 0.5 cm⁻¹ accuracy estimated for strong peaks if values from the same phase are compared but not otherwise. For mode υ₈α, SAC quote values 1538 (vapour i.r.), 1526 (liquid i.r.) and 1522 (crystal i.r.) and M-NS quote values 1527 (liquid i.r.) 1527 (liquid Raman) but the values reported in their summaries are 1538 (SAC) and 1527 (M-NS).

** For example, liquid phase results obtained for mode υ₂ are 2260 (SAC i.r.) 2275 (M-NS i.r. and Raman) 2266 and 2264 cm⁻¹ (in two Raman studies by Innes et al., 1969).
and Parmenter, 1979]. There are several other discrepancies between the assignments made by M-NS and those made by other authors (as well as uncertainties in the frequencies) as indicated in the notes accompanying table 6.1. They involve modes which are relatively unimportant in the SVL fluorescence spectral assignments.

6.4 DETAILS OF THE MEASUREMENT AND PRESENTATION OF THE SVL FLUORESCENCE SPECTRA OF PYRIMIDINE-d₄

In discussing the SVL fluorescence spectra of pyrimidine-d₄, the normal conventions of the literature have been followed. Each SVL fluorescence spectrum is labelled by the upper vibronic level of the absorption band excited, the positions and assignments of absorption bands being taken from Innes et al. (1969). Though substantial normal mode mixing is generally expected for a molecule of the size of pyrimidine-d₄ [e.g. cf. CO₂, H₂O Herzberg, 1945, pp. 217-219] and has been identified in the ground and excited states of pyrimidine-h₄ [KLP], it is convenient to use the xᵢⱼ notation which gives the number of vibrational quanta of a particular normal mode (x) in the upper and lower electronic states (i and j respectively) even though this suggests that the normal modes are harmonic and identical in the ground and excited states. Bands are identified according to their displacements (in cm⁻¹) from the excitation position. These displacements correspond to ground state fundamentals, overtones or combinations (table 6.1, column (iii)).

Innes et al. (1969) found that the rotational structure of each absorption band examined in the ³B₁ - ³A₁ transition had a very strong and sharp Q branch edge nearly coincident with the band origin. The only resolvable features seemed to be formed from superpositions of Q-branch transitions. For the fluorescence spectra described herein, the position of
excitation in a given vibronic absorption band was selected by tuning the laser wavelength to yield maximum fluorescence intensity, as described in chapter 3, and so was at the maximum of the Q branch. Innes et al. (1969) found that the Q branch maxima in absorption were within 0.2 cm⁻¹ of the band origins. Positions of fluorescence band maxima were used in determining displacements. It will be shown later that the nonequilibrium rotational distribution produced by the narrowband (ca. 0.4 cm⁻¹) excitation source means that nonequilibrium rotational contours are observed in fluorescence, electronic relaxation being the dominant collision induced decay process. Since the maximum intensity in each fluorescence band also occurs near the Q-branch edge, no significant distortions in the measured displacements should arise.

Most of the intensity of the 0-0 absorption band is contained within a range of 10 cm⁻¹ [Innes et al., 1969]. In fluorescence, the observed breadth of a vibronic band depends on the bandpass of the fluorescence resolving spectrometer as well as on the intrinsic band breadth. For the fluorescence spectra reported here, the spread in the contour extends from about 30 to 80 cm⁻¹ for easily observed bands*. Overlap of bands therefore occurs frequently in the spectra, especially at higher displacements from the excitation position where structure becomes severely congested. Where overlap does occur, assignments in the annotations of the spectra and especially in the tables of assignments of band maxima are usually referred to the centre of intensity of the composite band.

* This variation arises from the different intensities of the bands, e.g. 6a₅⁰ cf. 6a₁⁰ 12₀⁻ in the 0-0 spectrum. Fluorescence bands recorded under higher resolution are much narrower. Figure 6.5 shows the 6a₁⁰ band recorded with a collection bandpass of 2.4 cm⁻¹. The main peak is 7 cm⁻¹ wide but the overall width of the band, when the rotational tails are included, is 30 cm⁻¹.
The spectra referred to in this chapter were recorded with constant excitation intensity as described in chapter 3 and with constant wavelength collection bandpass and were corrected for the spectral response of the fluorimeter system by the method described in chapter 4. For the annotated spectra, the assignment markers refer to the positions of observed maxima and are not calculated displacements. In the assignment of progressions, the lower vibrational quantum number \( n \) increases (from right to left) from 0 (e.g. \( 6a^0_n,8a^0_1 \) of the \( 0^0 \) spectrum) or 1 (e.g. \( 6a^0_n,6a^0_1,10b^0_2 \)). Recorded intensities of the fluorescence band at the excitation wavelength are attenuated by reabsorption but masked by scattered excitation light. For all spectra reported here, it has been necessary to reduce the recorded intensity at the excitation position 1-3 times by editing intensity data for this band before plotting the spectra. Asterisks mark the position of excitation in the annotated spectra of this chapter. A constant value has been added to the intensities of each spectrum to avoid interference between the spectrum and the wavenumber markers. This shift has also been applied in the annotated spectra though the lower wavenumber scale is not shown.

Tables listing band maxima assignments include the majority of transitions indicated in the annotations of the spectra. For these tables, positions of band maxima were determined from computer listings of the smoothed and corrected intensities for each collection step of the spectra. For the tables of band positions, wavelengths were converted to wavenumbers in vacuum using the table of De Witt Coleman, Bozman and Meggers (1960). Uncertainties in the positions of the band maxima and hence in the displacements depend on uncertainties in the spectrometer wavelength*, the step size and fluorescence bandpass used in recording the spectra.

* The spectrometer was calibrated using the lines of a low pressure mercury lamp as reference.
and variations in the laser excitation wavelength. Tests of the wavelength stability of the laser/fluorescence resolving spectrometer have been described in chapter 3 and indicate variations in the positions of the observed maxima of ±0.25 cm⁻¹ when the step size is 0.37 cm⁻¹ and the collection bandpass is 2.4 cm⁻¹. When the additional uncertainties associated with the larger step sizes and collection bandpasses employed in obtaining the spectra are taken into account, the uncertainties in the positions of the bands are estimated to be ±2 cm⁻¹ for the 0⁰ spectrum and ±4 cm⁻¹ for the other spectra. Uncertainties in the positions of weak bands are higher.

As the spectra reported here were collected over 40-60 hours of pulsing with the laser, it is essential that the system be highly stable. As an indication of the stability of the system, the position of the exciting radiation observed when the spectrometer is scanned through to fourth order (second order of the dye laser's primary beam) is also given in the tables of band maxima.

Specific experimental conditions pertaining to the spectra are given in their captions. Step sizes and fluorescence collection bandpasses are reported over a range of wavenumbers because the spectrometer is linear in wavelength. This implies that resolution improves as the displacement from the excitation position increases. As the ratio of fluorescence collection bandpass to step size was always ≥ 3, a three point moving average scheme could be used to smooth the spectra. To enhance the appearance of peaks in the annotated spectra of this chapter,

* E.g. if the uncertainty in determining band maxima from the computer printout is ±1 step which is conceivable given the Poisson error associated with each intensity value, this translates as an uncertainty of 1.6-0.9 cm⁻¹ (the wavenumber step size varies throughout the spectrum) in the 0⁰ spectrum and 3.3-1.9 cm⁻¹ in the other (12¹ etc.) spectra.
a five point moving average scheme for smoothing was used. Examples of unsmoothed and three-point-smoothed plots of these spectra are given in the appendix. Also included in the appendix are spectra obtained in other runs. These were recorded using the same excitation wavelength and bandpass as used for their analogues in this chapter and are presented to show the extent of reproducibility and to indicate which peaks of weak intensity are "real".

6.5 GENERAL FEATURES OF THE SVL FLUORESCENCE SPECTRA OF PYRIMIDINE-d₄

The most striking features of the pyrimidine-d₄ fluorescence spectra are their greater discreteness and the involvement of fewer ground state vibrations in vibrational activity when compared with the fluorescence spectra of pyrimidine-h₄ and their remarkable superficial resemblance to the SVL fluorescence spectra of α-triazine [Knight and Parmenter, 1979]. The absence of ground state Fermi resonances accounts for the cleaner appearance of the pyrimidine-d₄ spectra and confirms that anharmonic coupling is responsible for irregularities observed in the electronic spectra of pyrimidine-h₄. Progressions in the modes $v''_{6a}$ and $v''_{12}$ account for the bulk of intensity in the fluorescence spectra of pyrimidine-d₄. This is consistent with the vibrational structure of the absorption spectrum. The two most active modes are ring breathing vibrations and their involvement in long progressions lends further support to the proposal that the geometry change for the molecule upon excitation to the first excited singlet state is as illustrated in figure 6.2 [Innes et al., 1969]. Of the totally symmetric modes, only five ($v'_{6a}$, $v_{12}$, $v_{8a}$, $v_{9a}$ and $v_{1}$ very weakly) are engaged in vibrational activity. Only two non-totally symmetric modes ($v_{6b}$ and $v_{10b}$) show significant activity. Nearly all the vibrational assignments were made using just these seven fundamentals, their overtones and combinations.
6.6 $O^0_0$ FLUORESCENCE SPECTRUM OF PYRIMIDINE-$d_4$

A. Assignments

The zero-point level fluorescence spectrum of pyrimidine-$d_4$ is presented in figure 6.3, band assignments being given in table 6.2. Progressions in the modes $v_{6a}$ and $v_{12}$ dominate the spectrum. Progressions in these two modes build on progression members of each other to form progressions of progressions [Herzberg, 1966, p. 143] and on totally symmetric transitions $9a^0_1$, $8a^0_1$, $10b^0_2$, $6b^0_2$ and form progressions of progressions built on these modes also, though of much weaker intensity. No other totally symmetric modes appear to form progressions. The third most active totally symmetric mode is $v_{8a}$. Its first overtone could be part of the composite band $9a^0_1 12^0_2 6a^0_3 10b^0_2$; its second overtone would occur at the position of the composite band assigned as $8a^0_1 12^0_3 6a^0_4 9a^0_1 12^0_1$. No bands appear which could be assigned as overtones of $9a^0_1(1^0_1)^*$. No transitions attributable to changes in the remaining ring breathing vibration $v_{19a}$ are observed and none of the totally symmetric CH stretching or bending vibrations are important in the $O^0_0$ spectrum.

Benzene-$d_6$ has been reported to yield identical vibrational structure to benzene-$h_6$ in SVL fluorescence spectra [Parmenter and Schuyler, 1970a], but the vibrational structure in the fluorescence spectra of pyrimidine-$d_4$ and -$h_4$ are notably different. Compared with the vibrational structure of

* The band appearing at 974 cm$^{-1}$ (table 6.2) should be assigned to the ring vibration $1^0_0$ but assignments in the pyrimidine-$d_4$ fluorescence spectra have been based on those of Sbrana, Adembri and Califano (1966) given in table 6.1. Mode $v_{9a}$ is a CH bending vibration of frequency $>860$ cm$^{-1}$ and is not expected to show significant activity in the fluorescence spectra reported here.
Figure 6.3. Fluorescence spectrum from \(^0\) level of pyrimidine-d\(_4\). Pressure 0.017 torr, collection bandpass 10-5 cm\(^{-1}\), step size 1.6-1.0 cm\(^{-1}\), NSM=5, constant excitation intensity collection intervals. Assignments in table 6.2.
Table 6.2 Assignments of band maxima observed in fluorescence from the zero-point level of pyrimidine-\textsubscript{d},
(spectrum in figure 6.3)

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<th>Calculated displacement</th>
<th>Band maximum (cm\textsuperscript{-1} vac.)</th>
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the $0_0^0$ fluorescence spectrum of pyrimidine-d$_4$, the $0_0^0$ fluorescence spectrum of pyrimidine-h$_4$ [KLP] is more congested and comprises more progression forming modes ($v_{6a}$, $v_{12}$, $v_{9a}$, $v_{1}$, $v_{19a}$, $v_{8a}$), though only modes $v_{6a}$ and $v_{12}$ form long progressions and progressions of progressions.

Congestion in the $0_0^0$ fluorescence spectrum of pyrimidine-h$_4$ has been attributed to the involvement of both the strong progression forming modes in Fermi resonances, $v''$ with $2v''_{16b}$ and $v''_{12}$ with $v''_{10b} + v''_{16b}$ [KLP]. Thus members of progressions in $v''$ and $v''_{12}$ have multiplet structure; for example, in the progression $6a_0^0$, the first member appears as a doublet, the second as a triplet, the third as a quartet and so on, with the intensity being concentrated towards the centre of the multiplet bands as they become broader and more complex. The absence of Fermi resonance multiplet structure in the $0_0^0$ fluorescence spectrum of pyrimidine-d$_4$ serves to confirm that the congestion of the corresponding pyrimidine-h$_4$ spectrum is due to Fermi resonance because the occurrence of Fermi resonances depends on the accidental degeneracy of vibrational levels of appropriate symmetry. The assignment of some hot bands in the high resolution electronic absorption spectrum of pyrimidine-d$_4$ in terms of Fermi resonances [Innes et al., 1969], will be challenged in the next section.

Modes $v_{9a}$, $v_{1}$ and $v_{19a}$ are more active in the $0_0^0$ fluorescence spectrum of pyrimidine-h$_4$ than in the corresponding spectrum of pyrimidine-d$_4$. In the spectrum of pyrimidine-h$_4$, mode $v_{9a}$ is prominent, with band $9a_1^0$ being of half the intensity of band $6a_1^0$ and with $v_{9a}$ forming short progressions; bands $19a_1^0$ and $1_1^0$ are also quite prominent but they are weaker than $9a_1^0$ and their higher progression members are obscured by stronger overlapping bands. Though, relative to the intensities of strong transitions such as
6a^0, the intensity of 8a^0 is about the same in the 0^0 fluorescence spectra of both pyrimidine-h_4 and -d_4, mode v_{8a} appears more prominently in the pyrimidine-d_4 spectrum where it is given greater emphasis by the lesser congestion.

Of the non-totally symmetric modes, only v_{10b} and v_{6b} appear in transitions in the 0^0 fluorescence spectrum of pyrimidine-d_4. The transition assigned as 10b^0_2 is particularly prominent, forming the origin for 6a^0_12^0_m progressions of comparable or greater intensity than those built on 9a^0_1. In the 0^0 fluorescence spectrum of pyrimidine-h_4, v_{10b} appears in combination with modes of the same symmetry (b_1) to form totally symmetric combination bands such as 4b^0_110b^0_1. According to table 6.1, the combination v''_{4b} + v''_{10b} would occur at a displacement of 1113 cm^{-1} in the 0^0 spectrum of pyrimidine-d_4. Mode v_{4b} is a ring mode and might be expected to be more active in the 0^0 spectrum than mode v_{10b} which is a CH bending mode. The occurrence of a band at 1105 cm^{-1} displacement in the 0^0 spectrum of pyrimidine-d_4 rather than at 1122 (2 x 561) cm^{-1} or 1113 (561 + 552) cm^{-1} perhaps suggests that the assignments for v_{10b} (552 cm^{-1}) and v_{4} (561 cm^{-1}) of table 6.1 be interchanged. Data from vibrational spectra on the frequencies of modes v_{10b} and v_{4} are inconclusive [SAC; M-NS]; the 0^0 fluorescence spectrum does confirm, however, a fundamental frequency of about 552 cm^{-1} for one non-totally symmetric mode.

The rationale for attempting to assign some of the very weak bands of less than 2000 cm^{-1} displacement from the excitation position is that it may assist in establishing some of the ground state fundamental frequencies which are uncertain. It is possible for modes which are only weakly active in infrared and Raman spectra to be relatively active and...
hence more readily observed in electronic spectra. Weaker bands which appear consistently in the \(0^0\) fluorescence spectrum of pyrimidine-d\(_4\), (as well as other SVL spectra), include the following:

(i) \(\sim 1387 \text{ cm}^{-1}\) (labelled \(Y\)) - this is perhaps attributable to the transition \(6a_{1}^{0}16a_{2}^{0} (659 + 2 \times 369)\) or the transition \(5b_{1}^{0}10b_{1}^{0} (830 + 552)\);

(ii) \(\sim 1495 \text{ cm}^{-1}\) - this may be due to the transition \(5b_{1}^{0}11^{0} (830 + 669)\) or the transition \(6a_{1}^{0}1^{0} (659 + 830)\);

(iii) \(\sim 1592 \text{ cm}^{-1}\) (labelled \(Z\)) - this relatively prominent band forms the origin of progression \(Z6a_{n}^{0}\) but it cannot be assigned to any of the totally symmetric modes or as an overtone of a non-totally symmetric mode; it is also the basis for progressions such as \(Z6a_{n}^{0}12_{1}^{0}\) etc. which overlap the higher members of progressions \(6a_{n}^{0}\) etc.; the assignment \(3_{1}^{0}6b_{1}^{0} (985 + 603)\) is suggested.

It should be noted that the assignments in (i) and (ii) require that the frequency for \(\nu_{5b}^{\prime}\) be \(\sim 830 \text{ cm}^{-1}\) rather than \(\sim 848 \text{ cm}^{-1}\) (cf. table 6.1).

In Appendix A6(i), the \(0^0\) fluorescence spectrum in figure 6.3 is given (a) plotted without any computer smoothing and (b) plotted employing a three point moving average scheme (chapter 3). Three other versions of the \(0^0\) fluorescence spectrum of figure 6.3 are given in Appendix A6(ii), together with tables listing the positions and assignments of some of the band maxima for comparison with table 6.2. In all three versions, fluorescence data were collected at each step of the wavelength scan for a constant time interval and not a constant excitation intensity as with the spectrum of figure 6.3 and considerable differences in the intensity distributions from that in figure 6.3 are apparent. In versions (a) and (c), the fluorescence collection bandpass was 9-4 \(\text{cm}^{-1}\). Version (b) was obtained with a fluorescence collection bandpass of 5.0-4.4 \(\text{cm}^{-1}\). Only the initial
portion of the $0^0$ fluorescence spectrum was measured in version (b) to
give emphasis to the rotational structure of each vibrational band. Some
parts of the spectrum in Appendix 6(ii) version (b) were not recorded
(completely flat sections) to reduce collection time. Those displacements
of band maxima which are compared in three of the versions of the $0^0$
fluorescence spectrum are all in excellent agreement.

B. Fermi resonance

Innes et al. (1969) attributed the multiplet structure near the
expected positions of bands $6a^0_1$ and $6a^1_0$ in their high resolution absorption
spectra of both pyrimidine-$h_4$ and -$d_4$ to Fermi resonance involving
($v''_6a$ with $2v''_{16b}$) and ($v'_{6a}$ with perhaps $2v'_{16b}$) respectively. Evidence
from the absorption spectra for the involvement of $v''_{6a}$ in Fermi resonance
comes from weak hot bands. In the $0^0$ fluorescence spectra (and other
SVL fluorescence spectra), such Fermi resonance interactions, if appreciable,
should be directly observable as multiplet structure in the region of the
$6a^0_1$ fluorescence band. For pyrimidine-$h_4$, multiplet structure has
indeed been observed in fluorescence spectra for the progression $6a^0_n$
[KLP]. Band $6a^0_1$ appears as a doublet astride the displacement 681 cm$^{-1}$
and this has been easily resolved in a higher resolution scan (collection
bandpass 2.5 cm$^{-1}$) of the $6a^0_1$ band of the $0^0$ fluorescence spectrum of
pyrimidine-$h_4$ obtained with our fluorimeter. Figure 6.4 clearly shows
the band as two almost equally intense peaks 7.8 cm$^{-1}$ apart. No such
multiplet structure is observed, however, near the $6a^0_n$ progression members
of the SVL fluorescence spectra of pyrimidine-$d_4$, (e.g. figure 6.3).
Figures 6.5, 6.6 and 6.7 show higher resolution scans, similar to the scan
of figure 6.4 for pyrimidine-$h_4$, of the $6a^0_1$, $6a^0_2$ and $6a^0_12^0_1$ fluorescence
Figure 6.4. Band 6a\textsuperscript{16b} in the O\textsubscript{2} fluorescence spectrum of pyrimidine-h\textsubscript{4}. Excitation 31073 cm\textsuperscript{-1}, pressure 0.04 torr, collection bandpass 2.5 cm\textsuperscript{-1}, step size 0.25 cm\textsuperscript{-1}, NSM=6.

Figures 6.5, 6.6, 6.7. Bands 6a\textsuperscript{1}, 6a\textsuperscript{9}, 6a\textsuperscript{12b} in the O\textsubscript{2} fluorescence spectrum of pyrimidine-d\textsubscript{4}. Excitation 31188 cm\textsuperscript{-1}, pressure 0.15 torr, collection bandpass 2.5-2.3 cm\textsuperscript{-1}, step size 0.3 cm\textsuperscript{-1}, NSM=4.

Constant excitation intensity collection intervals.
bands of pyrimidine-d$_4$ after zero-point level excitation. The "humps" on either side of the peak intensity in these figures reflect the non-equilibrium distribution of rotational levels excited in absorption (to be verified in section 6.10) and do not represent multiplet structure resulting from a Fermi resonance interaction. The absence of multiplet structure for 6a$_1^0$, 6a$_2^0$, ... in the Q$_0^0$ fluorescence spectrum of pyrimidine-d$_4$ implies that the interpretation by Innes et al. (1969) of some of the hot bands in the absorption spectrum of pyrimidine-d$_4$ must be incorrect.

In the analysis by Innes et al. (1969), the anharmonic term in the potential energy responsible for the proposed Fermi resonance was assumed to be of the form $V_{\text{anh}} = k q^2$ where the normal coordinate $q$ equals the $\gamma^2 Q$ of Wilson, Decius and Cross (1955, pp. 289-291). A perturbation theory appropriate for near degenerate interacting levels was used [Herzberg, 1950, pp. 282-283], the perturbed vibrational energy levels being given by the solution of a secular determinant whose diagonal elements are the zero order energy levels in the absence of the Fermi resonance interaction and whose off-diagonal elements are the perturbation interaction energies given by

$$W_{ij} = \int \psi_i^* V_{\text{anh}} \psi_j \, d\tau = W_{ji}$$

(6.1)

For interaction between vibrational levels of the same electronic state, this reduces to a vibrational integral of the form tabulated for harmonic oscillator vibrational eigenfunctions in Wilson, Decius and Cross (1955, pp. 289-291).
The secular determinant for the diads is

\[
\begin{vmatrix}
E^0_m - E & w_{mn} \\
w_{nm} & E^0_n - E
\end{vmatrix} = 0
\] (6.2)

where the \( E \) represent the observed energy values resulting from the perturbation. This equation is equivalent to equation 5.13. Equations 5.14 and 5.15 define the eigenfunctions of the resulting mixed states. Figure 6.8 illustrates the relevant energy levels (in cm\(^{-1}\)) for pyrimidine-d\(_4\) hot band absorption. The relative intensity of a transition \( 0' \leftrightarrow \psi_1, 0' \leftrightarrow \psi_2 \) is determined by the Franck-Condon factor. If only one of the levels in the mixture carries oscillator strength, the relative

![Diagram of energy levels](image)

Figure 6.8. Energy levels (in cm\(^{-1}\)) resulting from anharmonic mixing relevant to pyrimidine-d\(_4\) hot band absorption.
intensities of transitions involving these mixed states depends on the coefficient of that component in the mixture. For the levels 6a₁ and 16b₂, only 6a₁ has a significant overlap integral with the upper state zero-point level (vide infra) so only the component ψ₆ₐ contributes intensity. Therefore, the relative intensity of the bands will be

\[ \frac{I_1}{I_2} = \frac{a^2}{b^2} = \rho \]  

(6.3)

where a and b are given by equations (5.16). Substituting for a and b in equation (6.3) and using equations

\[ \delta = E_m^0 - E_n^0 \quad \text{and} \quad (4|W_{mn}|^2 + \delta^2)^\frac{1}{2} = E_1 - E_2 \]  

(6.4)

gives the equation

\[ \frac{\rho - 1}{\rho + 1} = \frac{(E_m^0 - E_n^0)/(E_1 - E_2)} \]  

(6.5)

in which the observed separation of the perturbed levels is related to the separation between the levels in the absence of the anharmonic perturbation under consideration. According to this theory, if the two components of the diad are of equal intensity, the separation of the levels in the absence of the Fermi resonance interaction, \( \delta \), would be zero, i.e. in the absence of anharmonicity the levels would be in resonance.

The secular determinant for the triads resulting from interaction of the three near resonant levels 6a₂, 6a₁6b₂, 16b₄ for the hot band absorption transitions is of the form

\[
\begin{vmatrix}
E_r^0 - E & W_{rs} & W_{rt} \\
W_{sr} & E_s^0 - E & W_{st} \\
W_{tr} & W_{ts} & E_t^0 - E \\
\end{vmatrix} = 0 
\]  

(6.6)
Innes et al. (1969) used the experimental information about the diads (the separation and relative intensity of component bands) to calculate the zero order energy values \( E_0 \), \( E_0' \) and the constant \( k \) of the perturbation \( V_{\text{an}} \). For the 30530.0 \( \text{cm}^{-1} \) and 30544.3 \( \text{cm}^{-1} \) hot bands of pyrimidine-\( d_4 \), \( E_1 - E_2 = 14.3 \text{ cm}^{-1} \) and \( \rho = 2 \) so \( E_0' - E_0' = 4.77 \text{ cm}^{-1} \) and the zero order energy levels, the \( E_0' \)'s of equation (6.2), are located 653.5 \( \text{cm}^{-1} \) and 648.8 \( \text{cm}^{-1} \) from the vibrationless level of the ground state. The integral \( W_{mn} \) of equation (6.2) for the mixing of levels \( 6a_1 \) and \( 16b_2 \) reduces to

\[
W_{mn} = \langle 6a_1 16b_0 \mid k \gamma_{6a}^2 16b_0 \mid 6a_0 16b_2 \rangle^+ \tag{6.7}
\]

\[
= k \langle 6a_1 \mid \gamma_{6a} \mid 6a_0 \rangle \langle 16b_0 \mid \gamma_{16b}^2 \mid 16b_2 \rangle \tag{6.8}
\]

\[
= k \langle 6a_1 \mid \gamma_{6a}^2 Q_{6a} \mid 6a_0 \rangle \langle 16b_0 \mid \gamma_{16b}^2 \mid 16b_2 \rangle \tag{6.9}
\]

\[
= k \gamma_{6a}^2 Q_{6a} \langle 6a_0 \rangle \langle 16b_0 \rangle \tag{6.10}
\]

\[
= k \gamma_{6a}^2 \left( \frac{1}{2 \gamma_{6a}} \right) \frac{1}{2 \gamma_{16b}} \tag{6.11}
\]

\[
= k/2 \tag{6.12}
\]

using the symbols and listed integrals for harmonic oscillator vibrational eigenfunctions of Wilson, Decius and Cross (1955, Appendix III).

\[\dagger\] Under the harmonic oscillator approximation, the product of the overlap integrals for all other vibrational modes \( x \) is unity since for all \( x, v_x'' = 0 \) and \( v_x' = 0 \). The factor \( \langle x' \rangle' x_0 | x_0 \rangle^2 \), the dash indicating that some of the \( 3N-6 \) normal modes are omitted from the product, has been omitted from equation (6.7) and similar equations.
Equation (6.2) then becomes

\[
\begin{vmatrix}
653.5-E & k/2 \\
k/2 & 648.8-E
\end{vmatrix}
= 0
\] (6.13)

in which the values of E are known \((658.3, 644 \text{ cm}^{-1})\). Substitution of one of the values of E in equation (6.13) yields a value of \(13.5 \text{ cm}^{-1}\) for k. Innes et al. (1969) used this value of k and the harmonic values determined from \(E_m^0, E_n^0\) for \(E^0_r, E^0_s, E^0_t\) to solve the cubic equation (6.6) for the values of E for the triad*. The agreement between the calculated and observed values of E for the triad was taken as confirmation of the proposed Fermi resonance interaction between \(6a_1\) and \(16b_2\) and of \(6a_2\) with \(6a_1 16b_2\) and \(16b_4\).

Some aspects of the above calculation for pyrimidine-\(d_4\) present difficulties. The calculation requires that \(E_n^0\), the energy of level \(16b_2\) in the ground state after all anharmonicities apart from the Fermi resonance interaction under consideration have been taken into account, be \(644 \text{ cm}^{-1}\), i.e. \(2\nu''_{16b} = 644 \text{ cm}^{-1}\). However, \(\nu''_{16b}\) has been securely assigned a frequency of \(304 \text{ cm}^{-1}\) (section 6.3) and that anharmonicity should cause the first overtone of \(\nu''_{16b}\) to be shifted so far from its harmonic value in the direction corresponding to an expansion rather than a contraction of the vibrational energy levels seems unreasonable. In view of this, the use of harmonic values for \(E_r^0, E_s^0, E_t^0\) in calculating the energy levels of the triad is inconsistent.

* In equation (6.6), the off-diagonal elements \(W_{rs}, W_{rt}, W_{st}\) are also proportional to k. If r represents \(6a_2\), s represents \(6a_1 16b_2\) and t represents \(16b_4\) then \(W_{st} = \langle 6a_1 16b_2 | kq_{6a_1 16b} \rangle 6a_0 16b_4 \rangle\) reduces to \((3/2)^{1/2}k\), \(W_{rs}\) to \((1/2)^{1/2}\) and \(W_{rt}\) vanishes.
When the perturbation theory equations are applied in the case of pyrimidine-\(H_4\), for which the proposed Fermi resonance interaction has been confirmed by the fluorescence spectrum, no such inconsistencies arise.

For pyrimidine-\(H_4\), transitions nominally assigned as \(16b_0^0\) and \(6a_1^0\) are observed in hot band absorption with equal intensity at 30388.6 cm\(^{-1}\) and 30395.4 cm\(^{-1}\) respectively, the 0-0 band being at 31072.7 cm\(^{-1}\) [Innes et al., 1969], and KLP observed the corresponding bands in zero-point fluorescence at displacements of 678 cm\(^{-1}\) and 685 cm\(^{-1}\) from the 0\(^0\) band. If a similar cubic term in the potential energy is responsible for the coupling, transition intensity is again only associated with \(6a_1^0\), since the Franck-Condon factor for \(16b_2^0\) is very small, and the relative intensity in the diad is given by \(a^2/b^2\). Since the bands are of near equal intensity, \(a^2 = b^2\) and \(\delta = 0\). Therefore, for pyrimidine-\(H_4\), \(E_m^0 = E_n^0 = 680.7\) cm\(^{-1}\) and \(v''_{6a} = 2v''_{16b} = 680.7\) cm\(^{-1}\). Substitution of one of the observed values of \(E\) in equation 6.2 yields \(k = 6.8\) cm\(^{-1}\). In this case, the fundamental frequency for \(v''_{16b}\) has been definitively determined to be 344 cm\(^{-1}\) so the value required for its first overtone is quite reasonable.

If the magnitude of the anharmonic perturbation mixing levels \(6a_1^1\) and \(16b_2^0\) in pyrimidine-\(D_4\) is estimated from the value of \(W_{mn}\) found for pyrimidine-\(H_4\), and if harmonic values are used for the energies \(E_m^0, E_n^0\) in equation 6.2 then (i) the energy levels \(E_1\) and \(E_2\) resulting from the Fermi resonance interaction between the levels \(6a_1^1\) and \(16b_2^0\) and (ii) the relative intensity of the transitions between these levels and the vibrationless level of the upper state can be calculated. The ratio of the integrals \(W_{mn}\) for pyrimidine-\(H_4\) and pyrimidine-\(D_4\) can be determined as follows [Fischer, 1979]:

\[
\frac{(W_{mn})_H}{(W_{mn})_D} = \frac{\langle 6a_1|Q_{6a}^0|6a_0\rangle \langle 16b_0|Q_{16b}^2|16b_2\rangle}{\langle 6a_1|Q_{6a}^0|6a_0\rangle \langle 16b_0|Q_{16b}^2|16b_2\rangle}
\]

(6.14)

\[
= (2\gamma_{6a,M_{6a}})^{-\frac{1}{2}} 2^{-\frac{1}{2}} (\gamma_{16b,M_{16b}})^{-\frac{1}{2}}
\]

(6.15)

\[
= \frac{(2\gamma_{6a,M_{6a}})^{-\frac{1}{2}} 2^{-\frac{1}{2}} (\gamma_{16b,M_{16b}})^{-\frac{1}{2}}}{(2\gamma_{6a,M_{6a}})^{-\frac{1}{2}} 2^{-\frac{1}{2}} (\gamma_{16b,M_{16b}})^{-\frac{1}{2}}}
\]

where \( \gamma = 4\pi^2v/h, \quad \nu = \frac{1}{2\pi}(f/M)^{\frac{1}{2}} \)

(6.16)

f being the force constant. The M's in the above equations are mass weighting factors and arise because the normal coordinates Q are mass-weighted. Equation (6.15) reduces to

\[
\frac{(W_{mn})_H}{(W_{mn})_D} = \frac{\nu_{6a}^h \nu_{16b}^d}{\nu_{6a}^d \nu_{16b}^h}
\]

(6.17)

With \( \nu_{6a}^h = 681.5, \quad \nu_{6a}^d = 659, \quad \nu_{16b}^h = 344 \) and \( \nu_{16b}^d = 304 \text{ cm}^{-1} \), the ratio is 1.15 and if \( (W_{mn})_H = 3.4 \text{ cm}^{-1} \), then \( (W_{mn})_D = 3.9 \text{ cm}^{-1} \). Solution of the secular equation

\[
\begin{array}{ccc|c}
659-E & 3.9 & & 0 \\
3.9 & 608-E & & \\
\end{array}
\]

(6.18)

then yields: \( E_1 = 659.3 \text{ cm}^{-1}, \quad E_2 = 607.7 \text{ cm}^{-1} \) so that \( \rho = 171 \). Thus the expected energy shifts are 0.3 cm\(^{-1}\) and the relative intensities are 1:0.006; the failure to observe any evidence of the Fermi resonance interaction in the fluorescence spectrum is quite reasonable. In deriving a value for \( (W_{mn})_D \) in this manner, it has been assumed that the force constants and the potential energy function (and hence k) are changed by a negligible amount by isotope substitution because they are determined by
the electronic structure of the molecule and that deuteration produces changes in the frequencies of vibration solely by changing the mass of the molecule.

C. Franck-Condon factors

Franck-Condon factors were determined from the $0^0_0$ fluorescence spectrum by integrating the intensity of vibrational bands using a computer listing of corrected intensities for each step of the collection spectrometer scan (chapter 4). Corrections were made for background, consisting mainly of underlying sequence congestion and the tails of nearby bands and for overlap with nearby bands. The background estimate can sometimes be very uncertain* and the identification of higher progression members can be difficult because of congestion**. Since the observed intensity of a vibronic band $(v',v'')$ corresponds to $I_{v',v''}^{em}$, where

$$I_{v',v''}^{em} = v_{v',v''}^4 <v'/v''>_2^2$$

(6.19)

the required Franck-Condon factor, $<v'/v''>_2^2$, can be extracted from $I_{v',v''}^{em}$ once the frequency factor for the transition is taken into account.

Though the Franck-Condon factors for all the members of a progression sum to unity [Sponer and Teller, 1941], for convenience here the Franck-Condon factors for the members of a progression $x^0_n$ have been normalised relative to the value of the Franck-Condon factor for the second member $x^0_1$.

---

* This applies even to strong bands such as $6a^0_2 12^0_2$ but especially to weaker bands such as $6a^0_5 12^0_2$ (see figure 6.3).

** These peaks appear more prominently in the uncorrected spectrum of figure 4.16.
Neither the true intensity of the $O^0_0$ band nor the Franck-Condon factor for the first member of a progression $x^0_0$ can be determined directly from the $O^0_0$ spectrum. Estimates for these quantities can be obtained, however, by using the Harmonic Oscillator approximation for the vibrational motion if there are no intensity anomalies for the transitions involved in obtaining the estimation (caused either by anharmonic mixing or by vibronically induced contributions from another electronic transition such as in the case of phenanthrene (section 5.4C)).

$I_c(O^0_0)$, the intensity of the $O^0_0$ band, can be estimated from the ratio of intensities of bands clearly observed in the spectrum viz.:

$$I_c(O^0_0) = \frac{I_c(6a^0_1)I_c(12^0_1)}{I_c(6a^0_1 12^0_1)} = \frac{I_c(6a^0_2)I_c(12^0_1)}{I_c(6a^0_2 12^0_1)} = \ldots = \frac{I_c(6a^0_1)I_c(12^0_2)}{I_c(6a^0_1 12^0_2)}$$

$$I_c(6a^0_1)I_c(12^0_3) = \ldots = \frac{I_c(8a^0_1)I_c(12^0_1)}{I_c(8a^0_1 12^0_1)} = \ldots = \frac{I_c(10b^0_2)I_c(12^0_1)}{I_c(10b^0_2 12^0_1)}$$

$$= \ldots$$ (6.20)

where the subscript $c$ is used to denote that the intensities are corrected for the $\nu^4_\nu^\prime\nu^\prime\prime$ factor (equation 6.19) and so are proportional to the Franck-Condon factor for the band. That these relationships hold can be seen by expanding the intensities ($I_c$'s) in terms of all the Franck-Condon factors for the band viz.:

$$I_c(6a^0_1)I_c(12^0_1) = \frac{\langle 6a^0_1 \mid 6a^0_2 \rangle^2 \langle 12^0_1 \rangle^2 \langle x^0 \mid x^0 \rangle^2 \langle x^0 \mid x^0 \rangle^2}{\langle 6a^0_1 \mid 6a^0_2 \rangle^2 \langle 12^0_1 \rangle^2 \langle x^0 \mid x^0 \rangle^2 \langle x^0 \mid x^0 \rangle^2}$$ (6.21)
Estimates of the relative Franck-Condon factor for the first member of a progression such as \(6a_0\) i.e. \(6a_0\) can be obtained from ratios of intensities such as

\[
\frac{I_c(12_0)}{I_c(6a_{012})} = \frac{I_c(12_2)}{I_c(6a_{120})} = \cdots = \frac{I_c(8a_{1})}{I_c(6a_{112})} = \frac{I_c(8a_{120})}{I_c(6a_{18a_{120}})} = \cdots
\]

\[
= \frac{I_c(10b_{0})}{I(6a_{10b_{0}})}
\]

because, for example

\[
\frac{I_c(12_0)}{I_c(6a_{112})} = \frac{<6a_0|6a_0>^2<12_0|12_1>^2\int_x<x^0|x_0^2>}{<6a_0|6a_1><12_0|12_1>^2\int_x<x^0|x_0^2>} = \frac{<6a_0|6a_0>^2}{<6a_0|6a_1>^2} = \frac{1}{<6a_0|6a_1>^2}
\]

(6.25)

If the Harmonic Oscillator approximation holds and if the spectrum is properly corrected, all the ratios for \(I_c(0_0^0)\) and for \(<6a_0|6a_0>^2\) etc. should agree exactly. This does not occur for the \(0_0^0\) spectrum and is possibly a manifestation of the breakdown of the Harmonic Oscillator approximation. Errors in the collection and correction of the spectrum and incorrect estimation of band intensities could also account in part for the discrepancies. In obtaining an estimate of \(I_c(0_0^0)\), the average of
several available estimates was taken*. To obtain an estimate of the Franck-Condon factors $<6a^0|6a^0>_2$ and $<12^0|12^0>^2$ in the progressions $6a^0_n$ and $12^0_n$, several estimates were averaged but to obtain the Franck-Condon factor for the first member of progressions such as $6a^0_n12^0_2$, the estimate arising from the ratio containing the intensity of a band in that progression, viz. $I_c(12^0_2)/I_c(6a^0_112^0_2)$, was used.

Franck-Condon factors were determined for several progressions in each of the modes $v''_{6a}$ and $v''_{12}$ and compared with theoretical Franck-Condon factors determined from the tables of Henderson et al. (1964) as indicated in section 5.4B. Higher members of progressions $6a^0_n12^0_16a^0_n$, $12^0_26a^0_n$, $12^0_36a^0_n$ overlap with members of the progression $12^0_16a^0_n$ and corrections were made for this overlap. Again several estimates for the intensities of $12^0_1$, $12^0_36a^0_1$ etc. were averaged in making these corrections. For example, $I_c(12^0_1)$ can be estimated from several ratios including $I_c(12^0_1)I_c(6a^0_12^0_1)/I_c(6a^0_1)$, $I_c(12^0_1)I_c(8a^0_12^0_1)/I_c(8a^0_1)$ and $I_c(12^0_1)I_c(10b^0_12^0_1)/I_c(10b^0_1)$ and contributions such as $I_c(12^0_36a^0_1)$ can be obtained from the ratios $I_c(12^0_3)I_c(6a^0_12^0_3)/I_c(12^0_3)$ and $I_c(12^0_3)I_c(6a^0_1)/I_c(0^0_0)$. Greater uncertainties attach to estimates derived using other estimated intensities, e.g. $I_c(0^0_0), I_c(12^0_3)$.

Relative Franck-Condon factors for progressions in $6a^0_n$ built on the origins $0^0_0$, $12^0_1$, $12^0_2$, $12^0_3$ are presented in figure 6.9 where they are

---

* For example, 13 estimates of $I_c(0^0_0)$ ranging from 1634 (using $I_c(12^0_46a^0_1)$) to 3233 (using $I_c(6a^0_12^0_3)$) give an average of 2411 and a standard deviation of 498 and 2340 ±450 if the outlier 3233 is rejected (the second highest estimate being 2907 using $I_c(10b^0_26a^0_112^0_1)$). There is no trend in the estimates of $I_c(0^0_0)$ obtained across the range of the spectrum.
Figure 6.9. Observed (bars) and calculated (points) relative Franck-Condon factors (FCFs) for $6a_0$ progressions in the $0^0$ level fluorescence of pyrimidine-$d_4$. Origins: (a) $0^8$, (b) $12^7$, (c) $12^9$, (d) $12^8$. Calculated FCFs determined using parameters $\delta=1.1$, $D=1.5-1.9$. FCFs observed without correcting for overlapping transitions shown as dashed bars.
Figure 6.10. Observed (bars) and calculated (points) relative Franck-Condon factors (FCFs) for $6a_0^\pi$ progressions in the 00 level fluorescence of pyrimidine-d$_4$. Origins: (a) 08, (b) 12, (c) 12, (d) 12. Calculated FCFs determined using parameters $\delta=1.0$, $D=1.5-1.9$. FCFs observed without correcting for overlapping transitions shown as dashed bars.
compared with Franck-Condon factors for a harmonic oscillator with \( \delta = 1.1 \) (A in the figures) and \( D = 1.5-1.9 \) and also in figure 6.10 where they are compared with theoretical Franck-Condon factors for \( \delta = 1.0 \) and \( D = 1.5-1.9 \). Franck-Condon factors obtained without correcting the observed intensities of higher members of the progressions for overlap with members of progressions built on the transition labelled \( Z \) are shown as dashed bars. For \( \nu_{6a} \) the parameter \( \delta \) of Henderson's tables is 1.052 but available tables only list overlap integrals for \( \delta \) values in increments of 0.1. Though assignments are given in figure 6.3 for very high members of progressions (up to 11 for \( 6a^0_n \)), only peaks of certain identity and of measurable intensity were considered in assessing Franck-Condon factors. Overlap with other transitions is more prevalent at higher displacements from the excitation position and, in several cases, assignment markers have been continued for only one contribution to the intensity of peaks*. Assignments given for peaks at large displacements are only offered as suggestions in any case.

It is apparent from figures 6.9 and 6.10 that the intensity profiles for the \( 6a^0_n \) progressions, with maxima at \( n = 1 \) and with \( I_c(n = 0) > I_c(n = 2) \) are best replicated by the Franck-Condon factors of a harmonic oscillator with parameters \( \delta = 1.0-1.1 \) and \( D = 1.6-1.7 \). These results for pyrimidine-\( d_4 \) are in good accord with the results obtained for pyrimidine-\( h_4 \) where it was found that the observed intensity pattern for the \( 6a^0_n \) progression was well replicated using \( \delta = 1.0 \) and \( D = 1.6 \) to obtain the theoretical Franck-Condon factors [KLP]. Greater congestion in the pyrimidine-\( h_4 \)

* This is not necessarily for the strongest contributor. For example, in figure 6.3 assignment markers \( 6a^0_8,9,10,11 \) are given to peaks which possibly derive most of their intensities from the transition \( 10b^0 \) \( 12^0 6a^0_0,1,2,3 \). The number of lines of assignment markers must be limited in figures such as figure 6.3.
spectra prevented the more extensive analysis of Franck-Condon factors possible for pyrimidine-d₄ spectra.

A notable feature of the Franck-Condon factors for 6a₀ⁿ progressions in pyrimidine-d₄ is the tendency for observed Franck-Condon factors not to decrease as rapidly with increasing n as do the theoretical Franck-Condon factors*. This may be due to a trivial mechanism, such as overlap with unassigned transitions of higher intensities or a further manifestation of the breakdown of the Harmonic Oscillator approximation. If the uncorrected 0₀ spectrum (figure 4.16) or the 0₀ spectrum corrected for the changing wavenumber bandpass of the spectrometer (figure 4.17) is used to obtain Franck-Condon factors, the departure from harmonic oscillator behaviour is more pronounced as indicated in table 6.3. In preparing table 6.3, peak heights were used as measures of band intensities for cases (ii), (iii) and (iv). As demonstrated in table 6.3 for the corrected spectrum (figure 6.3 or 4.18), Franck-Condon factors obtained using peak heights, (ii), are in good agreement with those obtained using band areas, (i). For (ii), (iii) and (iv) of table 6.3, corrections for overlap with Z₆ₐ₀ⁿ₁₂₀ⁿ progression members and estimates of not directly derivable Franck-Condon factors were obtained by averaging the same ratios of νⁿ-corrected intensities as used for (i) i.e. as used in deriving the Franck-Condon factors of figure 6.9 (6.10).

* For example, relative Franck-Condon factors of a harmonic oscillator with ϵ = 1.0 and D = 1.6 for a progression ν = 0, ν = n are: 0.8, 1.0, 0.6, 0.3, 0.1, 0.02, 0.005, 0.001, 0.00002 which means that progression members with n>5 should be unobservable experimentally for a harmonic oscillator.
Table 6.3  Comparison of Franck-Condon factors for some $6a_n^0$ progressions of the $0_0^0$ level fluorescence spectrum of pyrimidine-d$_4$ obtained from: (i) the band areas of the corrected spectrum; (ii) the peak heights of the corrected spectrum; (iii) the peak heights of the uncorrected spectrum; (iv) the peak heights of the spectrum corrected for the changing (cm$^{-1}$) collection bandpass; (v) harmonic oscillator with $\delta = 1.0$ and $D = 1.6$; (vi) harmonic oscillator with $\delta = 1.1$ and $D = 1.6$

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<th>Progression</th>
<th>$6a_n^0$</th>
<th>$12_1^06a_n^0$</th>
<th>$12_3^06a_n^0$</th>
<th>H.O.</th>
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<td>.10</td>
</tr>
<tr>
<td></td>
<td>.03</td>
<td>.06</td>
<td>.12</td>
<td>.15</td>
</tr>
<tr>
<td></td>
<td>.001</td>
<td>.005</td>
<td>.01</td>
<td></td>
</tr>
</tbody>
</table>

Notes: "Spectrum" (i), (ii) as in figures 4.18 and 6.3; (iii) as in figure 4.16; (iv) as in figure 4.17.
Progressions in $6a_n^0$ built on other origins ($8a_1^0$, $8a_{12}^0$, etc., $10b_2^0$, $10b_{22}^0$, etc.) display qualitatively the same intensity profiles as the $6a_n^0$ progressions built on $12_n^0$. Franck-Condon factors determined from the first few members of progressions $8a_1^0 6a_1^0$, $8a_{12}^0 6a_1^0$, $8a_{12}^0 6a_{22}^0$, $10b_2^0 6a_1^0$, $10b_{22}^0 6a_1^0$ and $10b_{22}^0 6a_{22}^0$ are given in table 6.4. The intensities of higher members of these progressions are known to be enhanced by overlapping transitions (not all of which are indicated in the annotations to the spectrum of figure 6.3*). There are considerable discrepancies among the Franck-Condon factors of table 6.4 and between the Franck-Condon factors of tables 6.4 and 6.3 but these cannot be taken as evidence of the operation of any special effects involving these transitions because of the greater uncertainties associated with their intensities.

Table 6.4 Franck-Condon factors for $6a_n^0$ progressions built on minor origins in the $0_0^0$ level fluorescence spectrum of pyrimidine-d$_4$

<table>
<thead>
<tr>
<th>Progression</th>
<th>n=0</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$8a_1^0 6a_1^0$</td>
<td>0.68</td>
<td>1.00</td>
<td>1.01</td>
<td>0.42</td>
</tr>
<tr>
<td>$8a_{12}^0 6a_1^0$</td>
<td>0.67</td>
<td>1.00</td>
<td>0.70</td>
<td>0.34</td>
</tr>
<tr>
<td>$8a_{12}^0 6a_{22}^0$</td>
<td>0.61</td>
<td>1.00</td>
<td>0.96</td>
<td>0.51</td>
</tr>
<tr>
<td>$10b_2^0 6a_1^0$</td>
<td>0.50</td>
<td>1.00</td>
<td>0.47</td>
<td>0.63</td>
</tr>
<tr>
<td>$10b_{22}^0 6a_1^0$</td>
<td>0.77</td>
<td>1.00</td>
<td>0.45</td>
<td>0.67</td>
</tr>
<tr>
<td>$10b_{22}^0 6a_{22}^0$</td>
<td>0.52</td>
<td>1.00</td>
<td>0.39</td>
<td>0.55</td>
</tr>
</tbody>
</table>

Note: The numbers given in parentheses for the third member of the $6a_n^0$ progressions built on $10b_2^0$, $10b_{22}^0$ and $10b_{22}^0$ are the Franck-Condon factors obtained before the intensities of the transitions were corrected for overlap with members of the progression $Yl_{22}^0$.

* For example, $6a_{31}^0 10b_{22}^0$ appears to be inordinately intense but, like $6a_{31}^0 10b_{22}^0$, it owes part of its intensity to a member of the progression $6a_{31}^0 9a_{21}^0$ with which it coincides.
Relative Franck-Condon factors for progressions in $12^0_n$ built on the origins $0^0_0, 6a^0_1, 6a^0_2, 6a^0_3, 6a^0_4$ are presented in figure 6.11 where they are compared with harmonic oscillator Franck-Condon factors for $\delta$ (A in the figures) = 1.0 and $D = 1.7-2.0$. For mode $v_{12}$, the parameter $\delta$ of Henderson's tables is 1.02. It was necessary to correct the intensities of members of the progression $6a^0_412^0_n$ for overlap with members of the progression $712^0_n$ (just as with the higher members of the $6a^0_n$ progressions) and the Franck-Condon factors derived if this correction is not made are shown in figure 6.11 as dashed bars. The good agreement apparent in the figure between the pattern of $6a^0_412^0_n$ and the other $12^0_n$ Franck-Condon factor patterns attests to the validity of the correction for the overlapping bands.

The Franck-Condon factors of a harmonic oscillator with $\delta = 1.0$ and $D = 2.0$ best replicate the Franck-Condon factors for the $12^0_n$ progressions in figure 6.11. These results contrast with the results obtained for pyrimidine-$h_4$ for which the observed intensity patterns for $12^0_n$ progressions were found to match theoretical Franck-Condon factors obtained using $\delta = 1.0$ and $D = 1.4$. Franck-Condon factors for the progressions $12^1_n$ obtained from $12^1$ level spectra of pyrimidine-$h_4$ and -$d_4$ are also well matched by theoretical Franck-Condon factors obtained with $\delta = 1.0$, $D = 1.4$ and $\delta = 1.0$, $D = 2.0$ respectively. For pyrimidine-$h_4$, a minimum is observed at $12^{1}_{1}(KLP)$ whereas, as will be shown in section 6.8, for pyrimidine-$d_4$, a minimum is observed at $12^{1}_{2}$. Thus there is a major difference between the Franck-Condon factors for mode $v_{12}$ in the $^1B_1-^1A_1$ transition of pyrimidine-$h_4$ and -$d_4$ which reflects quite a large change in the form of the normal mode upon deuteration. In effect, the geometry change in the electronic transition is mirrored more closely by the $v_{12}$ mode of vibration in pyrimidine-$d_4$ than it is in pyrimidine-$h_4$. 
Figure 6.11. Observed (bars) and calculated (points) relative Franck-Condon factors (FCfs) for $12_n^0$ progressions in the $0^0$ level fluorescence of pyrimidine-d$_4$. Origins: (a) $0^0_0$, (b) $6a_1^0$, (c) $6a_2^0$, (d) $6a_3^0$, (e) $6a_4^0$. Calculated FCfs determined using $\delta=1.0$, $D=1.7-2.0$. In (e), FCfs observed without correcting for overlapping transitions are shown as dashed bars. ((b), (c), (d), (e) on following page).
Figure 6.11(continued)
Table 6.5  Comparison of Franck-Condon factors for some $\frac{12^0_n}{12^0_n}$ progressions of the $0^0_0$ level fluorescence spectrum of pyrimidine-$d_4$ obtained from: (i) the band areas of the corrected spectrum; (ii) the peak heights of the corrected spectrum; (iii) the peak heights of the uncorrected spectrum; (iv) the peak heights of the spectrum corrected for the changing (cm$^{-1}$) collection bandpass; (v) harmonic oscillator with $\delta = 1.0$ and $D = 2.0$

<table>
<thead>
<tr>
<th>Progression</th>
<th>$\frac{12^0_n}{12^0_n}$ (i)</th>
<th>$\frac{6a_1^012^0_n}{12^0_n}$ (i)</th>
<th>$\frac{6a_2^012^0_n}{12^0_n}$ (i)</th>
<th>H.O. (v)</th>
</tr>
</thead>
<tbody>
<tr>
<td>&quot;Spectrum&quot;</td>
<td>(i) (ii) (iii) (iv)</td>
<td>(i) (ii) (iii) (iv)</td>
<td>(i) (ii) (iii) (iv)</td>
<td>(v)</td>
</tr>
<tr>
<td>n = 0</td>
<td>.51 .48 .47 .43</td>
<td>.68 .61 .66 .62</td>
<td>.51 .43 .40 3.7</td>
<td>.50</td>
</tr>
<tr>
<td>1</td>
<td>1.00 1.00 1.00 1.00</td>
<td>1.00 1.00 1.00 1.00</td>
<td>1.00 1.00 1.00 1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>2</td>
<td>.98 1.01 1.02 1.10</td>
<td>1.00 .99 1.13 1.21</td>
<td>.93 .93 1.22 1.32</td>
<td>1.00</td>
</tr>
<tr>
<td>3</td>
<td>.66 .68 .84 .97</td>
<td>.58 .61 .90 1.03</td>
<td>.57 .65 1.03 1.20</td>
<td>.67</td>
</tr>
<tr>
<td>4</td>
<td>.26 .38 .60 .74</td>
<td>.45 .49 .90 1.11</td>
<td>.38 .42 .84 1.06</td>
<td>.33</td>
</tr>
<tr>
<td>5</td>
<td>.14 .16 .31 .41</td>
<td>.16 .18 .41 .55</td>
<td>.07</td>
<td>.13</td>
</tr>
</tbody>
</table>

Notes: "Spectrum" (i), (ii) as in figures 4.18 and 6.3; (iii) as in figure 4.16; (iv) as in figure 4.17.
In Table 6.5, $^{12^0}_{n}$ Franck-Condon factors derived from the corrected (i) and (ii), uncorrected (iii) and partly corrected (iv) $^{0^0}_0$ level fluorescence spectrum of pyrimidine-d$_4$ are compared. Table 6.5 is the $^{12^0}_{n}$ progressions counterpart of table 6.3 and, as in table 6.3, the greatest consistency in the results and best matches with theoretical Franck-Condon factors are obtained using the intensities of the completely corrected spectrum (i) and (ii). The results of tables 6.3 and 6.5 illustrate the need to correct fluorescence spectra and vindicate the attention given to obtaining corrected fluorescence spectra.

Progressions in $^{12^0}_{n}$ built on other origins ($^{8a^0}_{11}$, $^{10b^0}_{2}$, etc.) display qualitatively the same intensity profiles as the $^{12^0}_{n}$ progressions built on $^{6a^0}_{n}$ progression members but, as with the $^{6a^0}_{n}$ progressions built on origins of low intensity, the Franck-Condon factors for the first few members of progressions $^{8a^0}_{11}12^0_n$, $^{8a^0}_{11}6a^0_{11}12^0_n$, $^{8a^0}_{11}6a^0_{2}12^0_n$, $^{10b^0}_{2}12^0_n$, $^{10b^0}_{2}6a^0_{11}12^0_n$ show considerable discrepancies among themselves and with the Franck-Condon factors built on $^{6a^0}_{n}$ origins as evidenced in Table 6.6. The poor correspondence of the Franck-Condon factors of Table 6.6 with those in Figure 6.11 (and Table 6.5) once again probably reflects the greater uncertainty in the measured intensities from which they were derived.

Table 6.6 Franck-Condon factors for $^{12^0}_{n}$ progressions built on minor origins in the $^{0^0}_0$ level fluorescence spectrum of pyrimidine-d$_4$

<table>
<thead>
<tr>
<th>Progression</th>
<th>$n=0$</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{8a^0}_112^0_n$</td>
<td>0.44</td>
<td>1.0</td>
<td>0.98</td>
<td></td>
</tr>
<tr>
<td>$^{8a^0}<em>116a^0</em>{11}12^0_n$</td>
<td>0.43</td>
<td>1.0</td>
<td>1.07</td>
<td></td>
</tr>
<tr>
<td>$^{8a^0}<em>116a^0</em>{2}12^0_n$</td>
<td>0.62</td>
<td>1.0</td>
<td>1.47</td>
<td></td>
</tr>
<tr>
<td>$^{10b^0}_212^0_n$</td>
<td>0.44</td>
<td>1.0</td>
<td>0.86</td>
<td>0.86</td>
</tr>
<tr>
<td>$^{10b^0}<em>26a^0</em>{11}12^0_n$</td>
<td>0.69</td>
<td>1.0</td>
<td>1.29</td>
<td>1.15</td>
</tr>
</tbody>
</table>
6.7 Fluorescence from the Resonance Pair \(6a^1 \ldots 6b^2\) \((0 + 595 \text{ cm}^{-1}, 0 + 645 \text{ cm}^{-1})\)

A. Assignments

Prominent \(\nu \approx 600 \text{ cm}^{-1}\) progressions with multiplet structure in pyrimidine-\(h_4\) and pyrimidine-\(d_4\) absorption spectra were assigned by Innes et al. (1969) as Fermi resonance diads, triads and so on, resulting from interaction between \(\nu'_6a\) and \(2\nu'_6b\), with all intrinsic intensity arising from \(6a^0\). For pyrimidine-\(h_4\), KLP confirmed that the levels of the diad \([0 + 613, 0 + 669 \text{ cm}^{-1}]\), identified by Innes et al. as the resonance pair \(6a^1 \ldots 16b^2\), were of mixed character from a quantitative analysis of the intensity distributions in fluorescence spectra generated by pumping each of the levels. The structure in emission was found to be a weighted mixture of the vibrational structure predicted from each of the upper state levels in the absence of Fermi resonance. It was shown that the major source of intensity in absorption is indeed due to \(\nu'_{6a}\) but that, to explain the intensity distributions of two progressions whose terminating levels are \(6a_n\) and \(6b_{2n}, n = 0, 1, 2, \ldots\), the other state participating in the interaction must be the second quantum level of a mode whose frequency changes from \(621 \text{ cm}^{-1}\) to \(320 \text{ cm}^{-1}\) on excitation. This led KLP to question the assignment by SAC of the \(621 \text{ cm}^{-1}\) fundamental as the ring mode \(\nu''_{6b}\) because, although for benzene-like molecules large frequency changes on excitation are not uncommon for out-of-plane modes, for example, \(\nu_4, \nu_{10}\) and \(\nu_{16}\) in benzene \((\nu'' = 707, 846, 399 \text{ cm}^{-1}\) cf. \(\nu' = 365, 585, 237 \text{ cm}^{-1}\) respectively [Knight, Parmenter and Schuyler, 1975a,b]); \(\nu_{10a}\) and \(\nu_{16b}\) in pyrazine-\(d_0\) and -\(d_4\) \((\nu'' = 919, 416 \text{ cm}^{-1}\) cf. \(\nu = 383, 235 \text{ cm}^{-1}\) respectively for -\(d_0\) and \(\nu'' = 721, 399 \text{ cm}^{-1}\) cf. \(\nu'' = 292, 211 \text{ cm}^{-1}\) for -\(d_4\) [Innes, Byrne and Ross, 1967; Zalewski et al., 1974; Thakur et al., 1974]); and \(\nu_4, \nu_{10b}, \nu_{16b}\) and \(\nu_{16b}\) in aniline \((\nu'' = 691, \ldots\)
233, 419, 501 cm\(^{-1}\) cf. \(\nu' = 365, 177, 187, 387\) cm\(^{-1}\) [Brand \textit{et al.}, 1966; Varsanyi, 1974: Chernoff and Rice, 1979a]) they are not common for ring vibrations, for example \(\nu_1\) and \(\nu_6\) in benzene (\(\nu'' = 993, 608\) cm\(^{-1}\) cf. \(\nu' = 923, 522\) cm\(^{-1}\)); \(\nu_{6a}\) in pyrazine-h\(_4\) and -d\(_4\) (\(\nu'' = 596\) cm\(^{-1}\) cf. \(\nu' = 582\) cm\(^{-1}\) for -h\(_4\) and \(\nu'' = 586\) cm\(^{-1}\) cf. \(\nu' = 578\) cm\(^{-1}\) for -d\(_4\)); \(\nu_1, \nu_{12}, \nu_{6a}\) in aniline (\(\nu'' = 823, 1002, 530\) cm\(^{-1}\) cf. \(\nu' = 798, 953, 492\) cm\(^{-1}\)); and \(\nu_1, \nu_{12}, \nu_{6a}\) in pyrimidine-h\(_4\) (\(\nu'' = 991, 1065, 681\) cm\(^{-1}\) cf. \(\nu' = 941, 1012, 613\) cm\(^{-1}\) [table 6.1; KLP].

It will be shown in section 6.78 by an analysis similar to that by KLP that fluorescence spectra obtained by exciting each of the Fermi resonance pair \(6a^1 \ldots 16b^2\) in pyrimidine-d\(_4\) (31783.7 (0 + 595) cm\(^{-1}\) and 31833.7 (0 + 645) cm\(^{-1}\)), are exactly analogous to the corresponding spectra of pyrimidine-h\(_4\); thus the same conclusions as to the identity of the modes involved in the \(6a^1 \ldots 16b^2\) interaction in pyrimidine-d\(_4\) and pyrimidine-h\(_4\) apply.

The spectra obtained by exciting in the absorption bands labelled \(6a^1_0\) and \(16b^2_0\) by Innes \textit{et al.}, are given in figures 6.12 and 6.13 and the tables of assignments in Appendix A6(iii). For simplicity, the assignments have been made assuming that the originating levels are as labelled by Innes \textit{et al.} though they are known to be of mixed character. Both spectra were obtained using a larger fluorescence collection bandpass than used for the \(0^0\) spectrum (22-10 cm\(^{-1}\) cf. 11-5 cm\(^{-1}\)). Consequently, peaks are broader, overlap of adjacent peaks is more prevalent, and displacements from the excitation position are more uncertain.

Assigning some of the weaker peaks in the first 3000 cm\(^{-1}\) of both spectra is difficult partly because Franck-Condon factors for \(6a^0_n\)
Figure 6.12. Fluorescence spectrum from 6a$^1$(see text) level of pyrimidine-$d_4$. Pressure 0.061 torr, collection bandpass 22-10 cm$^{-1}$, step size 3.4-2 cm$^{-1}$, NSM=5, constant excitation intensity collection intervals. Assignments in Appendix A6(iii).
progression members \( n = 1, 2, 3 \) can be small in these spectra (see next section) making weak transitions indistinguishable from a background noisier and larger than the background in the \( 0_0^0 \) spectrum. This higher background arises from exciting bands built on greater sequence congestion. A low resolution absorption spectrum of pyrimidine-d\(_4\) vapour is given in Appendix A6(iv).

In both spectra, progressions in \( 1_2^n \) and \( 6a^1_n \) built on the same origins as were identified in the \( 0_0^0 \) spectrum provide the bulk of structure at large displacements from the excitation positions. The Franck-Condon factors for \( 6a^1_n \) progressions in these spectra are different from those of the \( 6a^0_n \) progressions in the \( 0_0^0 \) spectra and extend moderately intense structure to even larger displacements from the excitation position than in the \( 0_0^0 \) spectrum. (The intensity distribution within \( 1_2^0_n \) progressions in both spectra is similar to that observed in the \( 0_0^0 \) spectrum as expected). A further difference between the \( 0_0^0 \) spectrum and the \( 6a^1 \) and \( 16b^2 \) spectra is the strength of the band coincident with the calculated displacement for \( 2v_{16b}'' \) (1206 cm\(^{-1}\)). Whereas the band \( 6b^0_2 \) is exceedingly weak in the zero point fluorescence spectrum, in the \( 6a^1 \) and \( 16b^2 \) spectra it is intense, forming the origin for strong progressions in \( v_{6a}'' \) and \( v_{12}'' \) and combinations of them. Furthermore, in the \( 6a^1 \) and \( 16b^2 \) spectra, the intensity distribution within \( 6a^1_n \) progressions built on \( 6b_212_n \), \( n = 0, 1, \ldots \) origins, (to be referred to as Q progressions), differs significantly from that within \( 6a^0_n \) progressions not involving \( v_{6b} \) in the ground state (P progressions) and from that calculated for the progression \( 6a^1_n \) using the \( \delta \) and \( D \) parameters which gave the best match between observed and calculated Franck-Condon factors for the \( 6a^0_n \) progression in the \( 0_0^0 \) spectrum.
Figure 6.13. Fluorescence spectrum from $16b^2$ (see text) level of pyrimidine-$d_4$. Pressure 0.062 torr, collection bandpass 22-10 cm$^{-1}$, step size 3.4-2 cm$^{-1}$, NSM=5, constant excitation intensity collection intervals. Assignments in Appendix A6(iii).
In the $6a^1$ spectrum, peaks labelled $Y$ and $Z$ occur as in the $0^0$ spectrum (displacements $\nu 1384 \text{ cm}^{-1}$ and $1602 \text{ cm}^{-1}$ cf. $\nu 1387 \text{ cm}^{-1}$ and $\nu 1592 \text{ cm}^{-1}$) but of the other peaks of uncertain identity attention is drawn to those at displacements of $1282 \text{ cm}^{-1}$ (labelled $V$), $2317 \text{ cm}^{-1}$ ($V12^0_1$) and $2971 \text{ cm}^{-1}$. If the level mixing with $6a^1$ in forming the Fermi resonance doublet is $16b^2$, a peak of moderate intensity corresponding to a displacement of $16b^2_2$ ($608 \text{ cm}^{-1}$) from the excitation position would be expected in both the $6a^1$ and $16b^2$ fluorescence spectra (as will be shown in Franck-Condon factor calculations in section 6.7B). In the $6a^1$ spectrum, no peak is observed near $\nu 608 \text{ cm}^{-1}$ but the minor peaks at $1282 \text{ cm}^{-1}$, $2317 \text{ cm}^{-1}$ and $2971 \text{ cm}^{-1}$ are near the calculated positions for the transitions $6a^1_{1}16b^0_{2}$ ($1267 \text{ cm}^{-1}$), $6a^1_{0}16b^0_{2}12^0_1$ ($2315 \text{ cm}^{-1}$) and $6a^1_{1}16b^0_{2}12^0_1$ ($2974 \text{ cm}^{-1}$). In the $16b^2$ spectrum, among the peaks of uncertain identity, a peak corresponding to $Z$ of the $0^0$ and $6a^1$ spectra occurs at $1589 \text{ cm}^{-1}$ but, in contrast to the case of the $6a^1$ spectrum, peaks identifiable as $16b^2_{2n}$ progression members appear clearly, transitions to ground state levels $16b^2_2$, $6a^1_{1}16b^2_2$, $12^1_{1}16b^2_2$ occurring at $604$, $1254$ and $1643 \text{ cm}^{-1}$ compared with the calculated displacements $608$, $1267$ and $1656 \text{ cm}^{-1}$ respectively, for example. No transitions involving $2\nu_{16b}$ can be distinguished in the $0^0$ spectrum, so the activity of $2\nu_{16b}$ in the $16b^2$ spectrum constitutes some evidence for the second state coupled with $6a^1$ being $16b^2$. Transitions involving $2\nu_{6b}$ are much more intense than those involving $2\nu_{16b}$ in the $16b^2$ spectrum, however, and, the evidence from the Franck-Condon factor analysis of section 6.7B suggests that levels $6a^1$ and $6b^2$ are the main contributors to the mixed states excited in obtaining spectra "$6a^1n$" and "$16b^2n$" considered in section 6.7.
It is acknowledged that many of the assignments made for peaks at large displacements from the excitation position are uncertain but attempt has been made to account for most peaks in the annotations and the tables of assignments given for spectra 6a₁ and 16b². Portion of a second 16b² spectrum with a table of assignments is given in Appendix A6(v). A second 6a₁ spectrum is given in figure 7.13.

B. Calculation of progression intensity profiles

Assuming that the unperturbed 1B₁ vibrational levels 6a₁ and 6b² (16b²) are near degenerate, from perturbation theory the perturbed eigenfunctions "a" and "k" can be represented as linear combinations of the initial states (sections 5.40, 6.68). If the unperturbed states are represented by harmonic oscillator eigenfunctions |a₁⟩ and |b²⟩, the eigenfunctions of the states resulting from the anharmonic interaction are

\[
a = \beta |a₁⟩ - \alpha |b²⟩ \quad (6.26)
\]

\[
k = \alpha |a₁⟩ + \beta |b²⟩ \quad (6.27)
\]

where mixing coefficients α and β are both positive. Spectra "6a₁" and "16b²", henceforth referred to as A and K respectively, result from exciting absorption bands terminating in states a and k respectively. It is necessary to calculate the intensity profiles for progressions P and Q in these spectra. The energy level diagram in figure 6.14 indicates the participating levels.

Coefficients α and β, necessary for specifying states a and k, can be evaluated from a comparison of the intensities in the 6a₁ ... 6b²
Figure 6.14. Energy level diagram for fluorescence spectra 6a^1(A) and 6b^2(K).
States |a⟩ and |k⟩ result from anharmonic mixing of ν'_{6a} with 2ν'_{6b}.
Progressions P and Q are indicated.

doublet of the absorption spectrum. The absorption intensity of this
doublet (relative to the 0^0 absorption band) is necessarily equal to the
sum of the intensities expected for the transitions 6a^1_{0} and 6b^2_{0} in the
absence of resonance, i.e.

\[
S = \frac{I(6a_{0}^0)}{I(0_{0}^0)} + \frac{I(6b_{0}^2)}{I(0_{0}^0)} = \frac{\langle a_{0}^1 | a_{0}^1 \rangle^2}{\langle a_{0}^0 | a_{0}^0 \rangle} + \frac{\langle b_{0}^2 | b_{0}^2 \rangle^2}{\langle b_{0}^0 | b_{0}^0 \rangle} \quad (6.28)
\]

The Franck-Condon factors \(\langle a_{0}^1 | a_{0}^0 \rangle^2\) and \(\langle a_{0}^0 | a_{0}^0 \rangle^2\) may be determined using
δ and D parameters which gave the best match for observed and calculated
Franck-Condon factors for the 6a^1_{n} progression in the 0^0_{0} spectrum.
Initially \(δ = 1.0\) and \(D = 1.6\) will be used. Since \(ν_{6b}\) is non-totally-
symmetric, the displacement in the potential minimum on excitation must be zero if the symmetry of the molecule is to be maintained, i.e. $D_{6b} = 0$.

The unperturbed frequency can be determined from the condition

$$559 \text{ cm}^{-1} < 2
\nu_{6b} < 645 \text{ cm}^{-1}$$

(6.29)

i.e., $\nu_{6b}$ (unperturbed) $= 301 \text{ cm}^{-1}$. This gives $\delta_{6b} = \sqrt{603/301} = 1.42$.

Using the tables of overlap integrals $S$ is found to be

$$S = 1.283 + 0.053 = 1.34$$

(6.30)

The ratio of the bands $k$ and $a$ from the doublet in the absorption spectrum is

$$\frac{I(k)}{I(0^g_0)} / \frac{I(a)}{I(0^g_0)} = 0.65$$

(6.31)

and combining this equation with equation 6.28 yields

$$\frac{I(a)}{I(0^g_0)} = 0.61S \text{ and } \frac{I(k)}{I(0^g_0)} = 0.39S$$

(6.32)

The transition moments for $k \rightarrow 0_0$ and $a \rightarrow 0_0$ are given by the expressions

$$\frac{I(k)}{I(0^g_0)} = <k|0_0>^2$$

(6.33)

and

$$\frac{I(a)}{I(0^g_0)} = <a|0_0>^2$$

(6.34)

These can be expanded in terms of vibrational overlap integrals. For
I(k)/I(0), the expansion can be expressed as

\[
\frac{I(k)}{I(0)} = \frac{<\alpha|a^1> + \beta|b^2>|0>|^2}{<\alpha|a^1>|0>|^2} = \frac{<\alpha|a^1>|b^0> + \beta|b^2>|a^0|b^2|\chi^0|\chi^0>^2}{<\alpha|a^0|b^0>|^2} = \frac{<\alpha|a^0|b^0>|^2}{<\alpha|a^0|b^0>|^2} \frac{<\alpha|a^0|b^0>|^2}{<\alpha|a^0|b^0>|^2}
\]

Similarly, expanding the integral for I(a)/I(0) yields

\[
\frac{I(a)}{I(0)} = \frac{<\beta|a^1>|a_0> + \alpha|b^2>|a_0>|^2}{<\alpha|a^0|a_0>|^2} \frac{<\beta|b^2>|a_0>|^2}{<\alpha|b^0|a_0>|^2}
\]

Solving equations 6.35 and 6.36 simultaneously (with the constraint that \(\alpha\) and \(\beta\) are positive) gives

\[
\alpha = 0.46 \quad \text{and} \quad \beta = 0.89
\]

and these are the normalised mixing coefficients \((\alpha^2 + \beta^2 = 1)\).

It is also possible to evaluate \(\alpha\) and \(\beta\) using the ratio of intensities of bands observed in fluorescence from levels \(a\) and \(k\). For example, in spectrum A the relative intensities of band \(a \rightarrow 12\) and \(a \rightarrow 6b_2\) are given by
and solving these equations simultaneously leads to values $\alpha = 0.40$, $\beta = 0.91$. Similarly, using the intensities of bands $k \rightarrow 12_1$ and $k \rightarrow 6b_2$ in spectrum $K$ leads to values $\alpha = 0.50$, $\beta = 0.87$. These values of $\alpha$ and $\beta$ as determined from the fluorescence spectra are in reasonable agreement with the values of $\alpha$ and $\beta$ determined from the absorption spectrum given the error associated with intensities of fluorescence bands.

For spectrum $A$, the relative intensities within type P progressions and type Q progressions can be determined from expressions of the form

$$\frac{I(a \rightarrow 12_1)}{I(0^0)} = \left[ \frac{\beta <a^1|a> <12^0|12> - \alpha <b^2|b> <12^0|12>}{<a^0|a<12^0|12> - <b^0|b<12^0|12>} \right]^2$$

(6.38)

$$\frac{I(a \rightarrow 6b_2)}{I(0^0)} = \left[ \frac{\beta <a^1|a> <b^0|b> - \alpha <b^2|b> <b^0|b>}{<a^0|a<b^0|b> - <b^0|b> b^0|b>} \right]^2$$

(6.39)

and

$$\frac{I(a \rightarrow 6a_n)}{I(0^0)} = \frac{(\beta |a|^2 - \alpha |b|^2)|a_n|^2}{<a^0|0> <a^0|0> = \frac{(\beta |a|^2 |b|^2 - \alpha |b|^2 |a|^2)|a_n|^2}{<a^0|b^0|a_n|^2}$$

(6.40)

i.e. $\frac{I_n(a)}{I(0^0)} = \left[ \frac{\beta <a^1|a_n> - \alpha <b^2|b> <a^0|a_n>}{<a^0|a_b> <b^0|b> <a^0|a_b>} \right]^2$

and

$$\frac{I(a \rightarrow 6a_n 6b_2)}{I(0^0)} = \frac{I_n^0(a)}{I(0^0)} = \left[ \frac{\beta <b^0|b_2> <a^1|a_n> - \alpha <b^2|b> <a^0|a_n>}{<b^0|b_2> <b^0|b_2> <a^0|a_n>} \right]^2$$

(6.41)

P and Q progressions built on $12_n$, $n = 1, 2, \ldots$ origins have the same relative intensity distributions. For example, for the progression whose terminating levels are $6a_n 6b_2 12_2$, the expression for the intensity of various members is
Similarly for spectrum K, the expressions for the relative intensities within type P and type Q progressions are

$\frac{I(k \rightarrow 6a_n, 6b_n)}{I(0^0_0)} = \frac{I_P(n)}{I(0^0_0)} = \left[ \frac{\alpha <b^0|b_2> <a^1|a_n>}{<a^0|a_0>^2} + \frac{\beta <b^2|b_0> <a^0|a_n>}{<b^0|b_0> <a^0|a_0>} \right]^2$ (6.43)

$\frac{I(k \rightarrow 6a_n, 6b_n)}{I(0^0_0)} = \frac{I_Q(n)}{I(0^0_0)} = \left[ \frac{\alpha <b^0|b_2> <a^1|a_n>}{<b^0|b_0> <a^0|a_0>} + \frac{\beta <b^2|b_0> <a^0|a_n>}{<b^0|b_0> <a^0|a_0>} \right]^2$ (6.44)

and again P and Q progressions built on $12_n$, $n = 1, 2, \ldots$ origins have the same relative intensity distributions.

Plots of these calculated intensity distributions are given in figure 6.15. There was some difficulty in matching theoretical and observed Franck-Condon factors for the $6a^0_n$ progression in the $0^0_0$ spectrum so the calculations have been performed using (a) $\delta_a = 1.0$, $D_a = 1.6$ and (b) $\delta_a = 1.1$, $D_a = 1.7$ and the results are shown in figure 6.15 as (a) solid and (b) dashed bars. For (b), the mixing coefficients determined from the absorption spectrum are $\alpha = 0.47$ and $\beta = 0.88$ (which compare favourably with the values obtained from fluorescence intensities: $\alpha = 0.42$, $\beta = 0.91$ from spectrum A; $\alpha = 0.48$, $\beta = 0.88$ from spectrum K). Figure 6.15 shows that in all 4 progressions, cases (a) and (b) result in similar intensity distributions.
Figure 6.15. Calculated relative Franck-Condon factors for (i) type P and (ii) type Q type progressions in spectrum A and (iii) type P and (iv) type Q progressions in spectrum K. From equations 6.40-6.44. The results, obtained using (a) $\delta = 1.0$, $D = 1.6$ (with $\delta = 1.4$, $D = 0.0$) and (b) $\delta = 1.1$, $D = 1.7$ (with $\delta = 1.4$, $D = 0.0$) are shown as solid and dashed bars respectively.
The intensities within type P and type Q progression calculated so far have been derived assuming \( b^2 = 6b^2 \) which gives \( \delta_b = 1.4 \). If \( b^2 = 16b^2 \), however, quite different results for the relative intensities are obtained because then \( \delta_b = 1.0 \) and harmonic oscillator overlap integrals \( \langle b_i | b_f \rangle \) for \( \delta = 1.0 \), \( D = 0.0 \) are zero except when \( i = f \). The mixing coefficients determined from the doublet in the absorption spectrum are then \( \alpha = 0.63 \), \( \beta = 0.78 \) and the relative intensities within type P and Q progressions are given by \( \langle a_1 | a_n \rangle^2 \) and \( \langle a_0 | a_n \rangle^2 \) respectively for both spectra A and K. These progression profiles (dashed) are compared with those derived for case (a) of the above paragraph in figure 6.16. Very marked differences in the intensity profiles are apparent.

Unfortunately, comparison of observed and calculated Franck-Condon factors for the P and Q type progressions in spectra A and K is hampered by the occurrence of overlapping transitions. For example, in spectrum A, the P type progression \( 6a^1_n \) built on the excitation position overlaps with \( 212^0_1 6a^1_{2} \), \( \ell > 0 \) for \( n > 4 \) and with \( 6b^0_{2} 212^0_{2} 6a^1_{m} \), \( m > 0 \) for \( n > 5 \) and the Q type progression \( 6a^1_n 6b^0_2 \) overlaps with \( 6a^1_{1} 12^0_{1} \), \( \ell > 0 \) for \( n > 1 \) and with \( 6a^1_{m} 10b^0_{2} 12^0_{2}, m > 0 \) for \( n > 3 \); in spectrum K, the P type progression \( 6a^0_{n} 16b^2_0 \) overlaps with \( 212^0_1 16b^2_{0} 6a^0_{\ell} \), \( \ell > 0 \) for \( n > 4 \) and with \( 6b^0_{2} 12^0_{2} 16b^2_0 6a^0_{m}, m > 0 \) for \( n > 5 \) and the Q type progression \( 6a^0_{n} 6b^0_2 16b^2_0 \) overlaps with transitions tentatively assigned as \( 10^0_{1} 6a^0_{\ell} 16b^2_0, \ell > 0 \) for \( n > 1 \) and with \( 6a^0_{m} 10b^0_{2} 12^0_{2} 16b^2_0, m > 0 \) for \( n > 3 \). Other unidentified overlaps are also

* For simplicity, progressions \( 6a^1_n \) in spectra A and K are referred to as if the originating levels were \( 6a^1 \) and \( 16b^2 \) respectively. Thus, there is reference to \( 6a^1_n \) etc. progressions in spectrum A and \( 6a^1_n \) etc. progressions in spectrum K.
Figure 6.16. Comparison of calculated relative Franck-Condon factors for (i) type P and (ii) type Q progressions in spectrum A and (iii) type P and (iv) type Q progressions in spectrum K obtained using $\delta_b=1.4$ (and $\delta_a=1.0$, $D_a=1.6$, $D_b=0.0$, i.e. case (a) of figure 6.15), shown as solid bars, and those obtained using $\delta_b=1.0$ (and $\delta_a=1.0$, $D_a=1.6$, $D_b=0.0$), shown as dashed bars.
possible, especially at higher displacements from the excitation positions*

Large uncertainties are associated with the corrections made for overlapping progression members because the origins of the overlapping progressions are of low intensity. In both spectra A and K, an undistorted view of the Franck-Condon factors for the first four members of the P type progressions is available but in all the Q type progressions only the intensity of the first member is undistorted by overlapping transitions. Thus, in estimating the intensities of overlapping bands, a combination of observed and theoretical Franck-Condon factors had to be used. The first four members of P type progressions were estimated from the Franck-Condon factors observed for the progressions $6a_{1}^{1}12_{1}^{0}$ and $6a_{1}^{1}12_{2}^{0}$ in spectrum A and for the progressions $6a_{1}^{0}12_{1}^{0}16b_{2}^{2}$ and $6a_{1}^{0}12_{2}^{0}16b_{2}^{2}$ in spectrum K and from the theoretical Franck-Condon factors for the remaining members but for Q type progressions, it was necessary to use theoretical Franck-Condon factors when evaluating the intensity of overlapping bands. Intensities within $12_{n}^{0}$ progressions were estimated using the Franck-Condon factors observed for $12_{n}^{0}$ progressions in the $0_{0}^{0}$ spectrum. The intensity of the fluorescence bands at the excitation positions in spectra A ("$6a_{1}^{1}12_{2}^{2}$") and K("$16b_{1}^{1}12_{2}^{2}$") were estimated using the relationships

* It should be noted that anharmonic interaction between levels such as $6a_{5}$ and $6b_{2}12_{2}$ would be negligible because the coupling matrix elements, being of the form $f_{5a2b2c} < a_{5} | Q_{a}^{5} | a_{0} > < b_{0} | Q_{b}^{2} | b_{2} > < c_{0} | Q_{c}^{2} | c_{2} >$, would be negligible. The coefficients would be of the form $(a^{5}V/aQ_{a}^{5})_{0}(a^{2}V/aQ_{b}^{2})_{0}(a^{2}V/aQ_{c}^{2})_{0}$ which would be negligible.
In both spectra A and K, the intensity profiles of several P type progressions (e.g. built on origins \(12^0_{n}(n = 0-4)\), \(8a^0_{1}12^0_{0-2}\) and \(10b^0_{2}12^0_{0,1}\)) and several Q type progressions (built on origins \(12^0_{0,1,2}\)) were measured and corrected for the contributions made by overlapping bands where necessary. The results for a few of the observed intensity profiles are shown in figure 6.17 where they are compared with the two sets of calculated intensity profiles shown in figure 6.16. The first set, represented in figure 6.17 by circles and henceforth referred to as "calculated (i)" is the focus of attention here and corresponds to the mixing of \(6a^1_0\) \((\delta_a = 1.0, D_a = 1.6)\) with a non-totally-symmetric mode \((D_b = 0.0)\) whose frequency changes by a factor of two on excitation \((\delta_b = 1.4)\). The second set, represented in figure 6.17 by triangles and henceforth referred to as "calculated (ii)", corresponds to the mixing of \(6a^3_1\) \((\delta_a = 1.0, D_a = 1.6)\) with a non-totally-symmetric mode whose frequency does not change appreciably on excitation \((\delta_b = 1.0)\) and is equivalent to the theoretical \(6a^1_n\) \((\delta = 1.0, D = 1.6)\) intensity profiles for the P type progressions and to the theoretical \(6a^0_n\) intensity profiles for the Q type progressions. Intensities obtained without correcting for the contributions made by overlapping bands are shown as dashed bars in figure 6.17 and it is apparent that the contributions made by the overlapping bands quickly become predominant for higher progression members especially for Q type progressions.

The agreement between observed and calculated (i) intensity profiles in figure 6.17 is only fair but it should be recognized that while the
Figure 6.17. Comparison of observed (bars) and calculated (points) relative Franck-Condon factors for type P and Q progressions in spectra A and K. Calculated FCs obtained using $\delta_b=1.4$ (referred to in text as "calculated (i)") and $\delta_b=1.0$ (referred to in text as "calculated (ii)") are shown as circles and triangles respectively. FCs obtained without correcting for overlapping transitions are shown as dashed bars.

(ii) Spectrum A, progression Q built on excitation position.

(i) Spectrum A, progression P built on origins (a) excitation position, (b) $12^0_1$, (c) $12^0_2$, (d) $12^0_3$.

(iii) Spectrum K, progression P built on origins (a) excitation position, (b) $12^0_1$.

(iv) Spectrum K, progression Q built on origins (a) excitation position, (b) $12^0_1$. 
Figure 6.17 (continued)
Figure 6.17 (continued)
observed intensity profiles have considerable uncertainties associated with them, even the estimation of the background to be subtracted is highly uncertain for many peaks (e.g. $12^0_3$ in spectrum K), the calculated intensity profiles with which the observed profiles are being compared are not ideal. The calculated intensity profiles are weighted mixtures of theoretical Franck-Condon factors $<6a_1^1|6a_n^0>_2$ and $<6a_0^0|6a_n^0>_2$ obtained using $\delta$ and $D$ parameters which did not give a good replication of the $6a_n^0$ progression intensity profile even in the $0_0^0$ spectrum. For the analogous A and K fluorescence spectra of pyrimidine-$h_4$, excellent agreement between observed and calculated intensity profiles is claimed for P and Q type progression [KLP]. This is surprising in view of the pyrimidine-$d_4$ results, notwithstanding the absence of overlapping transitions and the better agreement between observed and calculated intensity profiles for $6a_n^0$ progressions in the $0_0^0$ spectrum in the case of pyrimidine-$h_4$, because the A and K spectra of pyrimidine-$h_4$ are clearly much more congested than the A and K spectra of pyrimidine-$d_4$.

Although only the gross features of the calculated (i) intensity profiles are reproduced in the observed intensity profiles, the Franck-Condon factor analysis of this section confirms that the levels excited ("a" and "k") in obtaining spectra A and K are of mixed character with $6a^1$ coupling with the first overtone of a non-totally-symmetric mode whose frequency changes by a factor of two on excitation, ($6b^2$ ?). If states "a" and "k" were not of mixed character with "a" = $6a^1$ and "k" $\neq 6a^1$, the intensity distribution within P and Q type progressions would be given by $<6a_1^1|6a_n^0>_2$ in spectrum A (i.e. as shown by the triangles in the P type progression plots in figure 6.17) and by $<6a_0^0|6a_n^0>_2$ in spectrum K (i.e. as shown by the triangles in the Q type progression plots in figure 6.17). Observed intensity profiles for P and Q type progressions, however, are
clearly different from this. If the frequency of the mode mixing with \(6a_1^1\) did not change appreciably on excitation, the intensity profiles in the P and Q type progressions in both spectra A and K would be given by the triangles (calculated (ii) values) in figure 6.17. However, while the observed intensity profiles are only in marginally better agreement with the calculated (i) values than with the calculated (ii) values even for the P type progressions in spectrum A which are relatively free from overlapping transitions, only the calculated (i) intensity profiles reproduce the observed intensity profiles for P type progressions in spectrum K.

The magnitude of the coupling between levels \(6a_1^1\) and \(6b_2^2\) is of interest. Assuming that levels \(6a_1^1\) and \(6b_2^2\) are the only levels coupled, the matrix element coupling them is of the form

\[
V_{\text{anh}} = g_{ab} \langle 1^1|Q_a^0 b^2 a^0 |b^0 \rangle = g_{ab} \langle 1^1|Q_a^0 |a^0 \rangle \langle b^2 |Q_b^0 |b^0 \rangle
\]  

(6.46)

where \(g_{ab}\) is a cubic coefficient in the potential energy.

A perturbation theory calculation similar to that in section 6.6B* yields \(V_{\text{anh}} = 42 \text{ cm}^{-1}\). A similar calculation for pyrimidine-\(h_4\) yields \(V_{\text{anh}} = 28 \text{ cm}^{-1}\). As noted by KLP, cubic coupling energies of this magnitude are not unknown for aromatic molecules. In benzene, moderate coupling matrix elements (\(\sim 10 \text{ cm}^{-1}\)) have been found sufficient to produce measurable intensity perturbations in fluorescence from levels that are 121 cm\(^{-1}\) and 223 cm\(^{-1}\) apart [Parmenter, Tang and Ware, 1976]. As suggested by KLP, anharmonic interaction of levels separated by several hundreds of cm\(^{-1}\) with \(6a_1^1\) separately to a first approximation.

* The observed separation of the perturbed levels (\(\Delta E\)) is 86 cm\(^{-1}\) and the relative intensity of the diad in the absorption spectrum (\(\phi\)) is, from equation (6.31), 1.0/0.65 giving 18.5 cm\(^{-1}\) as the separation between the unperturbed levels (\(\Delta E^0\)).
wavenumbers may be significant if coupling energies of \( \approx 40 \text{ cm}^{-1} \) are possible although, as discussed by Fischer, Sharf and Parmenter (1975) and by Parmenter, Tang and Ware (1976), these interactions may only be readily detectable in favourable cases.

Progressions in \( 6a_n \) built on origins at displacements from the excitation position corresponding to levels \( 16b_2, 16b_2 12_1, 16b_2 12_2, 16b_2 6b_2 \) and \( 16b_2 6b_2 12_1 \) in the ground state are distinguishable in the \( 16b_2 \) spectrum of pyrimidine-\( d_4 \). If mode \( v_{16b} \) is indeed responsible for these transitions, its activity in this spectrum is significant as it appears to be completely inactive in other fluorescence spectra \( (0^0, "6a_1^n", 12^1) \) of pyrimidine-\( d_4 \). By analogy with the case of coupling between \( 6a_1 \) and \( 6b_2 \) just examined, the exceptional activity of \( 16b_2 \) in the "16b_2" spectrum suggests that the mixed state from which fluorescence originates contains \( 16b_2 \). If \( 16b_2 \) does mix with \( 6a_1 \) as does \( 6b_2 \), the transition \( 16b_2 \) should be evident as is \( 6b_2^2 \) because of the appreciable overlap integral for the transition \( (\delta = 1.0, D = 0.0) \) and, as a result of mixing \( 16b_2 \) with \( 6a_1 \), progressions in \( 6a_1 \) built on \( 16b_2 12_0 - n \) origins should have intensity distributions similar to that shown by the dashed bars in figure 6.16(d) and this is observed. The observed intensity pattern for progressions \( 6a_n 16b_2 6b_2 12_0,1 \) is similar, as would also be expected* . This distribution is simply that given by Franck-Condon factors \( <6a^0|6a_n>^2 \).

The different activity of mode \( v_{10b} \) in spectra from levels \( 0^0, "6a_1^n" \) and "16b_2" is also noteworthy. In the \( 0^0_b \) spectrum, progressions \( 6a_n 12_0 - n \)

* If it is valid to consider the mixing of \( 16b_2 \) with \( 6a_1 \) and the mixing of \( 6b_2 \) with \( 6a_1 \) separately to a first approximation.
built on origin $10b_2$ are less intense than those built on $8a_1$, in spectrum "6a"1", the reverse is true but in spectrum "16b"2" progressions built on $10b_2$ are much less intense than those built on $8a_1$. These differences in the relative activities of modes $\nu_{10b}$ and $\nu_{8a}$ may be further manifestations of the breakdown in the harmonic oscillator approximation.

Intensity profiles observed for $12_n$ progressions in spectra A and K are similar to the intensity distribution observed for the $12^0_n$ progression in the $0^0_0$ fluorescence spectrum and, as shown in figure 6.18, are reasonably well replicated by the intensity pattern calculated for a harmonic oscillator with $\delta = 1.0$, $D = 2.0$. This is as expected if the state from which fluorescence occurs does not contain any appreciable $12^1$ character.

6.8 FLUORESCENCE FROM THE LEVEL $12^1$ (0 + 1002 cm$^{-1}$)

Intense upper state progressions in the absorption spectra of pyrimidine-$h_4$ and -$d_4$ were assigned by Innes et al. (1969) as $8a_0^1$, on the basis of a qualitative application of the Franck-Condon principle and the assumption that the normal coordinates for pyrimidine are similar to those of pyridine. Innes et al. admitted that the progression could be $12^0_0$ if the normal coordinates for pyrimidine were quite different from those of related molecules.

For pyrimidine-$h_4$, KLP found that the SVL fluorescence generated by pumping the absorption band labelled $8a_0^1$ by Innes et al. (1969) corresponded to emission from upper state level $12^1$ and thus established unequivocally that the assignment $8a_0^1$ was incorrect. The analogous SVL fluorescence spectrum of pyrimidine-$d_4$ shows that the assignments $8a_0^n$, $n = 1, 2, ...$ made for this molecule must also be revised to $12^0_n$, $n = 1, 2, ...$
Figure 6.18. Observed (bars) and calculated (points) relative Franck-Condon factors (FCFs) for $12^0_n$ progressions in spectra A ((a),(b),(c),(d)) and K ((e),(f)) of pyrimidine-$d_4$. Calculated FCFs determined using $\delta=1.0$, $D=2.0$. Origins: (a) $6a_3^1$, (b) $6a_4^1$, (c) $6a_0^1$, (d) $6a_2^1$, (e) $16b_0^2$, (f)$16b_0^26a_1^0$, designating the excited levels as "$6a_3^1$" and "$16b_0^2$" (see text). ((c), (d), (e), (f) on following page).
Figure 6.18 (continued)
Fluorescence following excitation of the 32191 cm\(^{-1}\) absorption band of pyrimidine-\(d_4\) is shown in figure 6.19. A table of assignments of the \(12^1\) spectrum is given in Appendix A6(vi). Progressions \(6a_n\) and \(12_n\) and their combinations dominate the spectrum. They build on the excitation position and on the same origins involving other modes as identified in the \(0^0\) spectrum. Attention is focused on the intensity distribution within the \(12_n\) progressions. It differs markedly from the intensity profile observed for the \(12^0_n\) progressions in the \(0^0\) spectrum. In the \(12^0_n\) progressions, a maximum is observed at \(n = 1-2\) (figure 6.11) whereas in the \(12_n\) progressions of the \(0 + 1002\) cm\(^{-1}\) spectrum, a very pronounced minimum occurs at \(n = 2\) and maxima at \(n = 0\) and 4 as shown in figure 6.20. The intensity profile for the \(12^0_n\) progression in \(0^0\) fluorescence is governed by Franck-Condon factors of the type \(\langle 12^0_n | 12 >^2\) and it was found that the observed profile was best replicated by harmonic oscillator Franck-Condon factors using \(\delta = 1.0, D = 2.0\). If the emitting level in the \(0 + 1002\) cm\(^{-1}\) spectrum is \(12^1\), the intensity distribution within \(12^1_n\) progressions will be governed by \(\langle 12^1_n | 12 >^2\) Franck-Condon factors and the observed intensity distribution should be replicated by calculated Franck-Condon factors using \(\delta = 1.0, D = 2.0\). As shown in figure 6.20, the agreement between the observed and calculated Franck-Condon factors for the \(12^1_n\) progressions is very good, particularly at the \(n = 2\) member. The calculated intensity profiles using \(\delta = 1.0\) and \(D = 2.0\) are very distinctive for the \(12^0_n\) (equally intense maxima at \(n = 1, 2\)) and \(12^1_n\) progressions and the fact that the observed intensity profiles match the calculated profiles so well for both \(12^0_n\) and \(12^1_n\) progressions is unequivocal evidence that the \(0 + 1002\) cm\(^{-1}\) level is \(12^1\) and that mode \(v_{12}\) is very harmonic. This result for the \(12^1_n\) progression profile for pyrimidine-\(d_4\) further illustrates that the \(v_{12}\) modes in pyrimidine-\(d_4\) and \(-h_4\) are different.
Figure 6.19. Fluorescence spectrum from $12^1$ (see text) level of pyrimidine-d$_4$. Pressure 0.066 torr, collection bandpass 22-11 cm$^{-1}$, step size 3.5-2 cm$^{-1}$, NSM=5, constant excitation intensity collection intervals. Assignments in Appendix A6(vi).
Figure 6.20. Observed (bars) and calculated (points) relative Franck-Condon factors (FCfs) for $12^1_n$ progressions in fluorescence from the $12^1_n$ level of pyrimidine-$d_4$. Origins: (a) excitation position, (b) $6a_1^0$. Calculated FCfs determined using $\delta=1.0$, $D=2.0$. The observed FCfs for $n=2$ are shown dashed because the bands to which they refer occur $\approx 20$ cm$^{-1}$ from the expected harmonic positions. At the harmonic positions for $12^1_2$ and $6a_1^012^1_2$, no bands are observed (see text).
KLP found that the intensity distribution in the $12^1_n$ progression of pyrimidine-$d_4$ had a minimum at $n = 1$ and maxima at $n = 0$ and $n = 3$, in very good agreement with the intensity distribution calculated using the same $\delta$ and $D$ parameters which gave the best match between observed and calculated Franck-Condon factors for the $12^0_n$ progression in the $0^0$ fluorescence, $\delta = 1.0$ and $D = 1.4$. The occurrence of multiple maxima and minima in the intensity distribution of progressions in the spectra of other molecules and also within the framework of the Franck-Condon principle has been discussed in section 5.4B.

There are several other notable features in the $12^1$ spectrum. In figure 6.20 the intensities of the third members ($n = 2$) of the $12^1_n$ progressions are shown dashed because $12^1_2$ and members of the progression $12^1_6a^0_n$ do not occur as near to the calculated harmonic positions as expected. For example, the transition $12^1_2$ is expected to occur at a displacement of about 2096 cm$^{-1}$ from the excitation position but the only peak in the vicinity of 2096 cm$^{-1}$ is one of very low intensity nearly 20 cm$^{-1}$ away at 2077 cm$^{-1}$. The peak at 2077 cm$^{-1}$ cannot be assigned to any other combination of ground state fundamentals and it does not appear in any other SVL fluorescence spectra of pyrimidine-$d_4$ examined so far. It does appear in other $12^1$ spectra where it is accompanied by progression members $12^1_26a^0_n$ at displacements well removed from their harmonic positions, as the $12^1$ spectrum with its table of assignments in Appendix A6(vii) illustrates. Transitions in other SVL spectra of pyrimidine-$d_4$ corresponding to the $12^1_2$ transition of the $12^1$ spectrum occur within experimental error of the harmonic position (e.g. 2095 cm$^{-1}$ and 2098 cm$^{-1}$ in the $0^0$ and "6a$_1$" spectra respectively) and other members of the $12^1_n$ progression in the $12^1$ spectrum occur at their expected positions as the tables of assignments in Appendix
A6(vi), (vii) show. These observations rule out the possibility that the \(12^1_2\) transition occurs ~20 cm\(^{-1}\) from its harmonic position because of Fermi resonance. If the band at ~2077 cm\(^{-1}\) is due to \(12^1_2\) its occurrence at such an anharmonic position could have interesting implications for it suggests that the \(v_{12}\) potential wells in the ground and excited states are, on average, distorted at the time of the \(12^1_2\) transition from their shape at the time of other \(12^1_n\) transitions.

Another interesting feature in the \(12^1\) spectrum is the intensity distribution in the \(6a^0_0\) progressions. For harmonic vibrations, it is expected that the intensity profile of the \(6a^0_0\) progression in the \(12^1\) spectrum be very similar to its counterpart in the \(0^0\) spectrum where a fair match with the observed profile was obtained using parameters \(\delta = 1.0-1.1\) and \(D = 1.6-1.7\) in calculating a theoretical intensity profile. Figure 6.21 shows, however, that though in qualitative agreement with \(6a^0_0\) progression profile of the \(0^0\) spectrum, the \(6a^0_0\) progression profile of the \(12^1\) spectrum is best replicated using parameters \(\delta = 1.0-1.1\) and \(D = 1.9\). The choice of parameter \(D\) for achieving agreement between the observed and calculated intensity patterns of the \(6a^0_0\) progression in the \(0^0\) spectrum was based on the observation that the first member of the \(6a^0_0\) progression \((n = 0)\) was more intense than the third member \((n = 2)\). In the \(12^1\) spectrum, the reverse is true, suggesting that mode \(v_{6a}\) is slightly different in the two spectra. In fact, KLP concluded from their study of SVL fluorescence from several totally symmetric vibrational levels in \(^1B_1\) pyrimidine-d\(_4\) that every totally symmetric fundamental in the \(^1B_1\) state was involved in anharmonic coupling so the slightly different distribution of intensity in the \(6a^0_0\) progressions from what is expected, if not just an experimental artifact, may reflect this coupling. The
Figure 6.21. Observed (bars) and calculated (points) relative Franck-Condon factors (FCFs) for $6a^0_n$ progressions in fluorescence from the 12$^1$ level of pyrimidine-$d_4$. Origins: (a) excitation position, (b) 12$^1$. Calculated FCFs determined using $\delta=1.0-1.1$, D=1.9.
greater activity of modes $v_{8a}$ and especially $v_{9a}$ in the $12^1$ spectrum compared with their activity in the $0^0$ spectrum (e.g. cf. activity of $10b_2^0$) suggests that these modes may also be coupled in the excited state with the level excited. In progressions $6a_{n}^012^1_{0}$ and $6a_{n}^012^1_{1}$, members $n > 8$ are abnormally intense but the only transitions which may underlie them and so contribute intensity seem to be the combinations $6a_{m}^09a_{1}^08a_{1}^012^1_{2}$, $m > 0$ and $6a_{m}^09a_{1}^08a_{1}^012^1_{3}$, $m > 0$ respectively. This is puzzling since, in the $12^1$ spectrum, the progression $6a_{n}^09a_{1}^08a_{1}^012^1_{0}$ cannot be distinguished from background and the progression $6a_{n}^09a_{1}^08a_{1}^012^1_{1}$ is of relatively low intensity.

Because the intensity distribution in $12^1_n$ progressions extends to high progression members ($n = 4, 5, 6$) and because $v''_{12} > 1000 \text{ cm}^{-1}$, the $12^1$ fluorescence spectrum of pyrimidine-$d_4$ affords a view of anharmonicities in the ground state vibrational frequencies for vibrational levels well above the $0_0$ level, and provides an opportunity for examining line shapes for transitions to highly excited, $6000-7000 \text{ cm}^{-1}$, ground state vibrational levels. Table 6.7 shows the disparities between observed and calculated (harmonic) displacements for some of these transitions and confirms some of the assignments made for bands in the $0^0$ fluorescence spectrum which are of much lower intensity than their counterparts in the $12^1$ fluorescence spectrum. Heller and Mukamel (1979) have presented a general theory for vibrational overtone line shapes of polyatomic molecules based on the overtone spectra of the CH stretching modes in several isotopically substituted benzenes at pressures of a few torr. Among results for benzene explained by the theory of Heller and Mukamel were the observations that each observed overtone ($v = 5, 6, 7$) is a structureless band with a homogeneous width of $\approx 100 \text{ cm}^{-1}$ (compared with $30 \text{ cm}^{-1}$ for the rovibronic width of the fundamental, $v = 1$) and that the 0-v bands become narrower with
Table 6.7  Observed frequencies for some ground state overtones and combinations from the 12\( ^{1} \) and 0\( ^{0} \) level fluorescence spectra of pyrimidine-d\( _{4} \), (spectra in figures 6.19 and 6.3)

<table>
<thead>
<tr>
<th>Ground state level</th>
<th>Calculated frequency (cm(^{-1}))</th>
<th>Frequency from 12( ^{1} ) spectrum</th>
<th>Frequency from 0( ^{0} ) spectrum(^{c} )</th>
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<tr>
<td>( 12_{1} )</td>
<td>1048</td>
<td>1050</td>
<td>1049</td>
</tr>
<tr>
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<td>2077(^{a} )</td>
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</tr>
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<td>( 12_{3} )</td>
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<td>3142</td>
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<tr>
<td>( 12_{7} )</td>
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<td>7304</td>
<td>-</td>
</tr>
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</tr>
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<td>6156</td>
</tr>
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</tr>
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</tr>
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<td>( 6a_{6} )</td>
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<tr>
<td>( 6a_{7}^{b} )</td>
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<td>( 6a_{8} )</td>
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<td>( 6a_{9} )</td>
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<td>5918</td>
</tr>
<tr>
<td>( 6a_{10} )</td>
<td>6590</td>
<td>6572</td>
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</table>

\(^{a}\) This anharmonic value is discussed in the text.

\(^{b}\) Calculated Franck-Condon factors suggest progression members 6a\( _{7-10} \) should not be visible.

\(^{c}\) If the observed frequencies for the 12\( _{n} \) progression are fitted to an expression of the form \( \nu = A + B\nu + B\nu^{2} \) (cf. equation 5.11) where \( \nu \) represents the vibrational quantum number, parameters A, B and C have values of the order of -2., -1. and 1050. respectively.
increasing $v$ for $v = 5, 6, 7$ (109, 94 and 87 cm$^{-1}$). While the pyrimidine-d$_4$ fluorescence from level 12$^1_n$ would need to be examined at higher resolution before definite remarks could be made, the results obtained so far suggest that there is no appreciable broadening of line widths for higher members of the 12$^1_n$ progression. Thus, while there can be no doubt that, if the effective density of states and the anharmonic interactions are sufficiently large, rapid radiationless transitions lead to uncertainty determined line-broadening, the pyrimidine-d$_4$ results (for ring modes) raise some doubts as to the applicability of the Heller and Mukamel interpretation to vibrational overtone spectra in general.

The final comment on the 12$^1_n$ spectrum is of experimental rather than theoretical significance. Because distinctive bands of appreciable intensity extend over a range of 7000-8000 cm$^{-1}$ in the 12$^1$ fluorescence spectrum of pyrimidine-d$_4$, this spectrum may provide an ideal reference for determining and comparing the spectral response of vapour phase fluorimeters which employ multi-pass optical systems in the wavelength range 3100-4000 Å.

6.9 FLUORESCENCE FROM OTHER SVL'S OF PYRIMIDINE-d$_4$

KLP generated structured emission (prominent bands easily distinguishable from the background) by pumping levels 9a$^1_n$ and 1$^1_n$ (assigned 9a$^1_n$ and 12$^1_n$ respectively by Innes et al.) of pyrimidine-h$_4$. From the intensity distribution in progressions 9a$^1_n$ and 1$^1_n$ respectively they were able to confirm the identity of the levels excited as 9a$^1$ and 1$^1$. Anomalous intensity distributions in the 1$^1$ spectrum and the appearance in the 9a$^1$ spectrum of a progression not prominent in the 0$^0$ spectrum were interpreted as being due to anharmonic mixing of the excited levels with other $^1B_1$ totally symmetric levels: 9a$^1_n$ with 6a$^1_1$6a$^2_2$ ... 6b$^2_2$6a$^2_2$ and 1$^1_n$ with 12$^1_n$. 
For pyrimidine-d\textsubscript{4}, the most prominent absorption below \(\tilde{\nu}_32250\ \text{cm}^{-1}\), apart from bands 12\textsubscript{1} \((\text{labelled } 8\text{a}^1 \text{ by Innes et al.})\), 6\textsubscript{1} ... 16\textsubscript{2} and the 0-0 band, is the band at 32117.6 \((0 + 929) \ \text{cm}^{-1}\) \cite{Innes1969}. Innes et al. offered the assignment 12\textsubscript{1} \(0\) for this band but it was established in section 6.8 that \(\tilde{\nu}_1^{12} = 1002 \ \text{cm}^{-1}\) hence an alternative assignment must be sought for the \(0 + 929 \ \text{cm}^{-1}\) band. Unfortunately, the fluorescence spectrum obtained by pumping the \(0 + 929 \ \text{cm}^{-1}\) band (figure 6.22) does not resolve the issue because it is singularly devoid of any prominent bands. There may be several reasons for this. The absorption coefficient of the \(0 + 929 \ \text{cm}^{-1}\) band in pyrimidine-d\textsubscript{4} is smaller (relative to that of the 0,0 band) than those of 9\textsubscript{1} \text{a} and 1\textsubscript{1} in pyrimidine-h\textsubscript{4}. Modes \(\nu_{9a}, \nu_{1}\) and \(\nu_{8a}\) are more active in the \(0^0\) fluorescence spectrum of pyrimidine-h\textsubscript{4}, where they form progressions of appreciable intensity, than in the \(0^0\) fluorescence spectrum of pyrimidine-d\textsubscript{4}. A general congestion of bands, as in the "16\textsubscript{2}" spectrum and the use of a much broader fluorescence collection bandpass for the \(0 + 929 \ \text{cm}^{-1}\) spectrum (4 times that employed for the \(0^0\) spectrum and twice that for the "16\textsubscript{2}" spectrum) would also combine to produce a more diffuse spectrum. Variation of the laser excitation wavelength around the reported position of the absorption band in an attempt to tune the laser to the peak of the absorption band produced no appreciable improvement in the overall fluorescence intensity as measured by the photomultiplier tube monitoring the total fluorescence (chapter 3). Nevertheless, the failure to obtain any structure in the spectrum is puzzling especially since the 12\textsubscript{1} fluorescence spectrum corresponds to excitation at a higher energy but is composed largely of discrete and open vibrational structure. A similar result has been obtained in fluorescence spectra of isoquinoline vapour \cite{Fischer1976}. 
Figure 6.22. Fluorescence spectrum from $8a^1$ (see text) level of pyrimidine-$d_4$. Pressure 0.16 torr, collection bandpass 44-21 cm$^{-1}$, step size 7-4 cm$^{-1}$, NSM=5, constant excitation intensity collection intervals.

Figure 6.23. Fluorescence spectrum from $6a^112^1$ (see text) level of pyrimidine-$d_4$. Pressure 0.063 torr, collection bandpass 23-11 cm$^{-1}$, step size 3.6-2 cm$^{-1}$, NSM=5, constant excitation intensity collection intervals.
admittedly a more complex case. For isoquinoline, though discrete structured fluorescence is obtained by exciting a prominent absorption feature at 32657 cm\(^{-1}\), the fluorescence following excitation of a less prominent absorption band at 32548 cm\(^{-1}\) is completely congested. It was contended that, in addition to congestion arising from vibrational mode mixing, the predominant contribution to the congestion in the 32548 cm\(^{-1}\) spectrum of isoquinoline is from the large number of overlapping hot bands and sequence bands that fall in the absorption region excited. The failure to obtain any appreciable change in fluorescence intensity as the excitation frequency was varied about the reported position of the 0 + 929 cm\(^{-1}\) absorption band of pyrimidine-d\(_4\) suggests that the same trivial mechanism is also responsible for the congested fluorescence generated from that level.

Excitation of the absorption band 6a\(_{0120}\)\(^{1}\) (assigned 6a\(_{08a0}\)\(^{1}\) by Innes et al.) at 0 + 1521 cm\(^{-1}\) (figure 6.23) gives a more diffuse spectrum than did excitation at 0 + 929 cm\(^{-1}\). Innes et al. (1969) reported that diffuseness in the pyrimidine-d\(_4\) absorption spectrum becomes noticeable above 0 + 1300 cm\(^{-1}\) and quite marked above 0 + 1800 cm\(^{-1}\) whereas in the -h\(_4\) spectrum diffuseness begins at about 0 + 1800 cm\(^{-1}\) and increases less rapidly than in the -d\(_4\) spectrum. The diffuseness of fluorescence resulting from excitation in the region 0 + 1521 cm\(^{-1}\) is consistent, therefore, with the diffuseness observed in the absorption spectrum in this region. Increased congestion in the fluorescence spectra obtained by probing higher vibronic levels of other molecules has been noted in section 5.3II. In the majority of cases it has been attributed to the vibronic complexity of the states reached (even by narrow-band excitation) and the mixing of vibrational levels within the excited electronic state.
by anharmonic coupling and there is no reason to suspect that additional mechanisms operate in the case of pyrimidine. It has been demonstrated that totally symmetric fundamentals in the $^1B_1$ state of pyrimidine-$d_4$ and $-h_4$ are involved in anharmonic coupling. Once again no appreciable change in the overall fluorescence intensity upon varying the excitation frequency about $0 + 1521 \text{ cm}^{-1}$ was observed. The possible trivial causes of increased fluorescence congestion listed for the $0 + 929 \text{ cm}^{-1}$ spectrum in the paragraphs above could also apply to the $0 + 1521 \text{ cm}^{-1}$ spectrum.

6.10 OBSERVATION OF ROTATIONAL CONTOURS IN FLUORESCENCE

No measurements of absorption band contours were made in the course of this study and only the rotational fine structure of the Q branch of the 0-0 band of pyrimidine-$h_4$ has been displayed in the literature [Innes et al., 1969]. The 0-0 bands of pyrimidine-$d_4$, $-h_4$ are described as exhibiting the characteristic features of a parallel C-type band of an oblate symmetric top ($I_A > I_B = I_C$) similar in appearance to the C-type bands of pyrazine [Merritt and Innes, 1960; Innes and Merritt, 1967]. The only features resolved are $Q_Q$ branch peaks and there is little detail in the P and Q branches. By analogy with the bands in pyrazine spectra [Merritt and Innes, 1960], band widths extend over 40 cm$^{-1}$ with the major portion of the intensity concentrated in a 10 cm$^{-1}$ region of the Q branch.

In a partial rotational analysis of the origin bands of the pyrimidines, Innes et al. (1969) showed that the resolved features could arise from the regular superpositions of the strongest rotational transitions in the Q branch if $\Delta B_0 = 2\Delta C_0$ though the possibility was not tested by computer simulating the observed structure. Extensive asymmetric rotor band contour
analyses of bands in the spectra of pyrimidine-\textsuperscript{\textit{d}}\textsubscript{4}, -\textit{h} \textsubscript{4} and other azines [Innes, Kalantar, Khan and Durnick, 1972], performed in the hope of determining the excited state structures, showed that the same resolved Q branch features could also arise if $\Delta B_0 \neq 2\Delta C_0$ and the inertial defect parameters in the ground and excited electronic states ($\delta''_0$ and $\delta'_0$) were not equal. Anomalously large defects were observed. For pyrimidine-\textit{d} \textsubscript{4}, an anomalously large $\delta'_0$ ($\neq \delta''_0$) was obtained. All of the large $\delta'_0$ ($\neq \delta''_0$) values were attributed to rotational mixing (Coriolis interaction) of the analysed electronic states with perturbing nearby states which have not been directly identified.

While looking for evidence of a $6a_1 \ldots 16b_2$ Fermi resonance diad proposed from an analysis of high resolution absorption spectrum of pyrimidine-\textit{d} \textsubscript{4} [Innes \textit{et al.}, 1969] by scanning the $6a'_1$ fluorescence peak of the $0^0$ level spectrum of pyrimidine-\textit{d} \textsubscript{4} at higher resolution, it became apparent that rotational contours could be seen in the fluorescence bands. By pumping the origin band with narrow band ($\sim 0.4 \text{ cm}^{-1}$) radiation, a non-Boltzmann rotational distribution in the zero point level of $S_1$ will result because of the restrictive $\Delta J, \Delta K$ selection rules. The fluorescence band contours will reflect this nonequilibrium distribution, being different from the absorption band contour if the initial excitation is not redistributed among the available rotational levels of the $S_1$ zero point level by thermalising collisional interactions of the excited molecule prior to fluorescence. Furthermore, if the excitation position in the origin band is changed slightly, different $J'K'$ populations will be created in the $S_1$ state and the fluorescence band profiles should reflect these differences in the originating $J'K'$ distributions.
Figure 6.24 shows fluorescence band contours resulting from exciting different regions of the origin band of pyrimidine-d$_4$ at 0.15 torr. All the plots given in figure 6.24 are computer smoothed using a 4-7 point moving-average scheme (chapter 3). The step sizes employed were about one-eighth the collection bandpasses and the effect of the smoothing is illustrated in figure 6.24 for one of the contours displayed there. Excitation wavelengths (cm$^{-1}$ vac.) quoted in figure 6.24 were determined from the positions of maximum intensity in the $0^0_0$ fluorescence band contour and varied from 31186 cm$^{-1}$ to 31158 cm$^{-1}$. Also given in figure 6.24 are the collection bandpasses employed (in parentheses beside the excitation wavelengths) and the positions of the intensity maxima.

Besides the origin band, whose intensity profile is expected to be distorted due to reabsorption and scattered excitation light, bands $6a^0_1$, $6a^0_2$, $12^0_1$ and $6a^0_112^0_2$ were monitored. Quite marked changes in the band contours are apparent as the excitation shifts to lower wavenumber. These are accompanied by changes in the displacements of the band maxima from the excitation position which are greater than the experimental uncertainties for excitation at 31170, 31164 and 31158 cm$^{-1}$. Such large changes in the displacements are probably caused by the simultaneous excitation of the P branch tail of the origin band and the Q branch of a hot band at 31169 cm$^{-1}$ (vide infra).

The changing band profiles in figure 6.24 can be rationalised as follows: at 31186 cm$^{-1}$ the nonequilibrium rotational distribution in the $S_1$ vibrationless level will be biased towards higher $J'$ and $K'$ values via the strongest Q branch absorption transitions. As the excitation frequency is reduced levels of higher and higher $J'K'$ will be populated via Q branch absorption and levels of lower but increasing $J'$ will be
Figure 6.24(a)-(f) Higher resolution scans of some pyrimidine-d₄ fluorescence bands (cm⁻¹ vac.)

<table>
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<th>Band</th>
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Figure 6.24(g)-(l) Higher resolution scans of some pyrimidine-d₄ fluorescence bands (cm⁻¹ vac.)

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Figure 6.24(m)-(q) Higher resolution scans of some pyrimidine-d₄ fluorescence bands (cm⁻¹ vac.)

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* NSM = 4 (thicker line) overlaid on NSM = 1 plot
populated by P branch absorption. As the excitation is further reduced (31176 cm$^{-1}$) absorption occurs via the P branch of the origin band and perhaps via the R branch of the hot band $9a_1^1$ [Innes et al., 1969] if the rotational structure of pyrimidine absorption bands is closely akin to those of pyrazine [Innes et al., 1972], till at 31170 - 31158 cm$^{-1}$ absorption is primarily via the Q branch of the $9a_1^1$ absorption band.

A rotational band contour for the fluorescence transition $6_{\frac{1}{2}}$ of $s$-triazine following excitation at the Q branch peak of the $6_{0}^1$ absorption band showed a similar profile to the profiles in figure 6.22 for 31186 cm$^{-1}$ excitation except that the P and R branch minor peaks are not so symmetrically disposed about the major Q branch peak [Knight and Parmenter, 1979]. The rotational band contour observed in fluorescence was noticeably different from the $6_{0}^1$ absorption band contour (of similar type to the origin band of pyrimidine-d$_4$) and indicated that rotational relaxation in the excited state of $s$-triazine was largely incomplete at a pressure of 0.2 torr. Different contours were also observed for the fluorescence transition $1_{1}^{0}6_{1}^{0}$ after narrow band excitation at various positions within the $6_{1}^{0}$ absorption band of benzene [Coveleskie and Parmenter, 1978].

The fluorescence decay of pyrimidine-h$_4$ vapour has been shown to consist of two components [e.g. Spears and El-Manguch, 1977] which is consistent with intermediate case radiationless decay. Both components give an identical fluorescence spectrum. Similar fluorescence decay behaviour is expected for pyrimidine-d$_4$. At 0.15 torr pressure and 295 K a pyrimidine molecule on average undergoes $\sim$ 2 hard sphere collisions (with other pyrimidine molecules) in 1.2 $\mu$s which is approximately the zero
pressure lifetime of the long component of pyrimidine-$h_4$ fluorescence [Spears and El-Manguch, 1977] and 0.004 collisions in 2 ns, approximately the zero pressure lifetime of the short component [Uchida et al., 1976, 1978; Spears and El-Manguch, 1977]. Thus, there would seem to be ample opportunity to obtain evidence of excited state rotational relaxation in the long component of fluorescence. For pyrimidine, however, collisional perturbations are very effective in inducing electronic relaxation [Knight and Parmenter, 1976] so that the observation of collision induced $S_1$ vibrational relaxation is almost entirely precluded (chapter 7). Therefore, while it is possible that the fluorescence contours in figure 6.24 contain contributions from a partially relaxed rotational distribution, it is more probable that they correspond almost exclusively to emission from the initially established nonequilibrium distribution of rotational levels* (via the short component). Observation of fluorescence band profiles for different pyrimidine-$d_4$ pressures would be necessary to confirm this.

For benzene and glyoxal, collisional interactions induce excited state rotational relaxation more readily than other nonradiative decay processes, effective collision cross sections of 5-10 times hard sphere being observed [Coveleskie and Parmenter, 1978; Rordorf, Knight and Parmenter, 1978]. It would be of interest therefore, to ascertain whether or not milder intermolecular perturbations can engender rotational but not electronic relaxation in pyrimidine. The results reported here suggest that excited state rotational relaxation studies similar to those reported for benzene should be attempted for pyrimidine.

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* Presumably excited state rotational relaxation in pyrimidine, as in benzene and glyoxal, is not an intramolecular process.
For benzene, individual rotational levels cannot be resolved at 300K in either absorption or fluorescence, and relaxation from the nonequilibrium rotational distributions created by narrow-band (0.4 cm\(^{-1}\)) excitation to a Boltzmann-like distribution was monitored by following the dependence of rotational contours in fluorescence bands upon gas pressure. The striking difference between the nonequilibrium and equilibrium contours made the monitoring particularly convenient. At pressures low enough to prevent collisions during the \(S_1\) fluorescence lifetime of benzene, fluorescence bands were found to have contours corresponding to the initial nonequilibrium \(J'K'\) distribution. Pressures of about 10 torr of benzene were required to transform the contour so as to closely resemble the Boltzmann contour (taken to be that obtained from 0.1 torr of benzene by broad band (85 cm\(^{-1}\)) excitation at the centre of the absorption band). For benzene, the nonradiative excited state decay processes competing with rotational relaxation are electronic energy transfer, vibrational and electronic relaxation. Electronic relaxation does not dominate the radiationless decay behaviour of benzene as it does in the case of pyrimidine. Because for benzene it was impossible to consider individual \(J'K'\) levels in a kinetic model, the analysis had to be performed assuming a two-state model in which the initial nonequilibrium distribution is taken directly to a wide Boltzmann-like distribution in a single step. Evidence was presented that such a two-state model is a good approximation, with further support deriving from a study of excited state rotational relaxation in glyoxal [Rordorf, Knight and Parmenter, 1978].

The \(S_1-S_0\) absorption spectrum of glyoxal is sufficiently sparse for just a few rotational levels in a \(S_1\) vibrational level to be excited when
glyoxal is irradiated by a narrow-band (~0.1 cm\(^{-1}\)) source. At low pressures (10\(^{-4}\) torr) the resultant fluorescence spectrum is also sufficiently sparse, even at a fluorescence resolution of 1 cm\(^{-1}\), for individual rotational transitions to be resolved and identified as originating from the initially populated \(J^'K^'\) levels. Thus, the course of rotational relaxation could be followed more closely in the glyoxal study than in the benzene study. For glyoxal, it was found that the new fluorescence that appeared even in the earliest stages of relaxation (> 10\(^{-4}\) torr) was only a broad featureless background characteristic of a wide spread of new rotational levels. Close examination of an emission band at various pressures showed that there were no strong propensities for the occurrence of rotational changes with \(\Delta K^' = 0, \pm 1, \pm 2, \pm 3\) and small \(\Delta J^'\) but rather that, even in the one-collision regime, rotational energy flow in glyoxal occurred by large \(\Delta J^'\), \(\Delta K^'\) jumps with new levels appearing with a quasi-Boltzmann distribution. This is compatible with a two-state model of rotational relaxation.

Results obtained so far suggest that rotational relaxation in the ground and first excited electronic states of polyatomic molecules is different in that, while the observed cross sections are of similar magnitude, strong selection (propensity) rules apply to rotational state changes in the ground state but not in the excited state. The absence of strong propensity rules for rotational state changes in the excited electronic states of polyatomic molecules is consistent with results obtained for rotational relaxation in the upper electronic states of diatomic molecules [Rordorf et al.,1978].
CHAPTER 7

FIRST EXCITED STATE NONRADIATIVE RELAXATION PROCESSES IN PYRIMIDINE
PROBED USING SVL FLUORESCENCE SPECTRAL MEASUREMENTS

Classification of nonradiative transitions into three categories is discussed, studies by other workers of the $S_1$ excited state decay behaviour of pyrimidine are reviewed and theories used to interpret intermediate case decay behaviour are surveyed. Studies conducted here of pyrimidine-$d_4$ and pyrimidine-$h_4$ $0^0$ level fluorescence quenching and attempts to observe vibrational energy redistribution and electronic energy transfer from pyrimidine-$d_4$ to pyrimidine-$h_4$ are described.
7.1 INTRODUCTION

A. Classification of nonradiative transitions

In isolated or near isolated polyatomic molecules, $S_1$ excited state dynamics are determined by interaction of the initially prepared state with other nearly degenerate states, vibrationally excited levels of lower triplet (T) states or the ground ($S_0$) state, which provide channels for the nonradiative dissipation of the excitation energy. There has been a great deal of research in the field of nonradiative transitions during the last decade and several review articles have been devoted to the topic [e.g. Avouris, Gelbart and El-Sayed, 1977 and list therein]. Because only considerably simplified theoretical treatments of radiationless transitions in real molecules are possible, theoretical attention has focused on the various means of formulating the problem mathematically and on ascertaining which "mechanisms" [e.g. Siebrand, 1970; Lawetz, Orlandi and Siebrand, 1972; Siebrand and Zgierski, 1980] resulting from the theoretical developments are mainly responsible for the various features of nonradiative processes.

In the adiabatic Born-Oppenheimer approximation, the coupling of the initial and final states in a nonradiative transition arises from the spin-orbit coupling and nuclear kinetic energy terms of the full molecular Hamiltonian. Matrix elements for the coupling can be simplified to products of electronic factors and vibrational overlap or Franck-Condon factors. The latter are generally considered [e.g. Lim, 1969] to have the major influence on the rate of radiationless transitions though Siebrand and co-workers [Penner et al., 1978; Siebrand and Zgierski, 1980] have argued that a non-Condon mechanism may have a considerable effect.

It is generally accepted that at low excess energies in the $S_1$ state of molecules such as benzene, naphthalene and several of the azabenzenes,
\( S_{1}^{\nu\nu+S_0} \) internal conversion (IC) does not compete effectively with emission and with \( S_{1}^{\nu\nu+T} \) intersystem crossing (ISC) because Franck-Condon factors decrease rapidly as the difference in vibrational quantum numbers for the interacting states increases. The density of final states in the vicinity of the \( S_1 \) initial state is usually far higher for \( S_{1}^{\nu\nu+S_0} \) transitions than for \( S_{1}^{\nu\nu+T} \) transitions but a greater amount of electronic energy must be converted to vibrational energy for the \( S_{1}^{\nu\nu+S_0} \) process because of the larger energy gap between the zero point levels of the combining electronic states (e.g. \( S_{1} - S_0 : 38000 \text{ cm}^{-1} \) cf. \( S_{1} - T_1 : 8600 \text{ cm}^{-1} \) for benzene). In these cases, therefore, the Franck-Condon factors are much smaller for IC than for ISC and this more than offsets the effect of the final state density in determining the rates of IC and ISC at least at low excess energies in \( S_1 \). For benzene, rough theoretical estimates [Prais, Heller and Freed, 1974] suggest that, because of the huge energy gap involved, the ratio of \( S_{1}^{\nu\nu+S_0} \) to \( S_{1}^{\nu\nu+T_1} \) decay rates for the \( S_1 \) zero point level might be as small as \( 10^{-9} \).

Because the rate of \( S_{1}^{\nu\nu+S_0} \) increases so much faster with vibrational excitation, relative to that of \( S_{1}^{\nu\nu+T} \), however, it is possible that this process could become competitive with \( S_{1}^{\nu\nu+T} \) ISC at higher excess energies in \( S_1 \) and there is experimental evidence that supports this view. In naphthalene, at shorter excitation wavelengths where, as a function of excess energy, the radiationless rate increase becomes exponential rather than linear, the triplet yield is found to decrease significantly [Hsieh et al., 1974 a, b, c].

In the discussion that follows, concern will be with \( S_{1}^{\nu\nu+T} \) non-radiative relaxation and with the density of \( T \) states in the vicinity of the excited \( S_1 \) vibronic levels. For several of the azabenzences, the experimental evidence is that the result of nonradiative decay is triplet
formation in very high yield. In any case $S_1 \rightarrow S_0$ would lie in the statistical limit because of the large $S_0 - S_1$ zero point level energy gap.

In various theoretical treatments nonradiative transitions have been categorised into several cases and sub-cases according to the relative magnitude of parameters such as the radiative width of the initially excited level, the interaction energy ($\nu$) coupling the initial level to the final levels, and the density ($\rho$) of lower electronic state levels to which effective coupling can occur [e.g. Bixon and Jortner 1968, 1969; Robinson, 1967; Lahmani, Tramer and Tric, 1974; van der Werf and Kommandeur, 1976]. Lack of precise knowledge even of parameters such as $\nu$ and $\rho$ for actual molecules makes much of the delineating done in the theoretical treatments rather academic. Here, as in Parmenter (1972b) and Avouris et al. (1977), a relatively simple classification which has evolved since the work of Bixon and Jortner will be adopted.

Nonradiative transitions may be classified according to the density of interacting vibronic states in the lower (final) electronic manifold. Where the density of final states is high enough to generate a quasi-continuum of levels nearly degenerate with the ($S_1$) initial state of the transition, nonradiative transitions will occur in the statistical (or large molecule) limit; such nonradiative transitions are intramolecular being virtually insensitive to collisional perturbations except when the pressure is high enough for vibrational relaxation to occur within $S_1$. Fluorescence decay is (almost always) exponential and, even in the zero pressure limit, the rate of fluorescence decay is faster than the radiative decay calculated from the integrated absorption coefficient and the fluorescence quantum yield is less than unity. For benzene, where the $S_1 - T_1$ energy gap is $\approx 8600 \text{ cm}^{-1}$ and there are as many as $8 \times 10^5$ triplet
vibronic states/cm⁻¹ in the vicinity of the S₀ zero point level* [Ware, Selinger, Parmenter and Schuyler, 1970], a combination of theoretical opinion [Robinson, 1967; Bixon and Jortner, 1968] and experimental results suggests that ISC from the S₁ zero point level may only just be within the statistical limit.** The fact that the quantum yield of fluorescence from the S₁ zero point level of benzene is virtually identical (0.20) in the vapour phase [Parmenter and Schuyler, 1970b] and in the condensed phase at 77 K [Lim, 1962; Eastman, 1968], demonstrates the insensitivity of the S₁→T nonradiative transition in benzene to external perturbation.

When the density of final vibronic levels is too low to form a dissipative quasi-continuum yet high enough for many levels to interact with the initial state, as in small molecules with few vibrational degrees of freedom or when the energy gap between the zero point levels of the combining electronic states is small, nonradiative transitions in the resonance (or small molecule) limit may occur. As explained by Douglas (1966), fluorescence is anomalously long-lived, lifetimes considerably longer than the calculated radiative lifetimes being observed. Quenching cross sections are very large (> gas kinetic) and, in the zero pressure limit, fluorescence quantum yields of unity are obtained. In these cases

* Robinson (1967): 3 x 10⁵ states/cm⁻¹; Bixon and Jortner (1968): 7.8 x 10⁶ states/cm⁻¹.

** While recognizing that experimental evidence indicated that ISC from S₁ levels of benzene ~ 2000 cm⁻¹ above the S₁ zero point level occurred in the statistical limit, Robinson (1967) suggested, on the basis of theoretical estimates of the effective density of states and average interaction energies (both 10⁻⁵-10⁻⁶) that benzene was "on the verge of entering the statistical limit". Subsequent experimental evidence [e.g. Anderson and Kistiakowsky 1969, 1969; Parmenter and White, 1969; Ware et al., 1970] confirmed that ISC from the S₁ zero point level occurs within the statistical limit.
nonradiative transitions appear to be almost entirely collision-induced yielding simple Stern-Volmer quenching with every added gas. Nonradiative decay from the $S_1$ states of $SO_2$, $NO_2$ and $CS_2$, in which the number of vibronic states quasidegenerate with the excited singlet is of the order of one state per cm$^{-1}$ [Bixon and Jortner, 1969] is considered to be in the small molecule limit [Avouris et al., 1979].

Medium-size molecules (≤ benzene) which exhibit simultaneously characteristic features of the small molecule and the statistical limit cases in their $S_1$ decay are said to undergo intermediate case nonradiative transitions. Fluorescence decay in these systems is generally quasi-biexponential and displays complicated (non-Stern-Volmer) sensitivity to collisional interactions. The photophysics of the $S_1$ states of glyoxal [van der Werf, Schutten and Kommandeur, 1975], methylglyoxal [Coveleskie and Yardley, 1975a,b, 1976; van der Werf, Schutten and Kommandeur, 1976b] and biacetyl [van der Werf and Kommandeur, 1976a] have been explained on the basis of intermediate case $S_1$ - $T$ coupling. It is the intermediate case of nonradiative decay that has evoked a great deal of the more recent theoretical interest in radiationless transitions.

B. $S_1$ - $T$ nonradiative transitions in the azabenzences

Because of the presence of $n^\pi*$ states, all the azabenzences have $S_1$ - $T_1$ zero point energy separations of less than ~4500 cm$^{-1}$ (cf. 8600 cm$^{-1}$ in benzene) and fewer vibrational degrees of freedom than benzene. $S_1\leftrightarrow T$ nonradiative transitions in these molecules could thus occur outside the statistical limit. This would provide opportunities for testing various theories of radiationless transitions. On the other hand, the presence of $n^\pi*$ states in these molecules may enhance $S_1\leftrightarrow T$ ISC because

* Initial categorisations [e.g. Bixon and Jortner, 1969] placed molecules such as CN in the resonance limit and molecules such as $SO_2$ in the intermediate case.
the spin-orbit coupling component of the interaction matrix for ISC is much larger when \( \pi^* \) states are coupled to \( \pi^* \) states than when only \( \pi^* \) states are involved [El-Sayed, 1969; Siebrand, 1970]. It has now been established that ISC in at least two azabenzences, namely pyrazine and pyrimidine, fit the intermediate case of radiationless transitions. Of course it is possible to observe different types of nonradiative decay behaviour (e.g. intermediate case and statistical limit) for a molecule as excitation reaches different vibronic levels in \( S_1 \) because, for different initial \( S_1 \) states, the final state densities and even the electronic states available for dissipative coupling to \( S_1 \) may be quite different [e.g. as proposed for biacetyl by Nitzan et al. (1971)].

The radiative and nonradiative processes in the \( S_1 \) states of the azabenzences have been the subject of many investigations and Knight and Parmenter (1976a,b) combined the available data on fluorescence quantum yields, fluorescence quenching and triplet formation yields for the azabenzences to present a general view of the photophysics of their \( S_1 \) states. A slightly different picture of the \( S_1 \) state photophysics of pyrimidine has emerged since then.

C. Pyrazine - an intermediate case molecule

It has been well established by studies of emission from both the singlet and triplet states of pyrazine vapour following \( S_1 \) SVL excitation that the \( S_1 \) photophysics of pyrazine is consistent with nonradiative \( S_1 \) decay in the intermediate case. At high pressures and in condensed phases the photophysical behaviour of pyrazine corresponds to the statistical limit but at much lower pressures the behaviour is completely different.

Tramer and co-workers [Lahmani, Frad and Tramer, 1972; Frad, Lahmani, Tramer and Tric, 1974; Lopez-Delgado, Tramer and Munro, 1974] studied the
photophysics of pyrazine vapour upon excitation of approximately SVL's of its $S_1$ state at pressures between $10^{-2}$ and 100 torr. It was found that fluorescence decay is nonexponential, has a zero pressure quantum yield of $\sim 3 \times 10^{-3}$, deviates from simple Stern-Volmer kinetics and reaches, at pressures in excess of $\sim 5$ torr, a limiting quantum yield value $(\approx 10^{-3})$ close to the yield obtained in condensed phases. The intensity distribution in the fluorescence spectrum is unchanged from the lowest pressures used ($\sim 0.001$ torr) to $\sim 50$ torr total gas pressure so that vibrational relaxation in the $S_1$ manifold does not compete effectively with electronic quenching. Tramer and co-workers showed that nonexponential decay can be analysed in terms of two exponentials giving a short component, with a lifetime of $\sim 0.5 \pm 0.2$ ns in agreement with the decay time estimated from oscillator strength and fluorescence yield measurements, and a much weaker long component with a lifetime nominally $\sim 10^{-7}$ s which varies according to which levels are pumped initially and decreases (as does the relative intensity of the long component) with increasing pressure [see also Knight and Parmenter, 1976a; Nott and Selinger, 1978b].

Tramer and co-workers also found that the decline in fluorescence intensity with increasing pressure is accompanied by a growth in thermally equilibrated phosphorescence. This is completely collision-induced: it is detectable only at pressures in excess of 0.05 torr and its yield extrapolates to zero at zero pressure and reaches a constant value $(\approx 1.5 \times 10^{-3})$ for added SF$_6$ gas pressure beyond 20 torr. The phosphorescence spectrum shows no dependence on pressure or excitation wavelength. In the pressure range 0.2-10 torr, the phosphorescence lifetime is rigorously exponential and pressure independent and was determined to be $63 \pm 3$ µs. At gas pressures high enough for collisional channels to dominate $S_1$ decay, triplet formation as determined by the method of biacetyl phosphorescence sensitization reaches a maximum yield of unity for lower $S_1$ vibronic
levels (<1100 cm$^{-1}$) and decreases at higher excitation energies [Knight and Parmenter, 1976a; Frad et al., 1974; Jones and Brewer, 1972].

The fluorescence and phosphorescence results were explained by proposing that the total fluorescence intensity is composed of a fast pressure independent component and a slow pressure dependent component. The intensity of the fast component was assumed to be equal to the total fluorescence intensity observed at high pressures, $I_f(\infty)$. The intensity of the slow component was assumed to equal the difference between the fluorescence intensity observed at a particular pressure and the high pressure value, $I_f(\infty)$, and the pressure dependence of this component was found to follow Stern-Volmer kinetics. Collisional quenching of molecules in the state characterised by long fluorescence decay was proposed to transfer them to the energy levels from which the equilibrated phosphorescence could occur.

D. Studies of pyrimidine photophysics

Initial studies [Jones, 1973; Nott, 1975 in Nott and Selinger, 1978a; Knight and Parmenter, 1976a] suggested that $S_1 \rightarrow T$ transitions in the small molecule limit determined the $S_1$ decay behaviour of pyrimidine. Strictly single exponential fluorescence decays from the $0^0$ and $6a^1$ levels were reported for low pyrimidine vapour pressures ($< 0.12$ torr) and from a study of the pressure dependence of the $0^0$ level lifetime, the zero pressure lifetime of the $0^0$ level was estimated to be $1.7 \times 10^{-6}$ s which is longer than the radiative lifetime calculated from the integrated absorption coefficient, $2 \times 10^{-7}$ s [Mason, 1959]. The low pressure fluorescence quantum yield for pyrimidine was found to be at least two orders of magnitude higher than those of the other azabenzenes and it was considered the zero pressure yield might even be unity. The pressure
dependences of the fluorescence quantum yield and lifetime were reported to give linear Stern-Volmer plots in the low pressure region (< 1 torr). Triplet formation was found to reach a persistent limiting yield under conditions of high added gas pressure: unity for the $S_1 (0^1)$ level and $\approx 0.8$ for higher $S_1$ levels. All these features are characteristic of $S_1 \rightarrow T$ ISC in the small molecule limit. Furthermore, the $S_1 - T_1$ energy gap in pyrimidine (2542 cm$^{-1}$) is much smaller than that in pyrazine (4056 cm$^{-1}$),* for which intermediate case $S_1 - T$ ISC had been observed, suggesting that $S_1 - T$ ISC for pyrimidine might follow small molecule behaviour [e.g. Uchida, Yamazaki and Baba, 1976]. The results of subsequent investigations over greater pressure ranges (\~$10^{-3}$-10 torr)

* These $S_1-T_1$ energy gaps are evaluated from the energy difference between the 0-0 bands of the vapour phase fluorescence/absorption and phosphorescence spectra [Innes et al., 1967; Takemura et al., 1980]. It was thought [e.g. Knight and Parmenter, 1976a,b; Uchida et al., 1976], from data given in the review of the electronic states of the azabenzenes by Innes et al. (1967), that the $S_1-T_1$ energy gap was even smaller (\~$1800$ cm$^{-1}$) for pyrimidine. Vapour phase phosphorescence for pyrimidine-$d_4$ has not yet been reported but since the $S_1-T_1$ energy gaps determined from mixed crystal spectra at 4.2 K are 2454 cm$^{-1}$ and 2453 cm$^{-1}$ for pyrimidine-$h_4$ and -$d_4$ respectively [Hochstrasser and Marzzacco, 1972], the $S_1-T_1$ energy gap for pyrimidine-$d_4$ is expected to be \~2540 cm$^{-1}$. For pyrimidine, the $S_1-T_1$ energy gap determined from vapour phase spectra is in good agreement with that determined from rigid glass spectra at 77 K (2560 cm$^{-1}$) [Uchida et al., 1978]. This also applies for pyrazine (4056 cm$^{-1}$ cf. 4065 cm$^{-1}$ [Goodman, 1961]). Both pyrimidine [Uchida et al. 1978] and pyrazine [Frad et al. 1974] have at least two triplet states below $S_1 (n,n^*)$: $T_1 3(n,n^*)$ and $T_2 3(n,n^*)$. $S_1$ is expected to be coupled more strongly to $T_2$ than to $T_1$ because of the favourable spin-orbit coupling between $1(n,n^*)$ and $3(n,n^*)$. The $T_2$ states in pyrimidine and pyrazine are \~900 cm$^{-1}$ and \~1400 cm$^{-1}$ respectively above the $T_1$ states.
(vide infra) indicate that the $S_1$ decay of pyrimidine conforms more closely to intermediate case than small molecule limit behaviour. In many respects the photophysics of pyrimidine is similar to that of pyrazine.

Lifetime studies: Decay measurements performed in several laboratories show that each of six SVL's of pyrimidine ($0^0 - 6a^212^1$) gives a biexponential fluorescence decay with lifetimes in the limit of zero pressure of $\sim 1$ ns and $\sim 1$ µs [Uchida et al., 1976, 1978; Spears and El-Manguch, 1977; Reineccius and von Weyssenhoff, 1977]. Each component was found to have the same fluorescence spectrum. In perhaps the best of these studies [Spears and El-Manguch, 1977], a tunable dye laser providing stable, variable $\sim 5$ MHz rate, 1.5 ns fwhm or $\sim 15$ ns fwhm pulses of $\sim 1$ cm$^{-1}$ linewidth was used as excitation source to measure the lifetimes of the fast and slow components by the time-correlated single photon counting technique. Care was taken to ensure that no scattered light or filter emission interfered with measurements and it was claimed that lifetimes as short as 50 ps could be obtained accurately with the system. A capacitance manometer was used to measure pressures. At a pressure of 0.02 torr the state-dependent lifetimes were found to range from 2.7-0.7 ns and 0.41-0.23 µs. For a given level of excitation it was found that the lifetime of the fast component is essentially independent of pressure in the range 0-12 torr but that the lifetime of the long component decreases significantly as the pressure increases and gives linear Stern-Volmer plots. Effective collision diameters for self quenching were found to be nearly three times hard sphere for the lower vibronic levels ($0^0, 6a^1, 12^1, 6a^112^1$) and hard sphere for the $6a^212^1$ level. The hard sphere diameter of pyrimidine has been estimated to be 5.7 Å [Uchida et al., 1976].
Quantum yield measurements: Uchida et al. (1976, 1978) and Reineccius and von Weyssenhoff (1977) observed that the fluorescence quantum yield $\phi_F(P)$ of pyrimidine consists of a constant term $\phi_{F1}$ ($< 0.007$), the limiting yield at high pressure, and a Stern-Volmer term $\phi_{F2}(P)$; the Stern-Volmer term is large compared with the constant term up to pressures of $\sim 0.3$ torr and in the range 0-0.3 torr, a plot of $\phi_F^{-1}$ versus pressure approximates a straight line. The constant term was identified with the fast component of the fluorescence decay and is of similar magnitude to the fluorescence quantum yield of pyrimidine in solution* while the Stern-Volmer term was identified with the slow pressure-dependent component. Uchida et al. (1978) found that the radiative lifetime of the fast component of fluorescence ($\sim 3 \times 10^{-7}$s) derived from lifetime and yield measurements is consistent with the radiative lifetime calculated from the integrated absorption intensity (2 $\times$ $10^{-7}$s, Mason, 1959). Estimates of the $0^0$ level zero pressure quantum yield from pressure dependence studies, though ranging from 0.17 to 0.9, confirmed that it is orders of magnitude higher than those of the other azabenzenes. Uchida et al., (1976, 1978) found that at high pressures, where the slow fluorescence emission is quenched, $\phi_F(P)$ does not show any appreciable dependence on the vibrational energy in the $S_1$ state ($\Delta E$), but that under collision free conditions, $\phi_F(P=0)$ decreases with increasing $\Delta E$. This decrease is especially marked over the range

* The constant term is found to range from 0.0065 ($0^0$ level) to 0.002 ($6a^212^1$ level) which compares with values for the quantum yield of pyrimidine in solution of 0.0014-0.003 (hydrocarbon, 298 K) [Uchida et al. 1978; Cohen and Goodman, 1967] and 0.006 (glassy solution, 77 K) [Cohen and Goodman, 1967]. The lifetime of the fast component of fluorescence is also in good agreement with the lifetime of pyrimidine in solution, 1.5 ns [Innes et al., 1967].
\[ \Delta E = 0.613 \text{ cm}^{-1} (6a^1 \text{ level}), \]

where \( \Phi_F(0) \) drops by a factor of 7, and must be due to the dependence of the slow fluorescence component on \( \Delta E \).

Knight and Parmenter (1976a) also report that higher \( S_1 \) levels give lower \( \Phi_F \)'s.

Quenching studies: The exceptional susceptibility of pyrimidine fluorescence to self quenching especially for the lower \( S_1 \) vibronic levels (cross sections several times gas kinetic) have already been noted. Knight and Parmenter (1976a) observed Stern-Volmer kinetics and cross sections of the order of hard sphere for the quenching of fluorescence from low \( S_1 \) vibrational levels in pyrimidine by a wide variety of foreign gases. Details were not given. They found that pyrimidine is the most sensitive of all the azabenzences to collisional quenching and that over a total gas pressure range of 0-0.5 torr, the Stern-Volmer plots for the quenching of fluorescence from the \( S_1 \) zero point levels of pyrimidine and pyrazine are quite different. Simple Stern-Volmer kinetics (linear plot) were observed in the study of pyrimidine quenching (0.05 torr pyrimidine, 0-0.4 torr cyclohexane) - behaviour consistent with nonradiative decay in the small molecule limit - but not in the case of pyrazine where a markedly non-linear Stern-Volmer plot was obtained over the pressure range 0-0.6 torr cyclohexane added to 0.05 torr pyrazine.

Phosphorescence: Like pyrazine, pyrimidine in the condensed phase phosphoresces brightly. In frozen hydrocarbon solution at 77 K both have appreciable phosphorescence quantum yields (pyrazine: 0.3, pyrimidine: 0.14; Cohen and Goodman, 1967). In fact Hochstrasser and Marzzacco (1972) found that in benzene mixed crystals at 4 K, the phosphorescence spectrum is considerably stronger than the fluorescence spectrum for both pyrimidine-\( h_4 \) and \(-d_4 \). Until recently, however, pyrazine was the only
azabenzene to display phosphorescence in the vapour phase.* Takemura et al. (1980) used a method of time resolved spectroscopy, whereby only emission occurring within a desired time range (10-20 µs) after pulsed laser excitation is recorded, to obtain the phosphorescence spectrum of pyrimidine following excitation of the $S_1$ zero point level. The phosphorescence quantum yield ($10^{-4}$) and exponential decay curves (lifetime 50 µs) were observed to be independent of pressure in the range 1-160 torr, as was the phosphorescence spectrum. Delayed fluorescence, also having a pressure independent lifetime of 50 µs, accompanied the phosphorescence.

E. Theoretical interpretation of pyrimidine decay data

The biexponential decay data of pyrazine and pyrimidine have been interpreted on the basis of the mixed state model of Lahmani et al./van der Werf et al. as intermediate case molecules with strong S-T coupling [Lahmani, Tramer and Tric, 1974; van der Werf and Kommandeur, 1976a]. It is supposed that a radiative zero-order singlet state $|S>$ is coupled to $N$ weakly radiative zero-order triplet states of a manifold $\{|T>n\}$ via coupling matrix elements $v_{ST}$ resulting in $N+1$ quasistationary states described by the wavefunctions:

$$|n> = a_n|S> + \sum_{2=1}^{N} b_{2,n}^{|T>n}$$ (7.1)

It is considered that each of the $|S>$ and $|T>$ states has a total width consisting of radiative and nonradiative components and that the $|T>$ states have additional width due to bimolecular collisions to incorporate

* Of all the azabenzences, only pyrazine and pyrimidine have been reported to give detectable phosphorescence in the vapour phase. Phosphorescence from $\sigma$-tetrazine vapour (and in mixed crystal) is observed only after direct $T_1-S_0$ excitation and very weak phosphorescence has been reported for some other azabenzences in frozen solution [see Knight and Parmenter (1976a) for details and references].
pressure dependent quenching in the model. Nonradiative line broadening, 
$\Delta_{ST}$, also occurs as a result of the $|S\rangle - |T\rangle$ coupling. An appropriate 
excitation pulse prepares an initial nonstationary state $|S\rangle$ which can be 
represented as a superposition of the quasistationary states $|n\rangle$.

Lahmani et al. (1974) showed that, under certain well-defined conditions, 
the subsequent time behaviour of the $|S\rangle$ content of the excited state can 
be crudely simplified to a sum of two exponential decays: a fast 
fluorescence with lifetime corresponding to the sum of the radiative and 
nonradiative widths of the initially prepared state $|S\rangle$ and a slow 
fluorescence corresponding to the decay of the quasistationary states in 
which the singlet emission probability is now distributed among $n + 1$ levels 
each containing a triplet component. The lifetimes, pre-exponentials and 
quantum yields of the two components can then be expressed in terms of 
parameters $N$, $\Delta_{ST}$, level widths and densities so that by combining the 
experimental observables, estimates for some of the parameters of the 
model ($N$, $\Delta_{ST}$, $\nu_{ST}$, and the density of effectively coupled triplet states 
$\rho_T$) can be obtained [Lahmani et al., 1972; Frad et al., 1974; Spears 

As well as providing a basis for understanding the biexponential 
nature of the fluorescence decays, the model of Lahmani et al./van der 
Werf et al. has been used to explain more detailed aspects of the 
luminescence from SVL's of pyrazine and pyrimidine: the pressure and 
wavelength dependence of the fluorescence and phosphorescence quantum 
yields for example. Van der Werf et al. (1976a,b) demonstrated that the 
$S_1$ manifolds of biacetyl and methylglyoxal could be considered to consist 
of two regions in which the pressure dependence of the slow fluorescence 
and the dependence of $N$ on $\Delta E$ are different and Spears and El-Manguch 
(1977) found that a similar division could be applied to the $S_1$ manifold 
of pyrimidine.
According to van der Werf and co-workers, only quasistationary states within the zero order $S_1$ widths contain $|S>$ character and fluoresce; quasistationary states outside the widths ("black-holes") lack any resonantly coupled $|S>$ character and thus can only be populated by collisions and are non-fluorescent. At low $S_1$ vibrational energies ($\Delta E$) where the singlet widths are much smaller than their mean level separation ($\rho_S^{-1}$), the singlet levels may be considered as isolated. In this "black-hole" region, $N = 2n^2\nu_S^2\omega_T^2$ and so should increase as $\Delta E$ increases and the cross sections for the quenching of the slow fluorescence are expected to be large because collisions capable of removing a very small amount of energy (exceeding the width of the isolated singlet level $\sim 5 \times 10^{-4}$ cm$^{-1}$) are sufficient to transfer the molecule to a black-hole state. At higher $\Delta E$ where the $S_1$ widths overlap (overlap region), a much larger amount of energy needs to be removed to transfer the molecule to a non-fluorescent state so only head-on collisions can be effective in quenching and much smaller cross sections are expected. In the overlap region, $N = \rho_T/\rho_S$; calculated values of $\rho_T/\rho_S$ for the dicarbonyls [van der Werf et al., 1976a,b] illustrate that this ratio decreases as $E$ increases.

For biacetyl and methylglyoxal, van der Werf et al. (1976a,b) found that the expected dependences of $N$ on $\Delta E$ did occur (especially in the case of biacetyl) and that fluorescence quenching rates were up to 8 times the hard-sphere collision rate in the black-hole region and down to 25% of the hard-sphere collision rate in the overlap region, also as expected. For pyrimidine, according to the criterion of van der Werf et al., all the $S_1$ vibronic levels studied so far ($\Delta E < 3000$ cm$^{-1}$) lie within the black-hole region [Uchida et al., 1978]; therefore, $N$ should increase with $\Delta E$ and fluorescence quenching cross sections should be large.
However, Uchida et al. (1978) found that N increases rapidly with $\Delta E$ for the low-lying vibronic levels but only slightly for the higher levels and Spears and El-Manguch (1977) found that the quenching rates of the slow fluorescence were 6-8 times the hard-sphere collision rate for lower vibronic levels but approximately equal to the hard-sphere collision rate for the $6a_1^2$ $l_2^2$ $(\Delta E = 2642 \text{ cm}^{-1})$ level. This behaviour suggests that the $S_1$ manifold of pyrimidine can also be separated into two regions but on the basis of a slightly different criterion from that proposed by van der Werf et al. (1976a,b) and used to explain their results for biacetyl, methylglyoxal and glyoxal. Spears and El-Manguch (1977) proposed such a criterion to explain the fluorescence quenching rates of pyrimidine; their interpretation of collisional quenching yielded a condition for quenching rates $\ll$ the hard-sphere collision rate which explained the onset of $\ll$ hard-sphere quenching rates at the $6a_1^2l_2^2$ level.

A most interesting result consistently emerges from the analysis of emission data for intermediate case molecules within the framework of the Lahmani et al./van der Werf et al. model. It is found that $\rho^\text{eff}$ derived in the analysis far exceeds the density of triplet vibronic states $\rho^V_T$ calculated by using the Haarhoff (1963) formula.* The discrepancy may be greater for pyrimidine than for any other intermediate case molecule examined so far. In calculations of $\rho^V_T$ for pyrimidine, however, contributions from a possible second triplet state located $\sim 900 \text{ cm}^{-1}$ above

---

* The $\rho^V_T$ values have considerable uncertainties associated with them because the calculation neglects anharmonicity and relies on estimates of the vibrational frequencies in the triplet state and the $S_1$-$T$ energy gap. As estimates of $\rho^\text{eff}$, however, the values of $\rho^V_T$ obtained using all the vibrational modes must be regarded as upper limits, despite the neglect of anharmonicity etc., because it is not expected that all modes can be involved in coupling (e.g. because of symmetry restrictions) with the singlet state. For example, Coveleskie and Yardley (1975b) found that for methylglyoxal at 22000 cm$^{-1}$ the calculated density of states is $1.7 \times 10^{10}\text{ cm}^{-1}$ using all 21 vibrational modes and $6.5 \times 10^{6}\text{ cm}^{-1}$ using only the 12 "skeletal" modes.
\( T_1 \) [Hochstrasser and Marzzacco, 1968] have been neglected.\(^*\) Ratios \( \rho^\text{eff}/\rho_T \) determined by various workers are (for \( \Delta E \leq 2000 \text{ cm}^{-1} \)): 120-50 [Spears and El-Manguch, 1977] and 9000-3000 [Uchida \textit{et al}., 1978] for pyrimidine,\(^{**} \sim 10-100\) for pyrazine [Frad \textit{et al}., 1974], and \( \approx 10 \) for glyoxal, methylglyoxal and biacetyl [van der Werf \textit{et al}., 1975, 1976a,b].

In comparing \( \rho^\text{eff}/\rho_T \) values, van der Werf \textit{et al}. (1976a,b) considered that the average Boltzmann ground state energy (\( \sim 600 \text{ cm}^{-1} \) for methylglyoxal) is transferred to the excited state as an energy (\( \Delta E_t \)) in excess of the energy of the exciting light. Their \( \rho_T \) values were calculated at energies \( \Delta(S_1-T_1) + \Delta E + \Delta E_t \) for optical excitations \( \Delta E \) in \( S_1 \). This results in the \( \rho^\text{eff}/\rho_T \) ratios for the dicarbonyls\(^{**} \) being deflated by an order of magnitude compared with the ratios quoted for pyrimidine and pyrazine.

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\(^*\) See footnote on p. 342

\(^{**}\) Different approximations were required to obtain values for \( \rho_T^\text{eff} \) (and \( N \)): not enough experimental parameters were measured to determine \( \rho_T^\text{eff} \) uniquely and both groups did not measure the same experimental parameters. Part of the discrepancy between the two estimates of the ratio arises from the different values used for \( \tau_{\text{Slow}} \) (\( P = 0 \)), the zero pressure lifetime of the slow fluorescence (\( \rho_T^\text{eff} \propto \tau_{\text{Slow}} \) (\( P = 0 \))). The estimates for \( \tau_{\text{Slow}} \) (\( P = 0 \)) obtained indirectly by Uchida \textit{et al}. from Stern-Volmer plots were \( \sim 10 \) times larger than the \( \tau_{\text{Slow}} \) (\( P = 0 \)) values obtained directly from lifetime measurements by Spears and El-Manguch. Both groups obtained very similar \( \rho_T \) values.

\(^{**} \) For 4492 Å excitation of methylglyoxal, Coveleskie and Yardley (1975b) obtained a \( \rho_T^\text{eff}/\rho_T \) value of 160 and van der Werf \textit{et al}. (1976a) a value of 7. A major part of the discrepancy arises from the different \( \rho_T^\text{V} \) values used: 75/cm\(^{-1} \) for \( \rho_T^\text{V} \) (\( \Delta E \)) and 460/cm\(^{-1} \) for \( \rho_T^\text{V} \) (\( \Delta E + \Delta E_t \)).
Spears and El-Manguch (1977) and Uchida et al. (1976, 1978) found that the apparently larger S$_1$-T coupling for pyrimidine could be attributed to the relatively greater number of effectively coupled triplet levels, N, calculated for pyrimidine; coupling matrix elements, $v_{ST}$, were found to be of the same magnitude ($\sim 10^{-4}$ cm$^{-1}$) for the dicarbonyls as for pyrimidine. Uchida et al. (1978) showed that methyl derivatives of pyrimidine also give both fast and slow fluorescence at low pressures, that methyl substitution significantly reduces $\phi_{F2}(0)$ in essentially the same manner as increasing $\Delta E$ does in the unsubstituted pyrimidine and that the decrease in $\phi_{F2}(0)$ can be interpreted as being due to the increase of N. Both the increase in $\Delta E$ and the introduction of one or two methyl groups into pyrimidine give rise to an increase in $\rho^v_T$ and Uchida et al. (1978) found that for pyrimidine and its methyl derivatives there is a fairly good correlation between N and $\rho^v_T$.

The generally observed disagreement between $\rho^v_T$ and $\rho^\text{eff}_T$ (and between $\rho^v_S$ and $\rho^\text{eff}_S$ [van der Werf et al., 1976a,b]) has led several authors [Spears and El-Manguch, 1977; Uchida et al., 1978; van der Werf et al., 1976a,b; Coveleskie and Yardley, 1975b] to conclude that the S$_1$-T coupling is between rovibronic levels (i.e. the rotational part of the molecular Hamiltonian cannot be neglected when considering collisional quenching of fluorescence for intermediate case molecules). Using the Haarhoff (1963) formulae, Spears and El-Manguch (1977) calculated that, for pyrimidine, the density of rovibronic triplet levels, $\rho^\text{rv}_T$, is $\sim 6 \times 10^3$ times higher than $\rho^v_T$ for $\Delta E = 0-2600$ cm$^{-1}$. Values of $\rho^\text{eff}_T$ in the range $\rho^v_T < \rho^\text{eff}_T < \rho^\text{rv}_T$ are acceptable: the density of triplet rovibronic levels effectively coupled to a fluorescing singlet state is expected to be smaller than $\rho^\text{rv}_T$ because of symmetry restrictions.
Before concluding this section it should be pointed out that the Lahmani et al./van der Werf strong coupling model is not the only model that can be used to account for the photophysical behaviour of intermediate case molecules. Avouris et al. (1977) demonstrated that, although it involves a quite different parameterization of the experimental observables (lifetimes etc.) from the strong coupling model, a simple weak coupling model is also applicable. They emphasise that, because intermediate case decay behaviour can be analysed in terms of strong and weak coupling models, neither of the two should be taken to have quantitative significance until independent information is obtained about the relative magnitudes of interelectronic interactions, level densities etc.

A non-quantum mechanical kinetic scheme, first proposed by Ashpole et al. (1971), has also been used to interpret decay data of intermediate case molecules. It depends for its success on a reversible collision-free ISC step, $S_1 \leftrightarrow T$, with first order rate constants describing the rate of the forward and back exchange between $S_1$ and $T$. Lahmani et al. (1974) established the correspondence between the parameters of their conceptually more sound quantum mechanical formulation and the rate constants of the kinetic scheme; the kinetic scheme has been used in the analysis of data for methylglyoxal [Coveleskie and Yardley, 1975b], biacetyl [van der Werf et al., 1974] and pyrimidine [Reineccius and von Weyssenhoff, 1977]. Wassam and Lim (1980) analysed the experimental data of Uchida et al. (1976, 1978) and Spears and El-Manguch (1977) for pyrimidine within the framework of the same kinetic scheme and rationalised the effect of methylation and vibrational excitation ($\Delta E$) on the biexponential decay of pyrimidine in terms of "proximity effects" in radiationless transitions.

It has been demonstrated [e.g. Lim, 1977; Wassam and Lim, 1978a,b, 1979] that vibronic interactions between $n\pi^*$ and $\pi\pi^*$ excited electronic states of N-hererocyclic molecules are important in determining their
photophysical behaviour. Changes in the photophysical behaviour brought about by alterations in the vibronic interaction between excited electronic states are termed "proximity effects". Studies [referenced in Wassam and Lim (1980)] have shown (1) that a decrease in the energy gap between vibronically coupled electronic states leads to an increase in the vibronic interaction as manifested in an enhancement of the IC and ISC nonradiative decay rates for transitions originating from the lower state of a vibronically coupled pair, (2) that excitation of totally symmetric (t.s.)/non-totally symmetric (n.t.s.) modes should detune/amplify the effect of variations in the vibronic interactions on IC and ISC rates and (3) that this latter effect should be much more dramatic for large energy gap transitions than small energy gap transitions. For pyrimidine, there is evidence of $1,3^1B_1(n\pi^*) - 1,3^1A_1(\pi\pi^*)$ vibronic coupling and also that methylation reduces the $\pi\pi^*$-$\pi\pi^*$ energy gaps [Goodman and Shull, 1954, 1957]; therefore, methylation can be used to probe proximity effects in pyrimidine. Wassam and Lim (1980) consider that their analysis shows that methylation leads to an increase in the rate constants for IC and ISC (cf. conclusion (1) above) but that, upon exciting t.s. modes $v_{6a}$ and $v_{12}$, the effect diminishes for large energy gap transitions (cf. conclusions (2) and (3) above). Despite the questionable validity of the kinetic scheme they employed, Wassam and Lim (1980) argue that their results show the importance of vibronic interactions in governing the decay behaviour of pyrimidine and that the characterisation of molecular relaxation by use of theories (such as that of Lahmani et al./van der Werf et al.) which do not allow for the incorporation of the details of microscopic interactions is, therefore, tenuous.

* In pyrimidine n.t.s. modes $v_{6a}$ and $v_{12a}$ are of correct symmetry to induce $1,3^1B_1(n\pi^*) - 1,3^1A_1(\pi\pi^*)$ vibronic coupling and Wassam and Lim (1980) consider that the large reduction in the frequencies of modes $v_{6a}$ and $v_{12a}$ between $S_0$ and $S_1$ attests to their involvement in vibronic coupling.
F. **Orientation of this study**

The high sensitivity of pyrimidine-$h_4$ ($P-h_4$) fluorescence to collisional quenching which has led several authors to propose that rotational effects are involved in the mechanism of quenching, prompted us to undertake studies on the $0^0$ level fluorescence quenching of pyrimidine-$d_4$ ($P-d_4$), since for it the energy intervals separating rotational levels are smaller, and on electronic energy transfer from $P-d_4$ to $P-h_4$. The $0^0$ level fluorescence quenching of $P-h_4$ was also re-investigated in order to compare quenching data for $P-d_4$ and $P-h_4$ from the same instrument but also because different measurements of the self quenching of $P-h_4$ fluorescence, even by workers of the same laboratory, have yielded different results [Uchida et al., 1976, 1978; Knight, 1974] and because, whereas some workers reported a transition from Stern-Volmer to non-Stern-Volmer kinetics for the self quenching of $P-h_4$ fluorescence at $\approx 0.3$ torr [Reineccius and von Weyssenhoff, 1977*; Uchida et al., 1976, 1978**], others reported strictly Stern-Volmer quenching of $P-h_4$ fluorescence by a range of foreign gases at pressures up to 0.4 torr [Knight, 1975; Knight and Parmenter, 1976(a)] and 1.2 torr [Jones, 1973].

Rate constants for self quenching of fluorescence obtained by study of the pressure dependence of the relative quantum yield are usually less reliable than those obtained by study of the pressure dependence of the lifetime. The changing spatial distribution of fluorescence within the cell with sample pressure is a problem in the relative fluorescence method. This study commenced with an examination of its effect on the $P-h_4$ self quenching.

* They found that the Stern-Volmer component of the fluorescence quantum yield was large cf. the constant component up to pressures of $\approx 0.3$ torr.

** Quantum yield of slow Stern-Volmer component of fluorescence $\leq$ quantum yield of fast pressure independent component for pressures $\geq 0.47$ torr.
quenching data obtained using our multi-pass cell. The vibrational structure of fluorescence spectra from levels $0^0$ and $12^1$ of P-d$_4$ over a range of pressures was also examined.

7.2 COLLISIONAL VIBRATIONAL RELAXATION

The relative intensities of the 12 strongest bands of the $0^0$ level fluorescence spectrum of P-d$_4$ were compared at 10 pressures in the range 0.005-0.2 torr. There were no indications of a redistribution of intensities among these bands over this pressure range. A similar result was obtained for the $12^1$ fluorescence spectra of P-d$_4$ obtained at pressures of 0.02, 0.06 and 0.2 torr.

In view of the high pressures required to effect observable upward vibrational relaxation for the $0^0$ level fluorescence of P-h$_4$ (sections 6.1 and 6.2), the result for the $0^0$ level fluorescence of P-d$_4$ is not unexpected. Knight and Parmenter (1976a) reported that downward vibrational relaxation in $S_1$ P-h$_4$ is sufficiently fast to compete with $S_1$-$T$ crossing and Logan and Ross (1968) found that, for 12-150 torr of P-h$_4$ and 12 torr of P-h$_4$ plus up to 700 torr of added isopentane, the fluorescence spectrum of P-h$_4$, following excitation at $\sim 850$ cm$^{-1}$ above the $0^0$ band, changed from a resonance to an equilibrated type. However, it is not surprising that no change was detected in the intensity pattern of the $12^1$ spectrum of P-d$_4$ despite the P-h$_4$ results since our study was done over a very limited pressure range and at much lower pressures than used by Logan and Ross (1968). Table 7.1 indicates just how few collisions per lifetime occur for P-h$_4$ over the pressure range of our study, the maximum being only $\sim 0.2$ for the long dominant ($\phi_L/\phi_S^2$) component of decay from the $0^0$ level of P-h$_4$ at 0.2 torr, and similar results are expected for P-d$_4$. Collision induced vibrational
Table 7.1 Collisions per fluorescence lifetime for levels \(0^0\) and \(12^1\) of pyrimidine-\(h_4\) at pressures of 0.005 and 0.2 torr

<table>
<thead>
<tr>
<th>State</th>
<th>(P(\text{torr}))</th>
<th>(\tau_L(\text{ns})^a)</th>
<th>(\tau_S(\text{ns})^a)</th>
<th>(c_L^b)</th>
<th>(c_S^b)</th>
<th>(\phi_L/\phi_S^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0^0)</td>
<td>0.005</td>
<td>760</td>
<td>2.7</td>
<td>5\times10^{-2}</td>
<td>2\times10^{-4}</td>
<td>20</td>
</tr>
<tr>
<td>(0^0)</td>
<td>0.2</td>
<td>60</td>
<td>2.7</td>
<td>2\times10^{-1}</td>
<td>7\times10^{-3}</td>
<td>2.2</td>
</tr>
<tr>
<td>(12^1)</td>
<td>0.005</td>
<td>500</td>
<td>1.3</td>
<td>3\times10^{-2}</td>
<td>9\times10^{-5}</td>
<td>2.5</td>
</tr>
<tr>
<td>(12^1)</td>
<td>0.2</td>
<td>50</td>
<td>1.3</td>
<td>1\times10^{-1}</td>
<td>3\times10^{-3}</td>
<td>0.3</td>
</tr>
</tbody>
</table>

\(^a\) Lifetimes of long(\(L\)) and short(\(S\)) decay components of fluorescence estimated from Spears and El-Manguch (1977)

\(^b\) Collisions per lifetime calculated using equations (2.16)-(2.18) with \(d = 5.7\ \text{Å}\)

\(^c\) Quantum yield of long decay component relative to quantum yield of short decay component at pressure \(P\). Quantum yield values obtained from Uchida et al. (1978).

Redistribution should, therefore, not be significant in the spectra used in the detailed analyses of Franck-Condon factors (chapter 6) or over the pressure range of the \(S_1\) electronic relaxation and energy transfer experiments reported in this chapter.

7.3 COLLISIONAL QUENCHING OF FLUORESCENCE

A. Changing spatial distribution of emission with changes in sample pressure in self quenching studies

Stern-Volmer plots (next section) for the self quenching of \(P-h_4\) \(0^0\) level fluorescence obtained using (i) photon counting and (ii) charge integration fluorescence detection as described in section 3.4 are given in figures 7.1(a) and 7.2(a). The plots are markedly non-linear at pressures \(\geq 0.03\ \text{torr}\). Similar curves (Appendix A7(i)-(iii)) were obtained using
Figure 7.1. Stern-Volmer plot for the self quenching of pyrimidine-h₄ ₀ level fluorescence obtained using photon counting fluorescence detection. Shows: (a) curvature in the plot at higher pressures, (b) effect of applying correction factor for ε=161 (see text), (c) effect of applying correction factor for ε=262, (d) fit to the uncorrected data over the low pressure range.
Figure 7.2. Stern-Volmer plot for the self quenching of pyrimidine-H4 0° level fluorescence obtained using charge integration fluorescence detection. Shows: (a) curvature in the plot at higher pressures, (b) effect of applying correction factor for ε=161 (see text), (c) effect of applying correction factor for ε=262, (d) fit to the uncorrected data over the low pressure range.
different detection conditions (collection rates, bandpasses, integrator settings, constant time as well as constant excitation intensity collection intervals, etc.) indicating that the curvature was not an artefact of the detection system. The following analysis shows that the curvature can be attributed to changes in the effective excitation intensity in the multi-pass cell with sample pressure.

For the purpose of the analysis it was assumed that, for each traversal of the cell, the intensity of fluorescence generated in the region from which fluorescence is collected is proportional to the intensity of the excitation beam at the centre of the cell, and that the total collected fluorescence intensity is proportional to the summation of the excitation intensities at the mid-point of each traversal. For successful fluorescence quenching studies, the excitation intensity must be the same for each sample pressure.

The total excitation intensity at the centre of the cell for n traversals, \( I_T \), was determined as follows. If the excitation intensity on entry to the cell is \( I_0 \) and the only intensity losses are due to imperfect reflections in the cell, \( I_T \) is given by

\[
I_T = I_T^0 = I_0 + I_0 R + \ldots + I_0 R^{n-1} \quad (7.2)
\]

\[
= I_0 (R^n - 1)/(R - 1) \quad (7.3)
\]

(7.2)

(7.3)

(7.4)

(7.5)

(7.5)

(7.5)
where $b$ is the absorbance in the distance $l_b$ (11 cm) between the cell window and the entry point of the multi-pass system and $a$ is the absorbance in the distance $l_a$ (6.5 cm) from the mirror surfaces to the cell centre. For an absorbing gas sample with molar extinction coefficient $\varepsilon$ at 295 K and pressure $P$(torr), $a$ and $b$ are given by*

$$a = \varepsilon (5.4 \times 10^{-5})P a$$

$$b = \varepsilon (5.4 \times 10^{-5})P b$$

Thus, in the case of an absorbing sample, the total excitation intensity at the cell centre is very sensitively dependent on the sample pressure, the effective excitation intensity relative to the excitation intensity in the absence of absorption being $I_T/I^0_T$. Multiplying the measured fluorescence intensities at each pressure by the corresponding $(I_T/I^0_T)^{-1}$ factor compensates for the absorption effect.

The average absorbance ($A$) for the 0-0 band of P-h₄ at its 300 K equilibrium vapour pressure was 1.54 for a 10 cm path length. The absorbance (spectrum Appendix A6(iv)) was obtained using a Cary 219 spectrophotometer operated at a constant slit width of 0.5 nm. The vapour pressure of P-h₄ at 300 K was estimated to be 18 torr**, so

---

* Absorbance $A = \log_{10}(I_0/I) = \varepsilon cl$ (assuming the Beer-Lambert law holds) where $I$ is the transmitted intensity, $c$ is the molar concentration and $l$ is the path length. From the Ideal gas equation, the concentration of a gas sample at 295 K and pressure $P$ (torr) is given by $c = P1000/\left[760(82.0575)295\right]$.

** Using the equation

$$\log P(\text{torr}) = 2.8808 - S\Delta T/(T - 0.15\Delta T)$$

where $S$ is the entropy of vaporisation at 760 torr, $T$ is the temperature and $\Delta T$ is the difference between $T$ and the boiling point, [Hass and Newton, 1967]. $S$ was obtained by using the equation with $P = 12$ torr for P-h₄ at 293 K [Logan and Ross, 1968].
equation

\[ A = \varepsilon (5.34 \times 10^{-5}) 10P \]  

(7.8)

gave \( \varepsilon = 161 \) (litre mole\(^{-1}\) cm\(^{-1}\)). Table 7.2 gives the resultant \( I_T/I_T^0 \) values over a range of pressures for \( R = 0.9 \) and \( \varepsilon \) values of 161 and 262.

The effect of applying the \((I_T/I_T^0)^{-1}\) correction factors to the fluorescence intensities used to obtain the Stern-Volmer plots of figures 7.1(a) and 7.2(a) is apparent from figures 7.1(b), (c) and 7.2(b), (c). They show that a value for \( \varepsilon \) of 262 rather than the measured value of 161 mole\(^{-1}\) cm\(^{-2}\) gives linear plots over the higher pressure range. This is not necessarily indicative of defects in the analysis, approximate as it is, because the absorbance of the sample for the narrow bandwidth laser excitation light may be higher than that obtained for much broader bandwidth light. Table 7.2 indicates that the adverse effect of sample absorption on the excitation intensity and hence the measured fluorescence intensity should be insignificant at pressures less than \( \sim 0.01 \) torr for P-h\(_4\) in our multi-pass cell and this was found: figures 7.1(d) and 7.2(d) show that the Stern-Volmer plots for the self quenching of pyrimidine-h\(_4\) are quite linear at pressures \( \leq 0.03 \) torr and other examples are given in Appendix 7(i). Consequently, the fluorescence self quenching data for P-h\(_4\) and P-d\(_4\) were derived from measurements with sample pressures below \( \sim 0.03 \) torr.

* The DMS "UV Atlas of Organic Compounds", Vol 3 (Butterworths, 1967) gives \( \varepsilon = 54 \) for the 0-0 band (30900 cm\(^{-1}\)) of P-h\(_4\) in cyclohexane (bandpass 80 cm\(^{-1}\)).
Table 7.2  Relative total excitation intensities at the cell centre, \( \frac{I_T}{I_T^0} \), over a range of pressures for molar extinction coefficients of 161 and 262 litre mole\(^{-1}\) cm\(^{-1}\)

<table>
<thead>
<tr>
<th>P (torr)</th>
<th>( I_T/I_T^0(161) )</th>
<th>( I_T/I_T^0(262) )</th>
<th>P (torr)</th>
<th>( I_T/I_T^0(161) )</th>
<th>( I_T/I_T^0(262) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 1 \times 10^{-4} )</td>
<td>1.0</td>
<td>1.0</td>
<td>( 7 \times 10^{-2} )</td>
<td>0.84</td>
<td>0.76</td>
</tr>
<tr>
<td>( 1 \times 10^{-3} )</td>
<td>1.0</td>
<td>1.0</td>
<td>0.1</td>
<td>0.80</td>
<td>0.69</td>
</tr>
<tr>
<td>( 5 \times 10^{-3} )</td>
<td>0.99</td>
<td>0.98</td>
<td>0.3</td>
<td>0.54</td>
<td>0.41</td>
</tr>
<tr>
<td>( 1 \times 10^{-2} )</td>
<td>0.97</td>
<td>0.96</td>
<td>0.5</td>
<td>0.40</td>
<td>0.28</td>
</tr>
<tr>
<td>( 3 \times 10^{-2} )</td>
<td>0.93</td>
<td>0.89</td>
<td>0.7</td>
<td>0.32</td>
<td>0.20</td>
</tr>
<tr>
<td>( 5 \times 10^{-2} )</td>
<td>0.88</td>
<td>0.82</td>
<td>1.0</td>
<td>0.23</td>
<td>0.14</td>
</tr>
</tbody>
</table>

B.  **Stern-Volmer equations**

(i)  **Self quenching**

The fluorescence quantum yield,

\[
\phi_f = \frac{k_f}{k_f + k_n + k_S P}
\]  \hspace{1cm} (7.9)

(\( k_f \) and \( k_n \) are the rate constants for unimolecular \( S_1 \) radiative and nonradiative decay respectively, \( k_S \) is the rate constant for bimolecular self quenching and \( P \) is the pressure of the fluorescent sample) is related to the observed fluorescence intensity, \( I_f \), as

\[
\phi_f = K I_f / P
\]  \hspace{1cm} (7.10)

(\( K \) is a proportionality constant) in the pressure range where absorption of the exciting light is a linear function of sample pressure [Parmenter and White, 1969; Anderson, Parmenter and Poland, 1973].  Thus
so the slope (b)-intercept (a) ratio of a plot of \( P/I_f \) vs. \( P \) (Stern-Volmer plot) yields \( k_s\tau_0 \) where \( \tau_0 = 1/(k_f + k_n) \) is the zero pressure fluorescence lifetime. The data presented here were fitted to the equation

\[
I_f = \frac{P}{a + bP}
\]  

(7.12)

where \( a \) and \( b \) are variable parameters using a weighted least-squares routine (e.g. figure 7.3(a)) though most are displayed in the conventional Stern-Volmer form (e.g. figure 7.3(b) cf. figure 7.3(a)).

(ii) Foreign gas quenching

For different pressures \( Q \) of foreign gas added to the fluorescent sample at constant pressure \( P_0 \), the fluorescence quantum yield is

\[
\phi_f = \frac{k_f}{k_f + k_n + k_sP_0 + k_qQ}
\]  

(7.13)

where \( k_q \) is the bimolecular rate constant for the quenching of fluorescence by the added foreign gas. In these experiments the absorption of the excitation light is independent of variation in gas pressure so

\[
\phi_f = K'I_f
\]  

(7.14)

where \( K' \) is a proportionality constant. Thus the slope-intercept ratio of a plot of \( 1/I_f \) vs. \( Q \) yields \( k_q\tau \) where \( \tau \) is the lifetime of the fluorescent species at pressure \( P_0 \) in the absence of foreign gas quencher. It is conventional, however, to derive \( k_q\tau \) from the slope of a \( I_f^0/I_f \) vs. \( Q \) plot (where \( I_f^0 \) is the fluorescence intensity in the absence of quencher) which should yield an intercept of unity since
\[
\frac{I^0_f}{I_f} = \frac{(k_f + k_n + k_s P_0 + k_Q)}{(k_f + k_n + k_s P_0)}
\]

The foreign gas quenching data presented here were fitted to the equation

\[
I_f = \frac{c}{(1 + dQ)}
\]

where \(c\) and \(d\) are variable parameters, using a weighted least-squares routine (e.g. figure 7.7(a)) though most are displayed in the conventional Stern-Volmer form (e.g. figure 7.7(b) cf. figure 7.7(a))

\[
\frac{I^0_f}{I_f} = 1 + k_q Q
\]

Parameter \(c\) was used instead of \(I^0_f\) because the pressure \((P_0)\) of \(P-d_4\) and \(P-h_4\) decrease with time due to their absorption into the O-ring seal and adsorption on the cell's internal surfaces; cyclohexane displayed no such tendency (section 2.3.3). To counteract this effect, the initial \(P-d_4\) and \(P-h_4\) samples were left to equilibrate in the cell for about 30 min before starting the measurements and making additions of foreign gas. Parameter \(d\) gives \(k_q\).

C. Results

(i) \(P-d_4\) self quenching

The plot of figure 7.3 for the range 0.001-0.043 torr gave a \(k_{sT_0}\) value of 209 torr\(^{-1}\). This compares with values of 189 torr\(^{-1}\) and 165 torr\(^{-1}\) obtained from data (figure 7.4) recorded over pressure ranges of 0.001-0.06 and 0.015-0.06 torr respectively. The \(k_{sT_0}\) values have a very sensitive dependence on the small intercept values. As the plots for all three sets of data were linear over the pressure ranges (cf. \(P-h_4\)
Figure 7.3. Stern-Volmer plot for the self quenching of $0^0$ level fluorescence of pyrimidine-d$_4$. Data plotted (a) in the form of equation (7.12) and (b) in the usual form (see text).
Figure 7.4. Stern-Volmer plots for the self quenching of 0^0 level fluorescence of pyrimidine-d$_4$. Plots (a) and (b) are for the same data and fitted parameters. Plot (c) is for different data.
plots) the $k_{l0}$ value for $P-d_4$ was taken to be $190 \pm 20$ torr$^{-1}$. These studies were not extended to higher pressures to conserve the $P-d_4$.

(ii) $P-h_4$ self quenching

An average value for $k_{s10}$ of $180 \pm 20$ torr$^{-1}$ was obtained from a series of measurements at pressures less than 0.02 torr (e.g. figure 7.5(a)). Extension of the measurements to higher pressures produced curvature in the plots (figure 7.5(b)), as discussed in the previous section. Why this does not occur at similar pressures for $P-d_4$ which has a similar 0-0 band extinction coefficient is not clear.

(iii) $P-d_4$ quenching by $P-h_4$

The most reliable of a series of measurements of the fluorescence quenching of $P-d_4$ by $P-h_4$ (figure 7.6) yielded a $k_{q1}$ value of 63 torr$^{-1}$ for an initial $P-d_4$ pressure of 0.002 torr. These studies were hampered by the reduction in sample pressure with time.

(iv) Quenching of $P-d_4$ fluorescence by cyclohexane

The plot of figure 7.7, for 0.002-0.02 torr of cyclohexane added to $P-d_4$ at an initial pressure of 0.0034 torr, gave a value for $k_{q1}$ of 60 torr$^{-1}$. The fitted parameter c closely matched the measured $I_f^0$ value (6486 cf. 6491) for the plot of figure 7.7 but this was the only close match between c and $I_f^0$ for the whole series of studies of foreign gas quenching of $P-d_4$ and $P-h_4$ fluorescence. There is some evidence of curvature in the plot of figure 7.7 as the pressure of added gas increases, the $k_{q1}$ value for 0.01-0.02 torr of added cyclohexane being 32 torr$^{-1}$ for example, but it could not be ascertained whether this is a manifestation of the growing dominance of a non-Stern-Volmer component of fluorescence (i.e. $I_f$ in equation 7.17 not maintaining a sufficiently rapid decrease
Figure 7.5. Stern-Volmer plot for the self quenching of 0° level fluorescence of pyrimidine-$h_4$. The plot becomes non-linear at higher pressures ((b) cf. (a)).

Figure 7.6. Stern-Volmer plot for the quenching of pyrimidine-$d_4$ 0° level fluorescence by pyrimidine-$h_4$. 
Figure 7.7. Stern-Volmer plot for the quenching of pyrimidine-d₄ 0° level fluorescence by cyclohexane. Data plotted (a) in the form of equation (7.16) and (b) in the usual form (see text). Initial pyrimidine-d₄ pressure of 0.0034 torr.
with increase in the pressure of added gas), a decrease in the fluorescent sample pressure (and hence $I_f^0$ in equation 7.17), an instrumental artefact (e.g. changing gain of the PMT monitoring the excitation intensity) or a combination of these factors. The trend towards decreasing values of $k_{qT}$ for fits made over higher pressures of cyclohexane is further illustrated in the plots of figures 7.8 and 7.9. For figure 7.8, the initial $P-d_4$ pressure was 0.0027 torr and the $k_{qT}$ values for fits over the pressure ranges 0.001-0.03 torr (figure 7.8(c)) and 0.03-0.1 torr (figure 7.8(d)) were 91 and 61 torr$^{-1}$ respectively. Fitting the data for the pressure range 0.001-0.3 torr (figure 7.8(a)) gives a value for $k_{qT}$ of 71 torr$^{-1}$; the fit to the data for the higher pressures of cyclohexane appears poor because, in the fitting program, greater weight is given to the higher intensity values (cf. figure 7.8(b)). For figure 7.9, the initial $P-d_4$ pressure was 0.0035 torr and the $k_{qT}$ values for fits over the pressure ranges 0.02-0.11 torr (figure 7.9(c)), 0.15-0.35 torr (figure 7.9(d)), 0.4-0.9 torr (figure 7.9(e)) were 46, 10 and 3 torr$^{-1}$ respectively. Fitting the data for the range 0.02-0.9 torr gave a $k_{qT}$ value of 25 torr$^{-1}$ (figure 7.9(a), (b)).

(v) Quenching of $P-h_4$ fluorescence by cyclohexane

The value for $k_{qT}$ from the plot in figure 7.10 for an initial $P-h_4$ pressure of 0.0044 torr over a pressure range of 0.005-0.04 torr was 32 torr$^{-1}$. At higher pressures of cyclohexane the $k_{qT}$ values decreased to 21 torr$^{-1}$ (0.1-0.4 torr cyclohexane, figure 7.11(b)) and 11 torr$^{-1}$ (0.1-1 torr cyclohexane, figure 7.11(a)). The remarks made about the cyclohexane quenching of $P-d_4$ fluorescence also apply here.
Figure 7.8. Stern-Volmer plots for the quenching of pyrimidine-$d_4$, 0° level fluorescence by cyclohexane for fits over different cyclohexane pressure regions. Initial pyrimidine-$d_4$ pressure of 0.0027 torr. Plots (a) and (b) are for the same data and fitted parameters.
Figure 7.9. Stern-Volmer plots for the quenching of pyrimidine-d$_4$, 0° level fluorescence by cyclohexane for fits over different cyclohexane pressure regions. Initial pyrimidine-d$_4$ pressure of 0.0035 torr. Plots (a) and (b) are for the same data and fitted parameters.
Figure 7.9 (continued)
Figure 7.10. Stern-Volmer plot for the quenching of pyrimidine-h₄ 0° level fluorescence by cyclohexane. Initial pyrimidine-h₄ pressure of 0.0044 torr.

Figure 7.11. Stern-Volmer plots for the quenching of pyrimidine-h₄ 0° level fluorescence by cyclohexane for fits over different cyclohexane pressure regions. Initial pyrimidine-h₄ pressure of 0.0044 torr.
(vi) Summary of results

Table 7.3 presents a summary of the results of the P-d₄ and P-h₄ quenching studies. The $k_{s\tau}$ and $k_{q\tau}$ values were evaluated for the pressure ranges indicated. Also tabulated are the lifetimes of the long pressure dependent component of P-h₄ fluorescence, obtained from the work of Spears and El-Manguch (1977). There are marked variations in the results from different determinations. Uncertainties were only assigned to a result if several determinations of it were made. Exhaustion of the supply of P-d₄ and lack of time prevented many repetitions of the experiments.

Table 7.3 Summary of pyrimidine-d₄ and -h₄ fluorescence quenching studies. Parameters defined in text.

(a) Self quenching (pressure in torr)

<table>
<thead>
<tr>
<th>Species</th>
<th>Pressure range</th>
<th>$k_{s\tau} (\text{torr}^{-1})$</th>
<th>$\tau_0 (\mu s)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-d₄</td>
<td>0.001-0.06</td>
<td>190 ± 20</td>
<td></td>
</tr>
<tr>
<td>P-h₄</td>
<td>0.002-0.02</td>
<td>180 ± 20</td>
<td>1.8</td>
</tr>
</tbody>
</table>

(b) Foreign gas quenching (pressure in torr)

<table>
<thead>
<tr>
<th>Fluorescent species (initial pressure)</th>
<th>Quencher</th>
<th>Pressure range</th>
<th>$k_{q\tau}(\text{torr}^{-1})$</th>
<th>$\tau_0 (\mu s)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-d₄ (0.002)</td>
<td>P-h₄</td>
<td>0.02-0.08</td>
<td>60</td>
<td>?</td>
</tr>
<tr>
<td>P-d₄ (0.0034)</td>
<td>Cyclohexane</td>
<td>0.002-0.02</td>
<td>60</td>
<td>?</td>
</tr>
<tr>
<td>P-d₄ (0.0034)</td>
<td>Cyclohexane</td>
<td>0.02-0.1</td>
<td>45</td>
<td>?</td>
</tr>
<tr>
<td>P-d₄ (0.0027)</td>
<td>Cyclohexane</td>
<td>0.002-0.03</td>
<td>90</td>
<td>?</td>
</tr>
<tr>
<td>P-d₄ (0.0027)</td>
<td>Cyclohexane</td>
<td>0.03-0.1</td>
<td>60</td>
<td>?</td>
</tr>
<tr>
<td>P-h₄ (0.0044)</td>
<td>Cyclohexane</td>
<td>0.004-0.09</td>
<td>40</td>
<td>0.8</td>
</tr>
<tr>
<td>P-h₄ (0.0044)</td>
<td>Cyclohexane</td>
<td>0.1-0.4</td>
<td>20</td>
<td>0.8</td>
</tr>
</tbody>
</table>
D. Discussion

Bimolecular rate constants for quenching, $k_Q$, can be converted to observed collision cross sections, $s_Q$, or collision diameters, $d$, by means of the equations

$$k_Q = s_Q \bar{g} \text{ (cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$$

(7.18)

$$k_Q = \pi d^2 \bar{g}$$

(7.19)

$$\bar{g} = \left( \frac{8kT}{\pi \mu} \right)^{1/2}$$

(7.20)

where $\bar{g}$ is the average relative speed and $\mu$ the reduced mass of the quenched and quenching molecules. Equation (7.19) reduces to

$$k_Q = (3.31 \times 10^{10})d^2/\mu^{1/2} \text{(torr}^{-1} \text{ s}^{-1})^*$$

(7.21)

at 295 K, with $d$ in cm and $\mu$ in g molecule$^{-1}$. To extract $s_Q$ and $d$ data from $k_Q (k_s \tau_0)$ data the lifetime $\tau(\tau_0)$ must be known.

Some general conclusions can be drawn from the results presented here despite the already indicated defects in the experiments. The results for P-h$_4$ are compared with those obtained by other workers in table 7.4. The results from Jones (1973), Knight and Parmenter (1975) and Knight (1974) were obtained at the same laboratory. In the study by Jones (1973), foreign gases at pressures of 0.1-1.2 torr were added to 0.1 torr of P-h$_4$; in their study of collisional quenching of P-h$_4$ fluorescence by foreign gases, Knight and Parmenter (1975) used a P-h$_4$ pressure of 0.02 torr; the P-h$_4$ self quenching result of Knight (1974)

* To convert from torr$^{-1}$ s$^{-1}$ to cm$^3$ molecule$^{-1}$ s$^{-1}$ multiply by 1.035 x 10$^{-19}$ T.
Table 7.4 Rate constants and cross sections for quenching of 0° level fluorescence of pyrimidine-h₄ from various sources

<table>
<thead>
<tr>
<th>Collision partner</th>
<th>$k_q \tau$ or $k_s \tau_0$ (torr⁻¹)</th>
<th>$\tau$ or $\tau_0$ (µs)</th>
<th>$k_q$ or $k_s$ (torr⁻¹ s⁻¹)</th>
<th>$d_q$ or $d_s$ (Å)</th>
<th>$d_{HS}$ (Å)</th>
<th>$s_Q/s_{HS}$</th>
<th>Source $^f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ne</td>
<td>1.46</td>
<td>0.11</td>
<td>1.3x10⁷</td>
<td>4.5</td>
<td>4.24</td>
<td>1.1</td>
<td>J</td>
</tr>
<tr>
<td>CO</td>
<td>2.41</td>
<td>0.11</td>
<td>2.1x10⁷</td>
<td>6.1</td>
<td>4.64</td>
<td>1.8</td>
<td>J</td>
</tr>
<tr>
<td>i-C₅H₁₂</td>
<td>2.42</td>
<td>0.11</td>
<td>2.1x10⁷</td>
<td>7.2</td>
<td>5.73</td>
<td>1.6</td>
<td>J</td>
</tr>
<tr>
<td>Ne</td>
<td>6.3</td>
<td>0.41</td>
<td>1.5x10⁷</td>
<td>4.9</td>
<td>4.24</td>
<td>1.3</td>
<td>KP</td>
</tr>
<tr>
<td>CO</td>
<td>9.9</td>
<td>0.41</td>
<td>2.4x10⁷</td>
<td>6.5</td>
<td>4.64</td>
<td>2.0</td>
<td>KP</td>
</tr>
<tr>
<td>C₆H₁₂</td>
<td>11.1</td>
<td>0.41</td>
<td>2.7x10⁷</td>
<td>8.1</td>
<td>5.90</td>
<td>1.9</td>
<td>KP</td>
</tr>
<tr>
<td>Self</td>
<td>96</td>
<td>1.8</td>
<td>5.3x10⁷</td>
<td>11.0</td>
<td>5.70</td>
<td>4.2</td>
<td>KP</td>
</tr>
<tr>
<td>Self</td>
<td>190</td>
<td>1.8</td>
<td>10.6x10⁷</td>
<td>16.0</td>
<td>5.70</td>
<td>8.0</td>
<td>K</td>
</tr>
<tr>
<td>Self</td>
<td>-</td>
<td>-</td>
<td>8.5x10⁷</td>
<td>14.5</td>
<td>5.70</td>
<td>6.4</td>
<td>SE</td>
</tr>
<tr>
<td>Self</td>
<td>180</td>
<td>1.8</td>
<td>10x10⁷</td>
<td>15.7</td>
<td>5.70</td>
<td>7.6</td>
<td>this work</td>
</tr>
<tr>
<td>C₆H₁₂</td>
<td>40*</td>
<td>0.8</td>
<td>5x10⁷</td>
<td>11.1</td>
<td>5.90</td>
<td>3.5</td>
<td>this work</td>
</tr>
<tr>
<td>C₆H₁₂</td>
<td>20*</td>
<td>0.8</td>
<td>2.5x10⁷</td>
<td>7.8</td>
<td>5.90</td>
<td>1.8</td>
<td>this work</td>
</tr>
</tbody>
</table>

* See table 7.3

a Lifetimes of the pressure dependent component of fluorescence from Spears and El-Manguch (1977)
b Rate constants for collision induced quenching
c Effective collision diameter for foreign gas ($d_q$) or self ($d_s$) quenching
d $d_{HS}$ is the average of the Lennard-Jones diameters $d_{L-J}$ for pyrimidine and its quenching partner.
All $d_{L-J}$ values except those for pyrimidine (5.7 Å, Uchida et al. (1976)) and cyclohexane (Jones, 1973) were obtained from Beyer and Lineberger (1975).
e Derived quenching cross section/hard sphere collision cross section
f J = Jones (1973); KP = Knight and Parmenter (1975); K = Knight (1974); SE = Spears and El-Manguch (1977)
J, KP, K relative quantum yield measurements; SE lifetime measurements over the pressure range 0.01-0.05 torr.
was obtained from measurements over the pressure range 0.01-0.12 torr.
Our result for the cross section for P-h₄ self quenching (7-8 times gas kinetic) is in reasonable agreement with that obtained from the study of pressure dependence of the lifetime. Our result for cyclohexane quenching obtained for lower pressures of added cyclohexane, 0.004-0.09 torr (table 7.3, sections 7.3A (iv), (v)), is much higher than those obtained by the other workers whereas the result obtained for measurements for higher pressures of added cyclohexane (0.1-0.4 torr) are in reasonable agreement with their results. If the change in $k_q$ with pressure of added gas is not an experimental artefact (section 7.3A (iv)), it may be indicative of an increase in the proportion of a non-Stern-Volmer component in the total fluorescence at higher pressures observed by other workers (section 7.10).

Quenching rate constants and cross sections cannot be extracted from the P-d₄ quenching results because fluorescence lifetimes for P-d₄ are not available. The fluorescence lifetimes for P-d₄ are expected to be longer than those for P-h₄ because of the isotope effect which is interpreted as being due to a decrease in the non-radiative rate constant, $k_n$, upon deuteration [Avouris et al., 1977]. For example, a significant deuterium effect on the fluorescence lifetime has been observed for benzene, the ratio $\tau(C_6D_6)/\tau(C_6H_6)$ for fluorescence from different $S_1$ vibronic levels ranging from 1.4 to 1.8 [Selinger and Ware, 1970]. Thus the quenching rate constants for P-d₄ are expected to be comparable with those of P-h₄.

The most important conclusions to be drawn from the study is that the small changes in the rotational energy intervals do not have any major influence on the collisional quenching of fluorescence since there is no appreciable difference between the quenching efficiencies of P-h₄ and P-d₄ but that the absence of exact resonance between the levels of
colliding molecules has a very large effect, P-d₄ being quenched with approximately equal efficiency by P-h₄ and cyclohexane. From lifetime studies, Zittel and Lineberger (1977) also found that collisional quenching of glyoxal was strikingly isotope independent; strong isotope effects were observed for the collision free lifetimes.

7.4 ENERGY TRANSFER STUDIES

All attempts to measure the rate of electronic energy transfer from excited P-d₄ to P-h₄ by observing the fluorescence spectra following selective excitation of S₁ SVL's of P-d₄ in vapour mixtures of the two isotopes proved unsuccessful. No fluorescence could be attributed to P-h₄ following excitation of P-d₄ to levels 0°, 6a₁ and 12₁. In table 7.5 the near-resonance transitions of P-h₄ and the corresponding energy mismatches are listed. The P-d₄/P-h₄ combinations would appear to offer

<table>
<thead>
<tr>
<th>P-d₄ excitation</th>
<th>Nearest P-h₄* transitions</th>
<th>Energy mismatch</th>
</tr>
</thead>
<tbody>
<tr>
<td>0°</td>
<td>0°</td>
<td>115</td>
</tr>
<tr>
<td></td>
<td>16b₁</td>
<td>93</td>
</tr>
<tr>
<td>12₁</td>
<td>12₁</td>
<td>105</td>
</tr>
<tr>
<td></td>
<td>9a₂</td>
<td>9</td>
</tr>
<tr>
<td>6a₂</td>
<td>6a₂</td>
<td>98</td>
</tr>
<tr>
<td></td>
<td>16b₂</td>
<td>42</td>
</tr>
</tbody>
</table>

* From Innes et al. (1969)
a very good chance of observing electronic energy transfer because the
SVL fluorescence spectra of the two species are well resolved and
identifiably different and because only 115 cm\(^{-1}\) needs to be accounted
for by rotation and translation even at the worst energy mismatch of
the studies. Parmenter, Setzer and Tang (1977) observed collisional
electronic energy transfer between SVL's of \(\text{C}_6\text{D}_6\) and \(\text{C}_6\text{H}_6\) which were
203 cm\(^{-1}\) apart, the rate constant for the transfer being about 0.6 of
the gas kinetic collision rate and the observations being made on
mixtures of 0.15 torr of \(\text{C}_6\text{D}_6\) and 0-1 torr of \(\text{C}_6\text{H}_6\).

The gas mixture combinations used in attempts to observe energy
transfer from the \(0^0\) level of \(\text{P-d}_4\) to \(\text{P-h}_4\) ranged from 0.05-0.15 torr of
\(\text{P-d}_4\) with 0.05-0.9 torr of \(\text{P-h}_4\). Energy transfer to the \(0^0\) level of
\(\text{P-h}_4\), if detectable by the technique employed, would result, for
example, in an increased intensity in the \(\text{P-d}_4\) spectrum at a displacement
of about 795 cm\(^{-1}\)* from the \(0^0\) level excitation position (i.e. 30394 cm\(^{-1}\)),
a region of the \(0^0\) level \(\text{P-d}_4\) fluorescence spectrum devoid of structure.

Figure 7.12(b)-(f) illustrates the results of scans of the region for \(0^0\) level
excitation of 0.05-0.08 torr of \(\text{P-d}_4\) in combination with 0.15-0.9 torr of \(\text{P-h}_4\). No increase in intensity occurs in the 30400 cm\(^{-1}\) region from that recorded
in the absence of \(\text{P-h}_4\) (figure 7.12(a)). In none of the spectra obtained from
the \(\text{P-d}_4/\text{P-h}_4\) combinations used in the \(0^0\) level study, did any bands
appear apart from those attributable to \(\text{P-d}_4\) and none of the \(\text{P-d}_4\) bands
occurred with enhanced intensity. Only quenching of the \(\text{P-d}_4\) fluorescence
was apparent. In the \(0^0\) level energy transfer study, fluorescence from
the \(0^0\) level of \(\text{P-h}_4\) 1000 times less intense than the \(\text{P-d}_4\ \, 0^0\) level
fluorescence observed could have been detected easily. Fluorescence spectra

\* i.e. due to the \(\text{P-h}_4\ \, 6a_1^0 \ldots 16b_2^0\) transition.
Figure 7.12. Fluorescence spectra resulting from exciting mixtures of pyrimidine-$d_4$ and pyrimidine-$h_4$ vapour at the position of the pyrimidine-$d_4$ O$_2$ absorption band. (d)-(f) on following page.

(a) 0.14 torr of pyrimidine-$d_4$ alone
(b) 0.076 torr of pyrimidine-$d_4$ + 0.16 torr of pyrimidine-$h_4$
(c) 0.15 torr of pyrimidine-$d_4$ + 0.15 torr of pyrimidine-$h_4$

(a)-(c), collection bandpass 20-18 cm$^{-1}$, step size 3 cm$^{-1}$, constant excitation intensity collection intervals, NSM=3.
Figure 7.12 (continued)
(d) 0.15 torr of pyrimidine-d$_4$ + 0.15 torr of pyrimidine-h$_4$, constant excitation intensity collection intervals
(e) 0.05 torr of pyrimidine-d$_4$ + 0.5 torr of pyrimidine-h$_4$, constant time (10 s) collection intervals
(f) 0.05 torr of pyrimidine-d$_4$ + 0.9 torr of pyrimidine-h$_4$, constant time (10 s) collection intervals
(d)-(f), collection bandpass 20-16 cm$^{-1}$, step size 3.2-2.7 cm$^{-1}$, NSM=5.
resulting from exciting the 6a¹ and 12¹ levels of P-d₄ at 0.16 torr in the presence of 0.16 torr P-h₄ are given in figures 7.13 and 7.14 respectively. Detailed analyses of the structure in these and similar spectra revealed no additional bands to those observed in the spectra obtained in the absence of P-h₄.

The negative result obtained for the energy transfer experiments is not surprising in view of the exceptional sensitivity of P-d₄ and P-h₄ to collisional quenching.
Figure 7.13. Fluorescence spectrum resulting from exciting a mixture of 0.16 torr of pyrimidine-d₄, and 0.16 torr of pyrimidine-h₄ vapour at the position of the 6a½ [Innes et al., 1969] absorption band of pyrimidine-d₄. Collection bandpass 22-12 cm⁻¹, step size 3.4-2.1 cm⁻¹, constant excitation intensity collection intervals, NSM=6.
Figure 7.14. Fluorescence spectrum resulting from exciting a mixture of 0.16 torr of pyrimidine-d₄ and 0.16 torr of pyrimidine-h₄ vapour at the position of the 12½ absorption band of pyrimidine-d₄. Collection bandpass 22-11 cm⁻¹, step size 3.5-2.0 cm⁻¹, NSM=5.
Let the two curves MCN and ADE in figure A2.1 represent the reflecting surfaces of two spherical mirrors of equal radius of curvature, c, with their centres of curvature located at C and D. AB represents an incoming light beam which, upon reflection about the normal at B, (BD) images at E. The reflection from this point about the normal at E (EC) hits the opposite surface at G. Lines AF and DF are constructed such that BA = BF and other points are joined as shown.
BD = CA = EC = radius of curvature = r

For convenience angles are defined as follows:
\[ \hat{A}BD = \hat{E}BD = m, \hat{E}BC = w, \hat{A}CB = x, \hat{A}CD = y, \hat{B}DC = v, \hat{D}CE = p, \hat{B}EC = q \]

(A2.2)

From the cosine rule, for triangle ADC

\[ AD^2 = AC^2 + DC^2 - 2(AC)(DC) \cos y \]

(A2.3)

and for triangle BCD

\[ BC^2 = BD^2 + CD^2 - 2(BD)(CD) \cos v \]

(A2.4)

Since DB = DC, \( w + m = x + y \)

(A2.5)

and for triangle BDC

\[ w + m + x + y + v = 180 \]

(A2.6)

therefore from equations A2.5 and A2.6

\[ x = (90 - \frac{v}{2}) - y \]

(A2.7)

and

\[ \cos x = \sin \frac{v}{2} \cos y + \cos \frac{v}{2} \sin y \]

(A2.8)

Now

\[ \cos v = 2 \cos^2 \frac{v}{2} - 1 = 1 - 2 \sin^2 \frac{v}{2} \]

(A2.9)

therefore

\[ \cos \frac{v}{2} = \left(\frac{\cos \frac{v}{2} + 1}{2}\right)^{\frac{1}{2}} \quad \sin \frac{v}{2} = \left(\frac{1 - \cos \frac{v}{2}}{2}\right)^{\frac{1}{2}} \]

(A2.10)

From the cosine rule, for triangle BAC

\[ BA^2 = CB^2 + CA^2 - 2(CB)(CA) \cos x \]

(A2.11)

and combining equations A2.1-4, A2.8, A2.10 and A2.11 gives

\[ BA^2 = CB^2 + CA^2 - \left[ BC^2 \left(1 - \frac{AD^2}{2r^2}\right) + \frac{(CB)(AD)}{r} \right] \left[ 4r^2 + (BC)^2(AD)^2 - BC^2 - AD^2 \right]^{\frac{1}{2}} \]

(A2.12)

For triangle ADB the cosine rule gives

\[ AD^2 = BA^2 + BD^2 - 2(BA)(BD) \cos m \]

(A2.13)

and combining equations A2.1 and A2.13 gives

\[ \cos m = \frac{BA^2 + r^2 - AD^2}{2r(BA)} \]

(A2.14)
From equations A2.5 and A2.6

\[ w = 90 - \left( \frac{v}{2} + m \right) \]  

(A2.15)

therefore

\[ \sin w = \cos \left( \frac{v}{2} + m \right) \]  

(A2.16)

or \[ \sin w = \cos \frac{v}{2} \cos m - \sin \frac{v}{2} \sin m \]  

(A2.17)

Since \( \sin m = (1 - \cos^2 m)^{\frac{1}{2}} \)  

(A2.18)

equation A2.17 can be written as

\[ \sin w = \cos \frac{v}{2} \cos m - \sin \frac{v}{2} \left[ 1 - \cos^2 m \right]^{\frac{1}{2}} \]  

(A2.19)

Combining equations A2.4, A2.10, A2.14 and A2.19 yields

\[ \sin w = \left( 1 - \frac{BC^2}{4r^2} \right)^{\frac{1}{2}} \left[ \frac{BA^2 + r^2 - AD^2}{2r} \right] - \frac{BC}{2r} \left[ 1 - \left( \frac{BA^2 + r^2 - AD^2}{2r} \right)^{\frac{1}{2}} \right] \]  

(A2.20)

and \( \cos w = (1 - \sin^2 w)^{\frac{1}{2}} \)

For triangle BCE, the sine rule gives

\[ \frac{BE}{\sin q} = \frac{CE}{\sin w} = \frac{BE}{\sin (x + y + p)} \]  

(A2.21)

and \( x + y + p + q + w = 180 \)

(A2.22)

Rearranging A2.22 gives

\[ x + y + p = 180 - (w + q) \]  

(A2.23)

so \( \sin (x + y + p) = \sin (w + q) \)  

(A2.24)

and \( \sin (w + q) = \sin q \cos w + \sin w \cos q \)  

(A2.25)

From equation A2.21 and A2.1

\[ \sin q = \frac{BC}{r} \sin w \]  

(A2.26)

and, since \( \cos q = (1 - \sin^2 q)^{\frac{1}{2}} \),

\[ \cos q = \left[ 1 - \frac{BC^2 \sin^2 w}{r^2} \right]^{\frac{1}{2}} \]  

(A2.27)

Substituting equations A2.24, A2.25, A2.26 into a rearrangement of equation A2.21,

\[ BE = \frac{r}{\sin w} \sin (x + y + p) \]  

(A2.29)

yields \( BE = BC \cos w + r \left( 1 - \frac{BC^2 \sin^2 w}{r^2} \right)^{\frac{1}{2}} \)  

(A2.30)
For triangle BCE, the cosine rule gives
\[ DE^2 = BD^2 + BE^2 - 2(BD)(BE) \cos m \]  
(A2.31)
and combining equations A2.1, A2.30 and A2.31 yields
\[ DE^2 = r^2 + [BC \cos w + r\left(1 - \frac{BC^2 \sin^2 w}{r^2}\right)]^2 \]
\[ - 2r[BC \cos w + r\left(1 - \frac{BC^2 \sin^2 w}{r^2}\right)] \cos m \]  
(A2.32)

From equations A2.32, A2.20, A2.14 and A2.12, a value for DE can be obtained by substitution of the known values for \( r \) (radius of curvature), \( AD \) (distance from the light beam entry point to the centre of curvature of mirror 2), and \( BC \) (distance from the point where the incoming beam hits mirror 1 to the centre of curvature of mirror 1). For 3 combinations of \( r \), \( AD \) and \( BC \), values of DE are listed in table A2.1. The third row corresponds to the dimensions of the White system used in the equipment described in chapter 2.

<table>
<thead>
<tr>
<th>( r )</th>
<th>( AD )</th>
<th>( BC )</th>
<th>( DE )</th>
<th>( DE/AD )</th>
</tr>
</thead>
<tbody>
<tr>
<td>100.0</td>
<td>25.0</td>
<td>15.0</td>
<td>25.3675</td>
<td>1.0146</td>
</tr>
<tr>
<td>100.0</td>
<td>2.5</td>
<td>1.5</td>
<td>2.5009</td>
<td>1.0004</td>
</tr>
<tr>
<td>13.0</td>
<td>2.5</td>
<td>1.5</td>
<td>2.5548</td>
<td>1.0219</td>
</tr>
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</table>

Table A2.1. \( r \), \( AD \), \( BC \) and \( DE \) refer to figure A2.1, where \( r \) is the radius of curvature of both curves.
Outgassing rates quoted in Holland, Steckelmacher and Yarwood (1974)

<table>
<thead>
<tr>
<th>Material</th>
<th>Pre-treatment</th>
<th>Time in vacuo (hour)</th>
<th>Outgassing rate (torr litre cm$^{-2}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium</td>
<td>None</td>
<td>1</td>
<td>1.3 x 10$^{-6}$</td>
</tr>
<tr>
<td>Nickel</td>
<td>None</td>
<td>1</td>
<td>6 x 10$^{-7}$</td>
</tr>
<tr>
<td>Stainless steel</td>
<td>None</td>
<td>1</td>
<td>2 x 10$^{-7}$</td>
</tr>
<tr>
<td></td>
<td>None</td>
<td>10</td>
<td>2 x 10$^{-8}$</td>
</tr>
<tr>
<td></td>
<td>Polished,</td>
<td>10</td>
<td>1.4 x 10$^{-9}$</td>
</tr>
<tr>
<td>Kel F</td>
<td>None</td>
<td>1</td>
<td>4 x 10$^{-8}$</td>
</tr>
<tr>
<td>Epoxy resin</td>
<td>None</td>
<td>1</td>
<td>3 x 10$^{-6}$</td>
</tr>
<tr>
<td></td>
<td>None</td>
<td>20</td>
<td>6 x 10$^{-7}$</td>
</tr>
</tbody>
</table>

Outgassing rates recommended by Wheeler (1972)

<table>
<thead>
<tr>
<th>Material</th>
<th>Pre-treatment</th>
<th>Outgassing rates (torr litres cm$^{-2}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1 hour 10 hours 40 hours Bakeout (°C)</td>
</tr>
<tr>
<td>OFHC copper</td>
<td>None</td>
<td>2x10$^{-8}$ 1x10$^{-9}$ 3x10$^{-10}$ -</td>
</tr>
<tr>
<td>OFHC copper</td>
<td>Surface removed</td>
<td>8x10$^{-9}$ 1.5x10$^{-10}$ 4x10$^{-11}$ 4x10$^{-12}$ (500)</td>
</tr>
<tr>
<td>Aluminium</td>
<td>Anodised</td>
<td>2x10$^{-6}$ 1x10$^{-7}$ 3x10$^{-9}$ -</td>
</tr>
<tr>
<td>Aluminium</td>
<td>Clean but with some oxide</td>
<td>1x10$^{-8}$ 1x10$^{-9}$ 3x10$^{-10}$ -</td>
</tr>
<tr>
<td>Stainless steel</td>
<td>Standard Varian cleaning</td>
<td>3x10$^{-9}$ 1.5x10$^{-10}$ 4x10$^{-11}$ 4x10$^{-12}$ (150 or 300)</td>
</tr>
<tr>
<td>Viton</td>
<td>None</td>
<td>4x10$^{-7}$ - - 5x10$^{-10}$ (200)</td>
</tr>
</tbody>
</table>
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2.24 OD NON-ROTATABLE CONFLAT FLANGE

N.B. NOT FOCUSED ON CENTRE (Z) BUT ON POINTS X AND Y RELEVANT ANGLES AND DISTANCES GIVEN ABOVE

MULTIPLE PASS EMISSION CELL

SCALE full
DIMENSIONS mm UNLESS STATED
MATERIAL stainless steel

A.D.HEN CHEMISTRY SGS
AUSTRALIAN NATIONAL UNIVERSITY
BASE PLATE

ROTATABLE CONFLAT FLANGE: DIMENSIONS IDENTICAL FOR BOTH CONFLAT FLANGE MOUNTINGS.

CAJON VCR & GLAND WELDED ON WITH FEMALE NUT IN PLACE. DIMENSIONS IDENTICAL FOR BOTH CAJON VCR COUPLINGS.

24 HOLE #84 ON 284-B PCD.

MULTIPLE PASS EMISSION CELL

SCALE: full
DIMENSIONS: mm UNLESS STATED
MATERIAL: Stainless Steel

J. ORMER CHEMISTRY SGS
AUSTRALIAN NATIONAL UNIVERSITY
Appendix A2(v)

Automatic liquid nitrogen trap filler

Function

The device fills a liquid nitrogen (LN$_2$) trap from a LN$_2$ Dewar at pre-set intervals $\Delta T$ (e.g. 3h) by using the pressure of boil-off gas, generated in the Dewar when a heater is activated, to pump the liquid nitrogen into the trap.

Operation

The device consists of a control unit, LN$_2$ level sensors, a heater and LN$_2$ transfer facilities (figure A2(v)(a)). On each fill, liquid nitrogen transfer continues for a pre-set time $\Delta t$. If during time $\Delta t$ a diode $D_1$ near the top of the LN$_2$ trap filler tube senses that the trap is full, pumping is interrupted until the level of liquid nitrogen drops below the level of $D_1$. Filling is only attempted if a diode $D_2$ in the LN$_2$ Dewar senses that there is sufficient liquid nitrogen in the Dewar.
The timing circuit provides for interval $\Delta T$ to be any one of 12 equally spaced values between $\Delta T_1$ and $\Delta T_2$. $\Delta T$ is set by the position of a 12 position switch. The stage of the timing cycle is indicated by activation of the appropriate LED on the front panel of the control unit. $\Delta T_1$, $\Delta T_2$ and $\Delta t$ can be varied by making simple changes to the timing circuit. This degree of flexibility is provided to enable the filler to be matched with the particular LN$_2$ trap so as to conserve liquid nitrogen.

Additional fills can be made during the automatic operation by depressing switch $S_1$. The cycle can be reset by depressing switch $S_2$. The operation of the system can be tested by depressing switch $S_3$ which sets the time for a full cycle to ~30 s. External test points are provided to test the battery powering the CMOS IC's. These dissipate very little power (~10 nW). Further refinements of the electronic system were requested by the author but were not effected by the Electronics workshop.

The transfer tube connections are shown schematically in figure A2(v)(a) above. Stainless steel was used for robustness. The trap filler at the LN$_2$ trap had to be capped to prevent ice forming inside it. Parts were detachable for convenience. A special cryogenic epoxy resin was used to cap the tubing associated with the Dewar. The electrical connections at the bottom of the tubing in the Dewar were not sealed up to allow easy access for heater and diode replacement.

Circuit description (from D. Llewelyn)

```
<table>
<thead>
<tr>
<th>ELECTRONIC CONTROL UNIT</th>
<th>LN$_2$ TRANSFER CONTROL</th>
<th>Diode D$_2$ sensor</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LN$_2$ DEWAR</td>
<td></td>
</tr>
<tr>
<td></td>
<td>LN$_2$ COLD TRAP</td>
<td></td>
</tr>
<tr>
<td></td>
<td>with diode D$_1$ sensor</td>
<td></td>
</tr>
</tbody>
</table>
```

The electronic control unit contains 4 low power CMOS Time Base Generators which are used to suitably divide down the 50 Hz mains frequency. Outputs are selectable, the suitable one being applied to the shift registers and data being shifted from one output to the next for each clock-pulse applied. When the pre-selected time is reached, the output data from the particular shift register involved triggers a "one shot" device, the output of which remains high for an adjustable period of time. When this output goes high it activates a relay which turns on the heater in the LN$_2$ Dewar and keeps it on for the duration of the pre-set time $\Delta t$ (unless diode D$_1$ senses that the LN$_2$ trap is full in which case the timing control is over-ridden and the heater is turned off as indicated in the second paragraph above).

Author's note

The frequency divider part of the timing circuit of the control unit was based on that of a different device in the Chemistry department. Publication here of further details of electronic aspects of the LN$_2$ trap filler (e.g. circuit) was suppressed by order of the Head of the Chemistry Department, Professor Warrener, at the instigation of staff in the Electronics workshop.
APPENDIX A4

Obtaining appropriate correction factors for fluorescence spectral data

\[ \text{Corr}(\nu) \text{ is given by} \]
\[ \frac{dL_{q}}{d\nu} = \text{Corr}(\nu) \frac{dP_{q}}{d\nu} \]  
(A4.1)

and changing the variable to \( \lambda \) (and ignoring the change in sign as previously) gives

\[ \left( \frac{\lambda^3}{hc} \right) \frac{dL_{w}}{d\lambda} = \text{Corr}(\nu) \lambda^2 \frac{dP_{q}}{d\lambda} \]  
(A4.2)

Corr(\( \nu \)) may be then determined from the equation

\[ \text{Corr}(\nu) = \left[ \left( \frac{\lambda^3}{hc} \right) \frac{dL_{w}}{d\lambda} \right] / \left[ \lambda^2 \left( \frac{dP_{q}}{d\lambda} \right) \right] \]  
(A4.3)

This correction factor must be applied to spectral data in the form

\[ \frac{dQ_{qobs}}{d\nu}, \text{ viz.}: \]

\[ \frac{dQ_{q}}{d\nu} = \text{Corr}(\nu) \frac{dQ_{qobs}}{d\nu} \]  
(A4.4)

Since \( \frac{dQ_{qobs}}{d\nu} \) is equivalent to \( \lambda^2 \left( \frac{dQ_{qobs}}{d\lambda} \right) \), equation A4.4 can be rearranged to give

\[ \frac{dQ_{q}}{d\nu} = \left( \frac{\lambda^3}{hc} \right) \left[ \frac{(dL_{w}/d\lambda)/(dP_{q}/d\lambda)}{(dQ_{qobs}/d\lambda)} \right] \frac{dQ_{qobs}}{d\lambda} \]  
(A4.5)

If in equation (A4.2), \( \lambda^2 \) was incorporated in the correction factor to give \( \text{Corr}(\nu) \):

\[ \text{Corr}(\nu) = \left( \frac{\lambda^3}{hc} \right) \frac{(dL_{w}/d\lambda)/(dP_{q}/d\lambda)} \]  
(A4.6)

then this correction factor must be applied to spectral data in the form \( \frac{dQ_{qobs}}{d\lambda} \) viz.:

\[ \frac{dQ_{q}}{d\nu} = \text{Corr}(\nu) \frac{dQ_{qobs}}{d\lambda} \]  
(A4.7)

If the expression for \( \text{Corr}(\nu) \) is substituted into equation (A4.7), equation (A4.5) results as required.
APPENDIX A6(1)

Fluorescence spectrum in figure 6.3 plotted with and without smoothing.

(a) plotted without smoothing, NSM=1
(b) plotted using a three point moving average scheme, NSM=3.
(a) 0.185 torr, collection bandpass 9-5 cm\(^{-1}\), step size 1.6-1.0 cm\(^{-1}\), NSM=3, constant time (6 s) collection intervals, fluorescence collected through UG11 filter.
(b) 0.185 torr, collection bandpass 5.0-4.4 cm\(^{-1}\), step size 0.7-0.6 cm\(^{-1}\),
NSM=3, constant time (20 s) collection intervals
(c) 0.177 torr, collection bandpass 8-4 cm\(^{-1}\), step size 1.6-1.0 cm\(^{-1}\),
NSM=3, constant time (10 s) collection intervals.
Assignments of some band maxima observed in the pyrimidine-d$_4$ 0$^8$ fluorescence spectrum in figure (a) of Appendix A6(ii)

<table>
<thead>
<tr>
<th>Band maximum (cm$^{-1}$ vac.)</th>
<th>Displacement from 0$^8$</th>
<th>Assignment</th>
<th>Calculated displacement</th>
</tr>
</thead>
<tbody>
<tr>
<td>31187</td>
<td>-</td>
<td>0$^8$</td>
<td>excitation (3rd)</td>
</tr>
<tr>
<td>30529</td>
<td>658</td>
<td>6a$^1$</td>
<td>659</td>
</tr>
<tr>
<td>30213</td>
<td>974</td>
<td>9a$^2$</td>
<td>975</td>
</tr>
<tr>
<td>30138</td>
<td>1049</td>
<td>12$^3$</td>
<td>1048</td>
</tr>
<tr>
<td>30082</td>
<td>1005</td>
<td>10b$^2$</td>
<td>1104</td>
</tr>
<tr>
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<td>1205</td>
<td>6b$^3$</td>
<td>1206</td>
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<td>1317</td>
<td>6a$^2$</td>
<td>1318</td>
</tr>
<tr>
<td>29804</td>
<td>1383</td>
<td>Y</td>
<td>-</td>
</tr>
<tr>
<td>29651</td>
<td>1536</td>
<td>8a$^3$</td>
<td>1538</td>
</tr>
<tr>
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<td>1592</td>
<td>Z</td>
<td>-</td>
</tr>
<tr>
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<td>1633</td>
<td>6a$^1$9a$^1$</td>
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<td>29481</td>
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<td>1707</td>
</tr>
<tr>
<td>29425</td>
<td>1762</td>
<td>6a$^1$10b$^2$</td>
<td>1763</td>
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<tr>
<td>29209</td>
<td>1978</td>
<td>6a$^2$</td>
<td>1977</td>
</tr>
<tr>
<td>29185</td>
<td>2002</td>
<td>?</td>
<td>-</td>
</tr>
<tr>
<td>29165</td>
<td>2022</td>
<td>9a$^1$12$^1$</td>
<td>2023</td>
</tr>
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</table>

Assignments of some band maxima observed in the pyrimidine-d$_4$ 0$^8$ higher resolution spectrum in figure (b) of Appendix A6(ii)

<table>
<thead>
<tr>
<th>Band maximum (cm$^{-1}$ vac.)</th>
<th>Displacement from 0$^8$</th>
<th>Assignment</th>
<th>Calculated displacement</th>
</tr>
</thead>
<tbody>
<tr>
<td>31187</td>
<td>-</td>
<td>0$^8$</td>
<td>excitation (3rd)</td>
</tr>
<tr>
<td>30528</td>
<td>658</td>
<td>6a$^1$</td>
<td>659</td>
</tr>
<tr>
<td>30212</td>
<td>974</td>
<td>9a$^2$</td>
<td>975</td>
</tr>
<tr>
<td>30139</td>
<td>1048</td>
<td>12$^3$</td>
<td>1048</td>
</tr>
<tr>
<td>30081</td>
<td>1105</td>
<td>10b$^2$</td>
<td>1104</td>
</tr>
<tr>
<td>29982</td>
<td>1205</td>
<td>6b$^3$</td>
<td>1206</td>
</tr>
<tr>
<td>29869</td>
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Assignments of maxima observed in fluorescence from level 6a¹ [Innes et al., 1969] of pyrimidine-d₄.
(spectrum in figure 6.12)

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(a) Absorption spectrum of pyrimidine-d₄ vapour obtained using a Cary 219 spectrophotometer. Pressure about 18 torr (p.360), path length 10 cm, spectrophotometer bandpass 0.05 nm.
(b) Absorption spectrum of pyrimidine-h₄ vapour obtained using a Cary 219 spectrophotometer. Pressure about 18 torr (p.360), path length 10 cm, spectrometer bandpass 0.05 nm.
Assignments of band maxima in the accompanying fluorescence spectrum from level $16b^2$ [Innes et al., 1969] of pyrimidine-d$_4$. Collection bandpass 20 cm$^{-1}$, step size 3.2 cm$^{-1}$, pressure 0.062 torr, NSM = 5, constant excitation intensity collection intervals.

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<th>Calculated Displacement</th>
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41 3

Assignments of band maxima observed in fluorescence from level 12 1 o
{spectrum in figure 6. 19)

Band maximum
(cm- 1 vac.)

Displacement
from 12 J

Assignment

Calculated
displacemen

126

32190
31530

660

31395-

795-

31352

838

31214

976

31140

1050

31082

1108

30984

Band maximum
(cm- 1 vac.)

Displacement
from 12 6

pyr imid i ne-d.

Assignment

Calculated
displacement
3803

28393

3797

6a~12l

28353

3837

6ae6bn26

3842

29299

3891

6a~ 8a Y, 21

3904

28239

3951

6an26

3954

28193

3997

6a ~ 9a Y, 21

4000

1048

28129

4061

6a~12p

4073

1104

28061

4129

28006

4184

6a~1ob~121
12U 6a 28a Y, 2 A

4129

1206
1318

27963

4226

6a ~ 6bq, 2 l /

4231/4220

6a 1126
?

659

9a 112 6

975

12:
1Obj 126

1206

6bj 12 6

30871

1319

30807

1383

6aj12!
y'

30765

1425

X'

30650

1540

8a 112 6

4192/4174

6a ~ 8a 19a 1121
27912

4278

6a ~ 9a112A

4270

1538

27850

4341

6a ~ 12 I

4343

30601

1589

z'

27739

4451

6a~12\

4462

30556

1634

6a 19a 1126

1634

27638

4552

1708

6a 112 l

1707

27578

4612

6a~8a 112!
6a~126

4563

30482
30428

1763

6a1 lObj 126

1763

27525

4665

8a 112 l
6ae 12p

4682
4732

6an2u

4851/4833

30326

1864

6aY6b~12 A

1865

27467

4723

30211

1979

6a ~ 126

1977

27349

4841

30113

2077

12!?

2096
21 ')7

4613

6a~Ba!l2A

29998

2192

4883

6a ~ 8a Y9a Y121

4879

2249

6a1Ba1126
6 bj 121 / 6a yZI

27307

29941

2254/659+ 1590

27260

4931

6ai9aY12!

4929

29897

2294

6aj 9a Y12

2293

27195

4995

6ai 12 I

5002

29825

2365

6aj 121

2366

27080

5110

6a ~ 12 l

5121

29767

2423

6a ~ 1Ob~ 12! /

2422/1375

26961

5230

12V 6a eBa Y121

5240/5222

Yl 2l

1048

26927

5263

6a 8 12 A

26872

5318

5272
5341

29719

2471

X12l

1423+1048

6a16b~l26

2524

26783

5408

6a 1BaY12 l
6a ~ 12)?

26751

5439

6a ~ 1Ob~ 12 I

5391
544 7

26693

5497

6a112U

5510/5492

29666

2524

29609

2582

Ba~ 121

2536

29553

2637

6ae 126/Zl 21

2636/ 1589+

6ai8a1]2 1

1048
29509
29451

2681

6a 19a Y12 l

2682

26654

5536

6a~8a19aY 12!

5538

6a Y12! ?
6a j 8a Y126

2755

26600

5591

29343

2739
2847

2856

26536

5654

6a~9a1126
6a~ 121

5588
5661

29280

2913

26481

5709

Ba1121

5730

26306

5885

6a112u

5899/5881

2910

6a16bj 12 l

29235

2955

6a ~ 9a Y 12!

2952

29168

3022

6a ~ 12!

3025

5a~ 10b1126

3081

26272

5918

25217

5973

6a~Ba? 12!

29113

3077

29048

3142

12l

3144

28952

3238

6a 18aY 121

3245

28895

3295

6a ~ 126

3295

25034

5455

5a ~ 121

5169

28852

3338

Ga~ 9a1121

3341

25998

6192

5aeBaY9a1121

5197

28785
28725

3405

5a~12~?

3414

25920

5270

12l

5288

3465

5a~ 1Ob~ 12!

3470

25888

6302

Gag 121

5320

3509

5a~ 8aY 126

3515

25830
25649

5360
6542

6a18aY 121

6389
6558

28681
28621

3570

6a~6b 121/

3572/3561

6572
631

3684
3740

25377

3616

6ae 9a? 126

3611

28508

3682

6ae 12:

~4

3716

6a~ 1Ob? 126

I

25618

28574

5931

5a ~Ba112\/

5000/ 5977

5ai9a112!

25559
25442

8a19a?12I

5a ~ 12 A

6a~ 12 s
6,1100126

6590

6748

6a~SaY12\
Bay12

6659
6778

6813

6ae 121

6828


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<th>Assignment</th>
<th>Calculated displacement</th>
<th>Band maximum (cm⁻¹ vac.)</th>
<th>Displacement from 12(i)</th>
<th>Assignment</th>
<th>Calculated displacement</th>
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<td>6a(8a'[9a][12])</td>
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<tr>
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<td>6924</td>
<td>6a[12|</td>
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<td>7336</td>
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Appendix A6(vii). Fluorescence spectrum from $^{12}_1$ (see text) level of pyrimidine-$d_4$. Pressure 0.06 torr, collection bandpass 22-11 cm$^{-1}$, step size 3.5-2 cm$^{-1}$, NSM=5, constant excitation intensity collection intervals. Some band assignments are given in the accompanying table.
Assignments of some of the maxima observed in fluorescence from level $12^1$ of pyrimidine-$d_4$ for the spectrum in Appendix A6(vii)

<table>
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<tr>
<th>Band maximum (cm$^{-1}$ vac.)</th>
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<th>Assignment</th>
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<tr>
<td>25918</td>
<td>6274</td>
<td>$12^1$</td>
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</tr>
</tbody>
</table>
(i) Obtained using photon counting fluorescence detection (cf. figure 7.1). Shows: (a) curvature in the plot at higher pressures, (b) effect of applying correction factor for ε=161 (see text), (c) effect of applying correction factor for ε=262, (d) fit to the uncorrected data over the low pressure range.
(ii) Obtained using charge integration fluorescence detection (cf. figure 7.2). 439 DCI on 10^{-7} C/pulse setting.

(iii) Obtained using charge integration fluorescence detection (cf. figure 7.2). 439 DCI on 10^{-9} C/pulse setting.

Show: (a) curvature in the plot at higher pressures, (d) fit to the uncorrected data over the low pressure range.
Preliminary paper on part of the work on the vapour phase fluorescence lifetimes of deuterated phenanthrenes

PLATE 7(p.420) shows the thermostated compartment in which the all quartz Wood's horn containing the vapour phase fluorescence sample is housed. The compartment, vacuum system and Wood's horn shown were constructed to perform fluorescence lifetime studies of deuterated phenanthrenes subsequent to those described in the accompanying paper. The Wood's horn is kept attached via a demountable VRC coupling and a Nupro SS-8BK stainless steel isolation valve (table 2.10) to the vacuum system during lifetime measurements so that collision free conditions can be established and maintained for each lifetime measurement and to ensure that once a satisfactory position for the Wood's horn is attained it can be held. The amount of scattered excitation light in the fluorescence decay curves was found to be markedly dependent on the exact orientation of the Wood's horn so once an orientation giving minimum scattered light was achieved it could be maintained.
POSITION DEPENDENT DEUTERIUM EFFECTS
ON THE VAPOUR PHASE FLUORESCENCE LIFETIMES OF DIDEUTERO PHENANTHRENES

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Received 6 September 1976

The fluorescence lifetimes of phenanthrene and three of its deuterated isomers are measured in the vapor phase under isolated molecule conditions with a bandpass of 25 cm⁻¹. The lifetimes fall in the order phenanthrene > 2,4-d₂ > 1,3-d₂ > 9,10-d₂. It is suggested that the change in lifetimes is due to a resonance mechanism of intersystem crossing.

Position dependent deuterium effects have proven to be most useful in attempts to understand the mechanism of intersystem crossing from the lowest triplet state to the ground state in aromatic hydrocarbons. In naphthalene [1,2], anthracene [3] and phenanthrene [4], a comparison of the triplet deactivation rates in molecules having the same number of deuterium substituents but differing only in the position of deuterium substitution has allowed attention to be focussed on the effect of the inducing vibrational mode, since any inhibition of radiationless deactivation due to an effect on the Franck-Condon factor should be the same in such molecules. In the molecules studied to date, triplet deactivation has been most effectively inhibited for deuterium substitution at positions of highest π electron density in the highest energy bonding and lowest energy antibonding orbitals. This generalization and the lifetimes themselves have been quantitatively accounted for on the basis of two theoretical approaches. In the first [3,5], intersystem crossing is attributed to nonadiabatic coupling via the nuclear kinetic energy operator along with spin-orbit interaction, and, in the second [6], it is attributed to Herzberg-Teller type coupling, again with spin-orbit interaction. Both approaches involve zero spin-orbit coupling along with induction via out-of-plane hydrogen bending modes. In the first the dominant contributions come from one-center terms while the second approach involves two-center interactions. At the present time neither the available experimental data nor the calculations themselves [7] unambiguously establish which approach leads to the dominant contributions to radiationless deactivation.

It is of interest to attempt to observe such a position dependent deuterium effect on intersystem crossing from S₁ into the triplet manifold. Firstly such data should be important in establishing the precise nature of the coupling in this process itself. Secondly an understanding of the intersystem crossing from S₁ might allow a distinction to be made between the two suggested mechanisms for triplet deactivation. Lastly, if the mechanism was understood, the nature and direction of the position dependent deuterium effect should permit an assignment of the terminal triplet state in the transition.

Partial deuterium effects on intersystem crossing from S₁ have been studied previously by Rice and co-workers for styrene [8], aniline [9], and benzene [10]. However only in the latter case were fluorescence lifetimes determined for molecules with the same number of deuterium substituents but differing positions. Because of the absence of symmetry inequivalent positions in benzene, the results do not permit a critical assessment of different mechanisms for intersystem crossing.
crossing in the same sense as data for the less symmetric aromatic hydrocarbons. Benzene however does offer the advantage of single vibronic level excitation and so some of the ambiguities of interpretation associated with the larger molecules are avoided (vide infra). For benzene [10] and also generally for aniline [9], both the observed fluorescence lifetimes and the lifetimes for non-radiative decay increased with the degree of deuterium substitution. A slight trend in the opposite direction was noted for styrene [8].

Phenanthrene was purified as described by Fischer [11]. The deuterated phenanthrenes were synthesized by Charlton et al. [4,12] and were the same as those used in previous studies of triplet lifetimes [4].

The fluorescence lifetime of phenanthrene under collision free conditions in the vapor (0.03 torr) has been measured previously by Knight and Selinger [13] and the procedures and apparatus used in the present study were similar to theirs. The sample was contained in a Rayleigh horn at a temperature of 324 ± 1 K at which the equilibrium vapor pressure is 0.024 torr. In this study however the use of a more intense air-filled flash lamp permitted the excitation bandpass to be reduced from 20 Å to 2.8 Å at the excitation wavelength of 3371 Å. This wavelength was selected by a 1 m Czerny–Turner spectrometer (Spex 1704) used in the third order of a 102 x 102 mm, 1200 g/mm grating blazed at 10000 Å. Measurements were also carried out at a bandpass of 8.3 Å. A cyanine perchlorate filter solution (0.2 g/dm²) was again used to reduce scattered excitation light. Hexafluoroacetone (100 torr, 293 K) was used as a lifetime standard in calibrating the single photon counting system [14]. The count rate ranged from 30 to 90 s⁻¹ at the 2.8 Å bandpass with 350000 to 600000 counts collected over 127 channels in obtaining a single decay curve.

Because in some cases the differences in lifetimes for the series of compounds were small, great care was taken to ensure that all measurements were made under comparable conditions. In particular the lamp pulse was monitored throughout and the full width at half maximum held between 4 and 7 ns.

The vapor phase spectrum of phenanthrene has been studied by Craig and Gordon [15]. They found that even the S¹ → S₀ transition was mainly unresolved with an envelope that closely resembled the envelope of the solution spectrum. Excitation at 3371 Å would fall close to the S¹ origin but even with the relatively narrow bandpass of ≈25 cm⁻¹, several sequence bands would be excited.

Single exponentials were fitted directly to the decay curves by means of an iterative non-linear least square fitting technique as described by Nott [16]. As a measure of the exponential character of the curve the parameter $\chi^2$ was used where

$$\chi^2 = \sum \frac{(I(t) - I^0(t))^2}{(N-3)I^0(t)}.$$  

and where $I(t)$ is the number of counts accumulated in channel $t$, $I^0(t)$ corresponds to the fitted function, and $N$ is the total number of channels. For the number of channels chosen, the value of $\chi^2$ which corresponds to a reasonably good exponential fit should be in the range 0.73 to 1.27. The decay of hexafluoroacetone has been established to be a single exponential [14]. The $\chi^2$'s obtained for hexafluoroacetone during instrument calibration were in the range 0.74 to 1.09. However, probably because of the multilevel nature of the decay, the decay curves for the phenanthrene compounds generally exhibited some degree of non-exponenti-

![Fig. 1. Fluorescence decay curve of 1,3-d₂ phenanthrene in the vapor at 324 K. Excitation 337.1 nm, bandpass 25 cm⁻¹, 2.76 ns per channel, $\chi^2 (35 - 125) = 1.17$.](image-url)


tiality as evidenced in a slight curvature throughout the logarithmic plots (see fig. 1), and as reflected in the values of \( \chi^2 \). As a consequence, the lifetime obtained from any such curve could vary by up to 5% depending upon the region of fit. The lifetimes given in table 1 represent the average of two or three lifetimes obtained under uniform experimental conditions and result from fits over the same region of the decay curves (approximately four lifetimes). The errors given represent a range and could be interpreted as outside limits for the lifetimes. \( \chi^2 \) varied from 0.9 to 1.7 for the inverse deuteration compounds. However a more pronounced degree of non-exponentiality was evident in the decay curves of phenanthrene itself, and this was reflected in the values of \( \chi^2 \approx 10 \). A similar effect was observed in studies of the triplet state where the correlation coefficient for the \( T_1 \) lifetime, which is also a measure of the exponential character of the decay, was substantially lower for phenanthrene than for the deuterated compounds (0.9999 as compared with 0.9998 [14]).

The average lifetime obtained for phenanthrene is somewhat longer than the value of 58 ns obtained by Knight and Selinger at the same wavelength. This result is probably due to the narrower bandpass employed here. A similar effect has been observed for aniline where, like phenanthrene, sequence congestion also prevents the excitation of single vibronic levels. The fluorescence lifetime of aniline vapor has been studied by von Weyssenhoff and Kraus [17], Ware and Garcia [18], and by Scheps et al. [9] at excitation bandwidths of 2.7 A, 2 A, and 0.45 A respectively. Although the relative values of the lifetimes are the same, they are invariably longer the narrower the bandpass of the excitation light (e.g. for excitation in the 0.0 band the measured lifetimes were 7.07 ns [17], 7.32 ns [18], and 8.51 ns [9] respectively).

There are two possible interpretations for the trend in the lifetimes of table 1. The first is that deuteration induces small changes in the absorption spectrum with a consequent alteration in the balance of the sequence bands excited in the \( S_1 \) states of the different isomers. The second possibility is that we are observing an inverse deuterium effect on intersystem crossing due to a resonance mechanism of the type proposed by Lawetz et al. [19], and that this resonance mechanism is also responsible for the changes among the deuterated lifetimes. An inverse deuterium effect has been observed by Boesl et al. [20] in the vapor phase fluorescence lifetimes of some of the single vibronic levels of naphthalene-\( \text{H}_8 \) and \( \text{d}_8 \) excited with a resolution of 0.5 cm\(^{-1}\). Quantum yield data for the four lowest levels [21] indicate that the decrease in lifetime upon deuteration for two of the levels is due to an increase in the rate of intersystem crossing from \( S_1 \) into the triplet manifold.

The requirement for a resonance crossing mechanism is that there exists a triplet state close in energy to the initial state in \( S_1 \). The only likely triplet state at or near the energy of the initial state in our experiments (29665 cm\(^{-1}\)) would be a \( \pi\pi^* \) state since states of mixed \( \pi\sigma \) character would be expected to lie much higher in energy. In the point group \( C_{2v} \), the only possible symmetries for \( \pi\pi^* \) states are \( A_1 \) and \( B_2 \). Since the lowest singlet state of phenanthrene has orbital symmetry \( B_2 \), first order spin-orbit coupling (mechanism 4 of ref. [19]) would require the resonant triplet state to have orbital symmetry, \( B_1 \), \( A_2 \), or \( A_1 \). Thus for a first order resonance mechanism, the resonant triplet state would be of \( A_1 \) symmetry. Triplet state energy calculations of Orloff predict a low lying, triplet state of \( A_1 \) symmetry to lie slightly below \( S_1 \) at 27120 cm\(^{-1}\) [22]. Given the uncertainty of the calculations, this state could well be within the range required for resonance interaction. The next highest triplet state, is most likely the one at 33770 cm\(^{-1}\) which has been observed in triplet–triplet absorption spectroscopy and also assigned \( A_1 \) character [23]. The energy of this state would effectively eliminate it from a resonance type of mechanism.

If a resonance mechanism is responsible for intersystem crossing, then given the presence of a \( \pi\pi^* \) state of the correct symmetry at about the right energy, it is probable that a first order mechanism (i.e., mechanism 4 of ref. [19]) is dominant. The matrix element governing this mechanism is, in the notation of ref. [19],
\[ H^{(4)}_{mn} = \frac{i L_{in}^0 S_{in}}{2 \pi \hbar \rho_m S_{mi} \rho \sum_k (\hbar \omega_k^{(l)} / 2 \mu_k)^{1/2} P_{mi}^0(k)} \]

where \( L_{in}^0 \) is a spin–orbit coupling integral between the singlet state \( \Phi_1 \) and the intermediate triplet state \( \Phi_i \). The \( S \)'s are overlap integrals and \( P_{mi}^0(k) \) is a matrix element over the operator \( \partial/\partial Q_k \) which is responsible for the radiationless deactivation of \( \Phi_i \) into the lowest triplet state \( \Phi_1 \). If the assumption is made that the initial state in \( \Phi_1 \) is the same for all the deuterated phenanthrenes, then one would expect lifetime differences to occur through an effect on the inducing mode \( k \). Because the mode \( k \) couples two \( \pi \pi^* \) states, alterations in the rate of radiationless decay with changes in the position of deuterium substitution will be more difficult to account for than for the \( T_1 \rightarrow S_0 \) transitions where one is dealing with primarily local one-center effects. In this context it is intriguing that the lifetime ordering observed here is exactly the reverse of the triplet state lifetime ordering [4]. Moreover the same lifetime ordering for phenanthrene and the 2,4-dideutero and 9,10-dideutero isomers, despite alterations in the lifetimes themselves, occurs when a wider bandpass of about 75 cm\(^{-1}\) is employed. This latter result is certainly consistent with a resonance mechanism of intersystem crossing.

We are happy to acknowledge our indebtedness to Dr. James L. Charlton who generously made the valuable deuterated compounds available to us. We also gratefully acknowledge helpful discussions with Professor Ian G. Ross. One of us (BRH) would like to express his gratitude to the Royal Society and Nuffield Foundation for a Commonwealth sabbatical bursary and to the Chemistry Department at the Australian National University for their kind hospitality.

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