THE DECAY OF MOLECULAR LUMINESCENCE

by

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for the degree of Doctor of Philosophy

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"All phenomena in physics and chemistry are of course time-dependent ...."

Per-Olov Löwdin (1967)
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Alan E. W. Knight
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CHAPTER I

INTRODUCTION

This thesis is concerned with the time-dependence of molecular luminescence, with particular reference to the study of fluorescence emission from aromatic molecules. Molecular spectroscopy, in its more familiar time-independent form, has reached a stage of development which enables the detection of exceedingly small changes in the internal energy of molecules as they absorb or emit electromagnetic radiation. Only in recent years have significant advances been made towards studying the time dependence of emission processes with optical resolution approaching that which is accepted as commonplace in classical spectroscopy.

The development of new experimental techniques has played a major part in this advance. Chapter II of this thesis describes the application of single photon counting to fluorescence decay spectroscopy. In Chapter III, detailed attention has been paid to the aspects of data analysis which are essential if lifetimes are to be determined accurately to within correctly specified
confidence limits. The experimental studies in the remaining chapters have fallen naturally into an order which reflects the direction taken in this research.

The relatively low optical resolution needed for solution phase studies makes no great demand on instrumental sensitivity. Chapter IV involves a study of excited state molecular complexes in solution.

The study of lifetimes of molecules in the vapour phase affords a means by which the properties of individual vibronic states of an excited molecule can be studied. Low pressures are necessary to establish conditions under which the excited molecule can be treated as being essentially isolated during its mean lifetime. High instrumental sensitivity is needed to detect the emission; the excitation must be sufficiently well resolved to enable selection of individual vibronic bands of the absorption spectrum. These objectives have been pursued in Chapter V with considerable success.

Various workers have studied the dependence of lifetime of the isolated benzene molecule on the initially selected vibronic state. With naphthalene, optical selection of individual states is considerably more difficult to achieve because of the added complexity of its absorption spectrum. A study of the lifetimes of single vibronic levels of naphthalene and perdeutero naphthalene forms the major part of Chapter V. The
fluorescence decay of aromatic vapours at low pressure is largely an unexplored area of research. Lifetimes of phenanthrene and azulene vapour under collision-free conditions, determined with moderate optical resolution of the exciting light, are reported for the first time.

The concluding chapter deals with an aspect of molecular decay spectroscopy which has so far been virtually ignored. Low intensity nanosecond light sources and limited instrumental sensitivity have previously prevented the optical resolution of both excitation and emission with anything more than broad-band filters. It is shown that the ultimate aim of being able to use highly resolved excitation, together with spectral resolution of the emission, is a feasible proposition even at the present stage of development of decay spectroscopy.
CHAPTER II

DECAY SPECTROSCOPY

The principles involved in measuring the time dependence of fast photophysical processes have been known for some time. Ever since Norrish & Porter (1949) extended the accessible experimental time domain from the millisecond to the microsecond range, the advance in technology has accelerated rapidly and now it is even possible to directly monitor events on a picosecond time scale.

In this chapter, the measurement of the time dependence of molecular fluorescence will be discussed. Although fluorescence decay measurements have been possible, at least in principle, since Gaviola (1926) first introduced the technique of phase and modulation fluorimetry, it was not until Brody (1957) utilized pulsed excitation methods that reasonably accurate determinations of fluorescence lifetimes became possible.

For species with reasonable quantum yields of fluorescence, the relationship between spontaneous emission probabilities and transition moment (Einstein 1917) means
that the lifetimes of these states are generally longer than one nanosecond. Thus the time dependence of emission spectra in the range $10^{-9}$ to $10^{-7}$ seconds is of prime import.

The problems of optical geometry, dispersion, sample preparation and radiation collection are in common with other areas of spectroscopy from which suitable techniques can be adapted. For example, when working with gases at low pressure and with low optical density, scattered light is a primary concern and one uses a Rayleigh horn, as in Raman spectroscopy. However, the short times and low light levels encountered in decay spectroscopy require a different concept in detection methods.

1. THE PHASE METHOD

The phase shift method for determining fluorescence lifetimes has recently been reviewed by Birks and Munro (1967). A great deal of literature is available on the subject and it is therefore unnecessary to enter into a full description in this thesis. However, it is relevant for purposes of comparison to state some of the limitations of this method.

The technique involves exciting the sample with intensity modulated light, the result being that the fluorescence will be phase-shifted relative to the exciting light because of the finite lifetime of the excited state. The amplitude change in the modulation relative to the exciting light is also a function of the
excited state lifetime. Thus phase fluorimetry requires a modulated light source and a phase sensitive detector with instrumentation involving mainly radiofrequency circuits and techniques.

It is an inherent feature of phase and modulation fluorimetry that sources of serious systematic error are always present. The two major problems are scattered light and the variation of phase with wavelength. Scattered light, which reduces the apparent fluorescence lifetime, may be treated quantitatively (Lumry, Müller & Kokubun 1965), provided that the optical density of the system is so low that the scattered light is unaffected by the presence of the absorbing medium. However, it is apparent from errors in recent work (Schlag, Schneider & Chandler 1971) that scattered light is an exceedingly difficult problem with which to contend.

The variation in phase with wavelength produces an error due to the wavelength difference between the exciting light and the resulting fluorescence. The usual practice is to obtain an estimate of the erroneous phase shift by comparing intentionally scattered light with the fluorescence. However, photomultiplier transit times are also dependent on the energy of the incident radiation and must also introduce systematic error (of the order of a few nanoseconds if the difference in wavelength between excitation and fluorescence is large). Theoretically, only the modulation frequency determines the lower limit of lifetime that can be measured.
In order to interpret the data, a prior assumption must be made concerning the nature of the decay laws which relate phase shift and degree of modulation to the rate constants. Three types of decay laws have been found to yield relationships which are simple to analyse:

\[ I \propto e^{-at} \]
\[ I \propto Ae^{-at} + Be^{-\beta t} \]
\[ I \propto Ae^{-at} - Be^{-\beta t} \]

where \( I \) is the fluorescence intensity, \( a, \beta \) are the rate constants and \( A, B \) are constant coefficients.

Attempts have been made to generalise the method to more complex systems, for example by Schlag, Yao & von Weyssenhoff (1969), in studying multistep relaxation processes. However, it is difficult at present to judge whether the phase shift method is adequately able to indicate rejection of the hypothesised decay process, particularly in more complex cases. In studying the fluorescence decay of naphthalene vapour, Schlag, Schneider & Chandler (1971) interpreted their data by making use of the assumption that the decay followed a single exponential. This assumption has been proved to be incorrect (Sections V.3 to V.6) and was responsible, in part, for gross errors in their results. Direct methods of obtaining fluorescence lifetimes, in the form of intensity versus time, present far less doubt as to the interpretation of the data. Furthermore, the problem of scattered light is usually dealt with easily.
In nanosecond lifetime studies, where the fluorescence decay is monitored directly, the initial problem is to produce a light pulse of suitably short duration and sufficient intensity over the required region of the spectrum. The very first direct observation of fluorescence decay in the nanosecond region used an X-ray source for excitation because of the difficulty in obtaining intense light pulses of short duration (Phillips & Swank 1953). This limitation was overcome by using a spark discharge between two closely spaced electrodes in an atmosphere of hydrogen (Malmberg 1957) which allowed Brody (1957) to measure the fluorescence lifetimes of some chlorophylls.

In recent years, the pulsed laser has become an obvious (but expensive) choice for the production of high intensity pulses with a duration of 3-10ns full width at half maximum (fwhm). With the advent of Q-switched dye lasers, considerable spectral flexibility can also be provided. However, the pulse repetition rate with available instrumentation is generally considerably less than 1000Hz. This can sometimes be a limitation, as will prove obvious in the discussion below relating to photon-counting techniques. A gas discharge across a spark gap, either triggered by a thyratron or running as a relaxation oscillator, is far cheaper to construct and is in many ways a more versatile excitation source. With
suitable choice of gas and pressure, the spectral range from 200-500nm can be covered. The nature of the gas determines whether a continuum or band emission is observed and at high pressures, (\(\sim 30\text{atm}\))\(^\dagger\), a certain degree of pressure broadening extends the tunability of line spectra. In either case a monochromator is used to select the excitation band.

The shapes of fast pulses are difficult to measure because of the limited response time or bandwidth of the measuring equipment. In the case of repetitive pulse signals it is possible to use a so-called sampling procedure. A sample of the pulse intensity is taken at a given time interval after the pulse has started, i.e. the pulse triggers the taking of a sample after a given delay. The time point of sampling is moved along at small intervals with the result that subsequent pulses are sampled at consecutive time spots and a "profile" of the pulse is produced in the form of a number (say 100) of discrete samples. The sampling oscilloscope works on just this principle and is capable of displaying signals some orders of magnitude faster than its "mainframe" bandwidth would allow. A more sophisticated sampling correlation instrument is the boxcar detector. It allows for averaging each sample point for a given time before moving

\[^\dagger\] \(\text{latm} = 1.01 \times 10^5\text{Nm}^{-2}\).
along to the next. It has an adjustable gate width (i.e. time slit width) and the minimum gate width determines the highest frequency component of the input waveform that can be reproduced (i.e. the time resolution).

The method of noise averaging used in the boxcar detector suffers from the basic disadvantage that for a given amount of information, noise reduction must be paid for in the form of a longer scan time. The longer scan time necessitates long term stability. To avoid this requirement, one can use the so-called CAT (Computer of Average Transients) procedure which is common in nuclear magnetic resonance spectrometry. Here noise reduction and time are still traded at the same exchange rate but instead of one long slow period of accumulation over the whole time span of interest, a number of faster repetitive short runs over the whole time span are averaged. Hence, in addition to the noise reduction obtained above, there is also averaging of long term fluctuations (such as lamp intensity). The sampling oscilloscope lends itself easily to the CAT procedure and has been used in conjunction with a Digital PDP8-S computer to obtain a one hundred-to-one increase in signal to noise ratio in a few minutes (Selinger & Speed 1969).

3. SINGLE PHOTON COUNTING

The fastest pulse that the above methods can display is the pulse shape or anode response curve (to a δ-pulse excitation) of the photomultiplier tube. For example, the
Phillips 56DUVP operated at a gain of $10^8$ has an anode pulse of about 4ns fwhm. This then represents a limit on time resolution. Secondly, as the light intensity drops, the output of the photomultiplier is no longer a "macroscopic" pulse (whose intensity is a time dependent current) but a sequence of *single photon pulses*, the mean number of which in a given time interval is proportional to the photon intensity in that interval. It is thus desirable to dispense with the idea of measuring a time dependent photon current (d.c. detection) and count instead the occurrence of single photoelectrons produced by photons incident on the photocathode. An immediate improvement in time resolution can now be obtained. The mean transit time for a fourteen stage photoelectron multiplication is of the order of 40ns but the transit time spread is less than 0.5ns (Schonkeren 1970). So, instead of displaying a photomultiplied pulse of about 4ns fwhm, the time of arrival of single photons is measured, to within 0.5ns by timing when the leading edge of the pulse reaches a certain threshold. This task can be performed by a leading-edge type discriminator which produces a timing output whenever an incoming pulse crosses the input threshold. The pulse amplification of the photomultiplier depends on the energy of the incident photon and differs for photons incident on different parts of the photocathode. There is also a spread in secondary electron amplification factors. This resulting variation in pulse amplitude will lead to a timing "jitter" (Figure II.1a) which can be reduced if only a small part
of the photocathode is used. However, it is preferable to use "constant fraction timing" since maximum aperture can then be retained. In this method one uses a discriminator whose threshold for timing occurs when the pulse has reached a fixed fraction of its maximum. By assuming that the ratio of the heights of two pulses is the same at any point on the pulse, all the variation is removed (Figure II.1b).

Strictly speaking, the emission of photons from a black body source obeys Bose-Einstein statistics. However, in practice, negligible error is introduced if photons with energies corresponding to the ultraviolet and visible portion of the spectrum are described using Boltzmann statistics. In other words, the arrival of \( N \) photons at the photocathode within a particular time interval (whether from a steady source or a pulse-excited fluorescing molecule) follows a Poisson distribution with equal mean and variance \( \bar{N} = \mu \). The standard error in estimating the mean, when expressed as a percentage error, \( 100/\sqrt{\mu} \), decreases as the square root of the number of photons counted in that interval. (For further details regarding the statistics of photon counting, a review article by Morton (1968) is recommended).

In an ideal time correlation experiment, a flash of light excites a fluorescence species and the time at which each photon is emitted by the species is detected by the photomultiplier and recorded. This experiment is repeated to build up the time correlation or decay spectrum. In
Fig. II.1 Comparison between leading edge timing (a) and constant fraction timing (b). With the latter technique, variation in pulse height of the signal does not introduce a timing difference since triggering occurs at a fixed fraction of pulse height.

Fig. II.2 Schematic representation of time-correlated Single-Photon-Counting apparatus.
practice one cannot measure the time of arrival of all the photons emitted by the fluorescence species as a result of one single flash. The time of arrival of only the first photon is recorded and then only if it arrives in a given time interval after the flash. Each time there is a lamp flash, a synchronized pulse (START) initiates the time sweep of a time to amplitude converter (TAC), and if a pulse is received from the photomultiplier during the sweep it acts as a STOP. The TAC then generates an output signal whose voltage is proportional to the time difference between START and STOP.

The less frequent\(^\dagger\) photomultiplier pulses could equally well be used as a START while the lamp flash, via a suitable delay, can activate the STOP. This sequence reduces the number of unconsumated STARTS. There is an inherent delay between the flash and the earliest possible photon detection due to the photomultiplier transit time, light path length, cable delay and discriminator delay. On a short TAC range, only the latter half of the range would be used unless the START pulse is delayed to bring it closer to the STOP. On longer ranges account must be taken of the need for a finite time for the TAC to STOP after STARTing - i.e. the initial non-linear (low output amplitude) region of the TAC must be avoided by delaying the STOP. Thus both the START and STOP pulses must be

\(^\dagger\)\(\approx 1\%\) of light flashes yield a detectable photon in a typical experiment.
suitably delayed by cable or by a delay generator to ensure that the linear section of the full range of the TAC is utilized.

The pulse output of the TAC is fed to a biased amplifier (BA) whose gain is used to sample a section of the TAC range and expand it to cover the full range of a multichannel pulse height analyser (MCPHA or MCA). The bias level control may be used as a zero shift.

In the analyser, the counts in each channel are proportional to the probability of fluorescence emission in the time interval $\Delta t$ at time $n\Delta t$, where $n$ is the channel number and $\Delta t$ the channel width in nanoseconds. The analyser thus stores the distribution of time intervals, up to a given maximum, for the arrival of the first photon from successive flashes. The maximum is set by the range of the TAC-BA combination (2ns to 0.1ms) with an ultimate resolution at the short time end of 10 ps ($10^{-11}$s).

Pulses arriving outside the range during each sweep of the TAC are ignored and the signal to noise ratio is immediately increased by a factor: (TAC range) x (flash repetition rate): i.e. say $(5\times10^{-7})\times10^4 = 5\times10^3$. The time correlated photon counting system is shown schematically in Figure II.2. Details of commercially available equipment used in the apparatus are listed below.

- High voltage power supply: DEL Electronics PSC 10-10-1
- Stabilized power supply: FLUKE 415B
- Delay generator: ORTEC 416A gate and delay generator
Discriminators

ORTEC 417 fast discriminators
ORTEC 453 constant fraction discriminator

Time-to-amplitude converter

ORTEC 437A time-to-pulse height converter

Biased amplifier

ORTEC 408 biased amplifier

Display oscilloscope

Hewlett-Packard 120B

Multichannel analyser

Nuclear Data 1100 with 256 channel memory and ADC

Counters

Hewlett-Packard 5321A, Racal SA535

Teletype

ASR 33 with paper tape punch

Photomultipliers

Phillips 56DUVP/03 (detector)
RCA 1P28 (start pulse).

4. PULSE PILE-UP

The TAC records the time of arrival of the first photon. If another photon arrives after the first during the TAC sweep time, it will not be recorded and thus the TAC is biased towards early arriving photons. This phenomenon is termed "pulse pile-up". The easiest way to approach this problem is to consider first of all the arrival of photons uncorrelated in time with the START - i.e. steady state random emission, where the probability distribution for the number of photons arriving in a fixed time interval, is independent of where that time interval occurs with respect to the START. In our ideal experiment the distribution \( p(u) \) of time intervals \( u \) between successive photon arrivals (i.e. intervals of time containing
only one event) is exponential:

\[ p(u) = \frac{1}{\bar{u}} \exp\left(-\frac{u}{\bar{u}}\right) \]

\[ = \frac{1}{\bar{u}} \left[ 1 - \frac{u}{\bar{u}} + \frac{1}{2}(u/\bar{u})^2 - \ldots \right] \]

As \( u/\bar{u} \) becomes small \( p(u) \approx \frac{1}{\bar{u}} (1 - u/\bar{u}) \approx 1/\bar{u} \) and the probability of arrival of a photon is uniform over the range of the TAC. This also means, given that a photon arrives in the TAC range, the probability of any more photons arriving is negligible. Under these conditions the distribution of the arrival of first photons is an unbiased estimate of the distribution of time-of-arrival intervals. When photon arrival is correlated with the START as in a flash fluorescence experiment, the above condition \( u/\bar{u} \) small, is still the criterion for unbiased results.

The necessity to work at low P/F (photon count rate)/(flash repetition rate) ratios can be overcome by using a pile-up detector which rejects any TAC output for a first photon arrival if a second photon arrives within the TAC range. Instead of being compelled to work with P/F ratios of \( \leq 1\% \), it is now admissable to work with ratios up to the order of 100\% without the risk of pile-up. At higher count ratios, the data collection rate will fall since there will be a predominance of TAC start-stop cycles during which two or more photons are detected.

Commercially available pile-up inspectors, whilst suitable for coincidence counting, do not at present meet the requirements demanded in lifetime measurements. They
function in a "continuous" updating" mode. If at any time two photons are detected within a preset inspect time interval, the inspector inhibits MCA storage and is reset immediately. The device is now capable of being again activated by another two photon event. In lifetime measurements, it is necessary and sufficient for the inspect time intervals to coincide with (and only with) the TAC "open" period. Thus the inspector must be gated to inspect when the TAC opens and cease inspecting when the TAC sweep has finished. Otherwise, a multiphoton event occurring say, just prior to a TAC start, would initiate an inhibit pulse and prevent the recording of a legitimate single photon event which may occur during that TAC sweep. It was found that the use of an ORTEC 404A pile-up inspector resulted in an overall loss of data collection rate, even when working at low P/F ratios.

A pile-up inspector and gate generator has been designed to overcome this deficiency in commercial units (Williams & Sandle 1970). The unit is active only during the TAC "open" time. Alternatively, a theoretical correction for pile-up can be made (Coates 1968) which, however, becomes unsatisfactory at very high count rates (Davis & King 1970).

5. FLASH LAMPS

The advent of the laser has produced a new avenue for
the production of high power pulsed light sources. In
Section II.2, attention was drawn to the limited pulse
repetition rate of currently available UV-visible pulsed
lasers. With single photon counting, no more than one
photon can be recorded per light flash and, to prevent
pulse pile-up, it is necessary to work at P/F ratios of
1% or less (Section II.4). However, with the use of a
pile-up inspector, P/F ratios of up to 100% are permissible.
Thus, even if every laser pulse gives rise to a number of
fluorescence photons, the maximum rate of data collection
can be no more than the number of single photon events
which are recorded by the TAC, the upper limit being the
pulse repetition rate. It may arise that each laser
pulse is too intense, thereby initiating a predominance
of multiphoton events which will be inhibited. In this
case, attenuation of the laser beam will offer an improved
data collection rate. When comparing a pulsed laser with
a flash lamp, the figure of merit for single photon
counting is therefore not simply intensity, but the product
of pulse intensity and pulse repetition rate. With flash
lamps, repetition rates of the order of 50kHz are
attainable so that for a laser to be competitive it must
be two orders of magnitude more intense. Of course, a laser
is coherent, which adds much in its favour, and there is
little doubt that the laser will soon prove its potential
superiority as a pulsed excitation source for single photon
counting. However, the following discussion will refer only
to flash lamps.
The voltage necessary to produce a light-emitting discharge between two electrodes in a gas increases with increasing gas pressure. Devices such as thyratrons, needed to trigger a lamp, increase rapidly in cost as one increases the requisite anode stand-off voltage. It has therefore been found necessary to pursue the development of nanosecond flash lamps with the following distinction in mind -

a) Triggered lamps are used with a low pressure (< 1 atm) of filler gas and are operated at voltages below 15kV.

b) Free-running (relaxation oscillator) lamps are necessary if high pressures are to be used with correspondingly high voltages.

The relative advantages and disadvantages of triggered and free-run lamps have been discussed by Ware (1971). Although low pressure lamps can be operated successfully in the free running mode, triggering enables the use of a considerable overvoltage on the anode, (the applied voltage can be several times the breakdown voltage) with a resulting increase in intensity. Changes in gas or gas pressure do not require adjustment of the RC time constant as is the case for the free running lamp. Low pressure lamps are simpler to construct so that high pressure lamps need to offer a distinct advantage in intensity, repetition rate or spectral distribution if the added technical difficulties in their construction are to be justified.
Low Pressure Triggered Lamps

Because the performance is critically dependent on the cleanliness of the electrode environment (see Figure II.3), we require a lamp in which the gas and the electrodes can be rapidly changed. To reduce electrode evaporation, tungsten is the preferred electrode material. Although platinum electrodes are more easily shaped, they tend to deposit platinum black on the silica window, thus impairing UV transmittance. The tungsten electrode tips are rounded and polished and periodically cleaned. Cleaning is particularly necessary if hydrogen or deuterium is the filler gas since a deposit "grows" on the tip of the positive electrode, reducing the spark gap and hence the intensity. The deposit is likely to be caused by the strong electric field extracting impurities from the tungsten (Berlman, Steingraber & Benson 1968). An intense line emission is found to be superimposed on the usual H₂ or D₂ continuum and can be assigned to Fe, Fe⁺ and Mo.†

† A similar effect has been observed whilst using steady state deuterium light sources for taking absorption spectra with a Cary 14 double beam spectrophotometer. After a new lamp has been installed, the intense line spectrum (which can be similarly assigned) causes undue oscillation of the automatic slit control. Limiting pen response leads to spurious results. Ageing the lamp reduces the effect although electrodes made of ultra pure tungsten are the obvious solution.
Fig.II.3 Decay curves for the air flash lamp showing the broadening and build up of longer lived emission as a result of prolonged use without cleaning.

The time scale is 0.15ns/channel.

Fig.II.4 Low pressure flash lamp trigger circuit. High voltage resistor is a Victoreen type HPX. The complete unit is enclosed in a fully shielded housing to prevent RF pickup by the detection system. C can be stray or added capacitance.

Fig.II.5 Pulse generator suitable for gating HY-6 thyatron. (The diodes were kindly supplied by A. Halpern.)
Stable operation is enhanced if the electrodes maintain a fairly constant temperature and this is achieved by operating at high repetition rates (10-30kHz). With an anode voltage of 8kV and an electrode gap of 3mm, the flash lifetime is minimised at approximately 0.4atm gas pressure. At higher pressures, unless a greater overvoltage can be applied, firing stability decreases and the arc curves. A stable arc is desirable to enable maximum throughput of light when the lamp is focussed on to the slit of a monochromator. It is an obvious advantage to utilize a monochromator with higher resolving power so as to be able to use wider slits (for the same desired resolution) and a less critical arc.

Triggering is most conveniently accomplished by supplying the high voltage to one electrode of the lamp via a charging resistor and earthing the other through a thyratron whose grid is pulsed at the required frequency. A high voltage 1M\(\Omega\) resistor is used and charging normally accomplished with stray capacitance only. If the shortest possible lamp pulse is not essential, wider electrode spacing or added capacitance can increase output at the expense of lamp pulse width. Figure II.4 shows the lamp trigger circuit. A fast rising edge is needed to pulse the grid and the one point at which the grid draws current is seen as a spike on a display of the grid pulse. The stability of this firing point is desirable although not essential unless the START pulse is derived from the pulse generator. A ceramic-metal hydrogen thyratron (EG&G type
HY-2) has operated satisfactorily at 8kV, 15kHz for 2,000 hours before finally failing due to internal mechanical failure. A more robust thyratron (EG&G HY-6) is now used in place of the type HY-2 and is capable of withstanding a peak anode voltage of 16kV. Care must be taken, however, to ensure that the plate breakdown factor (pulse repetition rate x peak anode voltage x peak anode current) is not exceeded. This places an upper limit on the pulse repetition rate which can be used for a given pulse power. If ultimately greater intensity and repetition rate are necessary, one must proceed towards the development of a suitable high pressure free-running lamp.

Both the HY-2 and HY-6 are supplied with a positive 300 volt pulse of ~20ns rise time and ~50ns pulse width from a pulse generator. A circuit employing a blocking oscillator and glass hydrogen thyratron has operated successfully but requires in addition three separate power supplies (Ware 1971). A more compact circuit (Figure II.5) utilizes a string of thyristor diodes operating in the mode of a relaxation oscillator. In principle, a single diode could be used, provided that it had the requisite peak forward breakdown voltage and that it was capable of switching within 0.1µs. Each of the diodes used in the circuit shown in Figure II.5 have a peak forward breakdown of 14V.

The START pulse, synchronised with the firing of the lamp, is derived from a photomultiplier (RCA 1P28 is suitable) which views the flash through a fibre-optic light
guide. A 1MΩ load resistor and supply voltage of 950V produces a signal pulse in excess of one volt which can be used without amplification as input to the START discriminator or directly as input to the TAC.

The spectral output of the low pressure lamp is determined by the filler gas and provision is made to pump and fill the lamp whilst it is mounted in place in the photon counting unit. Optical alignment is facilitated by vertical and horizontal micrometer adjustment. The construction of the low pressure lamp is shown in Figure II.6 and Table II.1 summarizes its characteristics.

### Table II.1. Characteristics of the low pressure lamp using various filler gases

<table>
<thead>
<tr>
<th>gas</th>
<th>pressure (atm)</th>
<th>electrode spacing (mm)</th>
<th>fwhm (ns)</th>
<th>decay time (ns)</th>
<th>usable decades</th>
</tr>
</thead>
<tbody>
<tr>
<td>air</td>
<td>0.4</td>
<td>3</td>
<td>3.0</td>
<td>1.8</td>
<td>4</td>
</tr>
<tr>
<td>nitrogen</td>
<td>0.4</td>
<td>3</td>
<td>4.5</td>
<td>2.5</td>
<td>4</td>
</tr>
<tr>
<td>hydrogen</td>
<td>0.3</td>
<td>5</td>
<td>1.8</td>
<td>0.9</td>
<td>3.5</td>
</tr>
<tr>
<td>deuterium</td>
<td>0.3</td>
<td>5</td>
<td>2.2</td>
<td>1.1</td>
<td>3.5</td>
</tr>
</tbody>
</table>

The spectrum of the nitrogen or air lamp consists of intense bands, the most prominent being at 316, 337 and 358nm. There is a weaker group of bands at 286nm which are sufficiently intense to be used for excitation but have a strong tail emission. It is apparent from Figure II.7 that gross errors in decay time would result if decay curves obtained with 286nm excitation were used without correction for the shape of the exciting pulse. Such
Fig. II.6 Construction of the low pressure lamp

A. Retaining sleeve
B. Sleeve soldered to Kovar tubing
C. Pyrex-to-Kovar glass-to-metal seal
D. Brass electrode holder
E. Tungsten electrode
F. Neoprene 'O' ring
G. Connection to vacuum tubing
H. Electrical connector to high voltage power supply
J. Curved front surface mirror mounted in ball joint
K. Socket for ball joint
L. Suprasil window secured with Araldite
Fig.II.7a  Spectral output of the air flash lamp

Fig.II.7b  The 337.1nm band group measured at high resolution (photoelectric recording).

Fig.II.7c  Comparison between decay curves of the 337nm (ooooo) and the 286nm (.....) band groups.
correction procedures are discussed in Chapter III. Figure II.8a illustrates the decay curve of the 315.9nm band. The "cleanliness" of the low pressure lamp, (other than for the 286nm band) reigns over 4 decades of intensity.

In contrast to air, both hydrogen and deuterium show no change in lifetime with wavelength in the region studied. They are particularly suited to studies using a wide variety of excitation wavelengths since their spectra are continuous over the region 200-350nm. However, the relative intensity is some orders of magnitude less than a prominent line of the air lamp. Deuterium is more intense (by a factor of two) than hydrogen in the region from 200-280nm).

Although various other filler gases have been tried, at pressures less than one atmosphere the most useful (in terms of intensity and spectral versatility) appear to be air, nitrogen, hydrogen and deuterium.

High Pressure Lamps

Although high pressure lamps have been used extensively, (D'Alessio, Ludwig & Burton 1964; Franke & Schmeing 1967; Yguerabide 1965) very few appear to have achieved the objectives required for use in time correlated photon counting. Features such as high frequency operation, facility for rapid change of gas or electrodes, stable and trouble-free operation, ease of construction, can be readily incorporated in low pressure lamps. The high
Fig. II.8a Decay curve for low pressure air flash lamp. Operating conditions were:
- pressure 330 Torr;
- electrode gap 3mm;
- voltage 8kV;
- repetition rate 11kHz.

Fig. II.8b Decay curve for prototype high pressure lamp. Operating conditions were:
- pressure 30 atm;
- voltage 40kV;
- electrode gap 0.8mm;
- repetition rate 5kHz.

The time scale is 0.06ns per channel.
pressure lamp can only be justified if it offers considerably greater intensity than low pressure lamps whilst operating with comparable reliability at the same repetition rate.

The energy \( E \) dissipated in a spark discharge and partially emitted as light is given by \( E = \frac{1}{2} CV^2 \) where \( C \) is the capacitance and \( V \) the voltage. \( C \) is limited by the necessity for a short electrical pulse. However, if one increases the breakdown voltage \( V \) across the spark gap, the energy dissipated will correspondingly increase. The increase in breakdown voltage can be achieved both by greater electrode separation and by increasing the pressure of the gas.

A moderately successful lamp used by Selinger & Speed (1969) has been tested at 20atm air pressure with an applied voltage of 15-20kV. However, the small electrode gap (0.2mm) necessary to limit the breakdown voltage to the output capacity of the high voltage power supply, results in a usable intensity no greater than that of the low pressure lamp. Furthermore, there is the limitation that at a repetition rate of 10kHz, the electrodes are rapidly degraded, causing unstable operation after only a few hours of use.

A more robust lamp is being developed at present, capable of being used with electrode gaps of up to 5mm and pressures of up to 50atm. The design allows applied voltages of up to 80kV and operation at high repetition rates without loss of performance. Some preliminary measurements
reveal that subnanosecond pulses are readily attainable, together with at least an order of magnitude enhancement in intensity compared with the low pressure lamp. Figure II.8b shows the light pulse obtained (on a linear intensity scale). When compared with the low pressure lamp on a logarithmic intensity scale, it becomes apparent that a significant advantage of the low pressure lamp is its "cleanliness" over four or five decades of intensity. It is hoped that further development will alleviate this present disadvantage of the high pressure lamp.

6. PHOTOMULTIPLIERS

The detection system centres around the photomultiplier. The tube which has been chosen for photon counting is one of the Phillips 56 series, the 56DUVP/03, which incorporates a bialkali K-Cs-Sb photocathode. The 03 designation indicates that the tube has been specially selected for low background and high single photon efficiency. A comparison with one of the older tubes (Phillips 56UVP) is presented in Table II.2 below.

The topology and mechanical construction of the voltage divider circuit for the tube can be as critical as the circuit itself in assuring clean, fast response times for single photons. There are two types of base circuits -

a) "linear" dynode chain

b) "tapered" dynode chain.
In the first of these the interdynode voltages are the same over the 14 stages. Decoupling capacitors are used between the last 3 or 4 stages to maintain the voltages in the region of higher current drain. In the tapered base the interdynode voltage is increased sharply over the last stages and bypass capacitors from dynode to ground are added. With suitable adjustment of focusing voltage, both types give satisfying results. However, the linear circuit is preferable for single photon counting since it produces a higher gain for the same overall supply voltage. The signal to noise ratio is thus better. The tapered base is better suited to pulse height analysis in scintillation counting since the anode current is then more closely a linear function of the incident flux.

Common to all bases are the following considerations.

The output cable (50Ω) is shielded right down as close as possible to the anode socket pin. The braid is earthed at the anode end to a floating solid copper plate to which all other earth connections are made. The braid is then earthed to the inside of the base housing (at the point of exit of the output cable) using a good quality 50Ω crimp BNC connector so that no external pick-up can enter the base. Resistors are of the cracked carbon, low noise, variety. All components, especially those connected to the anode and last dynode, must be of low inductance. Wiring inductance should be minimised by using short leads. Such considerations are essential in the wiring of the base circuit if "ringing" of the output
signal is to be eliminated. Figure II.9 shows the linear and tapered circuits which have been used with the Phillips 56DUVP/03. The mechanical construction is depicted in Plate 1.

The tube dark pulse rate is reduced on "pump-out", i.e. leaving the high voltage applied to the tube (in the dark) when not in use and on cooling the photocathode to reduce thermal photon emission. There appears to be little benefit in cooling the tube below -40°C although even at these temperatures, care must be taken to avoid condensation on the tube or on the base connections. Blowing with dry nitrogen provides a satisfactory preventive measure. Best results are obtained if only the cathode (the window and a centimetre or so of the tube itself) is cooled.

The photomultiplier signal is used without amplification and can be fed directly (or preferably via a discriminator) into the TAC.

One photo-electron (charge $1.6 \times 10^{-19}$ coulomb) produces a charge packet at the anode (gain $3 \times 10^8$) which is spread over a period of about 3ns and thus represents an average pulse current of 16mA. Across the 50Ω anode load resistor this provides a mean pulse height of 800mV. a dark pulse rate of 20 counts sec$^{-1}$ thus corresponds to an equivalent d.c. current of 1mA. Of course, with a discriminator threshold of 150mV, these figures do not include the large number of small amplitude dark current pulses which are attributable to electrons that have not been fully amplified by the multiplier system. The pulse
TAPERED BASE CIRCUIT FOR PHILLIPS 56 DUVP/03 PHOTOMULTIPLIER

C = 0.01μF, flat ceramic with short leads to earth.
R_L = 50Ω, cracked carbon
Resistors are 1W, cracked carbon

LINEAR BASE CIRCUIT FOR PHILLIPS 56DUVP/03 PHOTOMULTIPLIER

C_1 = 2200pF, C_2 = 680pF, C_3 = 220pF, C_4 = 68pF (low inductance.)
R = 33kΩ, 1W, cracked carbon.
R_L = 50Ω, cracked carbon.

Fig.II.9 Voltage divider circuits used with the Phillips 56 DUVP/03 photomultiplier.
PLATE 1

Internal mechanical construction of voltage divider circuits for Phillips 56 DUVP/03 photomultiplier.

Above: Tapered circuit
Right: Linear circuit

Oscilloscope trace shows typical performance for a gain of $10^8$.

Vertical scale: 0.2 mv/division
Horizontal scale: 2ns/division
height distribution of photo-electrons and dark pulses provides a rationale for selecting a suitable discriminator level which will optimize the signal to noise ratio. The amplitude distribution of dark current pulses measured for the 56DUVP/03 is illustrated in Figure II.10. Cooling is seen to significantly reduce the thermionic emission. With a typical signal level (corresponding to approximately 100 counts per second) incident on the photocathode one obtains the pulse height distribution shown in Figure II.10. It becomes obvious that one cannot discriminate against thermionic emission which has been fully amplified.

Table II.2. Photomultiplier Noise Characteristics

<table>
<thead>
<tr>
<th>tube</th>
<th>cathode volts (kV)</th>
<th>gain $3 \times 10^8$</th>
<th>discriminator level (mV)</th>
<th>temperature (°C)</th>
<th>dark counts (sec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>56UVP</td>
<td>-2.5</td>
<td></td>
<td>150</td>
<td>25</td>
<td>2500</td>
</tr>
<tr>
<td>56DUVP/03</td>
<td>-2.4</td>
<td></td>
<td>150</td>
<td>-30</td>
<td>400</td>
</tr>
</tbody>
</table>

An important facet of decay spectroscopy is to provide adequate electrical shielding around both the lamp housing and the photomultiplier. Failure to do this can result in "oscillation" of short lifetime decay curves caused by the superimposed RF radiation which originates from the flash lamp and its associated circuitry. This artifact can be very persistent if careful attention is not paid to the details of shielding.
Fig. II.10 Pulse height distribution for Phillips 56 DUVP/03 photomultiplier.

- ambient temperature
- cooled to -30°C
- cooled tube with a typical incident light flux of \( \sim 100 \) photons/sec.

Fig. II.11 Fluorescence decay curve obtained for anthracene vapour at 20°C, 10^-4 Torr. The excitation flash (337.1 nm air lamp) is also included (less pronounced points)

The time scale is 0.32 ns per channel.
7. INSTRUMENTAL PERFORMANCE

Standards

Owing to the considerable variation in techniques of lifetime determination, a chemical standard has been chosen as a measure of sensitivity. Crystalline anthracene at 20°C has a vapour pressure of the order of $10^{-4}$ Torr.† Excitation with the 337.1 nm line of an air flash lamp operating at a frequency of 11 kHz produces an average count rate of 10 Hz on a TAC time range of 80 ns. The decay curve so obtained is shown in Figure II.11. The count rate for scattered excitation light (using a Bausch & Lomb double grating monochromator with 2 nm bandpass) is less than 0.5 Hz. The average photomultiplier dark pulse rate over all time is 20 Hz (for a photomultiplier voltage of $-2.4 kV$ and a discriminator threshold set at 150 mV.) On the time range of 80 ns, the average dark pulse count rate, as detected within the TAC 'open' period, is less than $2 \times 10^{-3}$ Hz.

After comparisons have been made with other laboratories, it is suggested that anthracene vapour should become an overall sensitivity standard. This compound is now generally available at high levels of purity and, owing to its fairly short lifetime, any quenching caused by residual oxygen will be minimal.

Calibration

Although the time calibration of such equipment is

† 1 Torr $=$ 133 Nm$^{-2}$
generally performed by using accurate delay lines, a chemical reference has again been the choice (for the longer time scales) because of cheapness and convenience. At pressures in excess of 15Torr, the fluorescence decay of hexafluoroacetone is independent of wavelength, pressure and the presence of oxygen and is strictly exponential over at least three (decade) orders of magnitude in intensity. The results are independent of the suppliers and the most common impurity, $SO_2$, is easy to remove. At pressures of $\sim 100$Torr, more than adequate light intensity is available when using the single photon technique. Complete agreement is found with the results of Halpern and Ware (1970) and it is suggested that hexafluoroacetone at 100Torr and 25°C with a lifetime of 84ns be accepted as a standard. This lifetime is accurate to better than 0.5ns and the available precision can more than match this.

Where the time scale was found to be too long for hexafluoroacetone to provide an accurate calibration, an ORTEC 416A gate and delay generator could be used. This was calibrated against hexafluoroacetone for delays of the order of 100ns and since the linearity over its delay range was better than 1% with a timing jitter of less than 0.02%, longer delays could then be accurately set. Very short time ranges were calibrated using accurate delay cables (e.g. Tektronix type 110).

The overall precision of the instrument for lifetimes ranging from $10^{-8}$ to $10^{-6}$ seconds can be stated as being better than 2%. 
Future Developments

Generally speaking, the limitations of the single photon technique for lifetime measurements are relatively few when compared with other methods. The shorter end of the time range is limited by the transit time spread for the photomultiplier, although this may be reduced to ~0.2ns by using only a small central portion of the photocathode. Further developments in photomultiplier technology may better this.

It is desirable that photomultiplier dark current be reduced even further if the weakest sources of emission are to be detected. In scintillation counting, a technique exists which can virtually eliminate the effect of background noise. The beta particle which is absorbed by the scintillator gives rise to a pulse consisting of many photons emitted within the decay time of the scintillator (usually 2-3ns for an organic liquid scintillator). The scintillator may therefore be viewed with two photomultipliers operating in coincidence. This ensures that only pulses which are "simultaneously" observed (i.e. within a typical coincidence resolving time of 10ns) will be recorded. Randomly occurring noise pulses, originating as a result of thermionic emission from the photocathode, will have a very low probability of occurring "simultaneously" in both photomultipliers and will not be recorded. The effect of background noise is thus virtually eliminated.

Such a procedure is intrinsically impossible in single
photon counting since the method involves individual detection of single photons. Reduction in photomultiplier dark current must therefore remain a worthwhile pursuit.

When studying weakly emitting gas phase samples, scattered excitation light is often many orders of magnitude more intense than the fluorescence emission. Optical filters are usually successful in removing a large part of the unwanted scatter. Any residual scatter can be readily differentiated from the decay curve, and corrected for, if the lifetime being measured is long in comparison with the excitation pulse. However, when short lifetimes are to be determined, scattered light is intolerable. An appreciable increase in the excitation intensity can increase the signal-to-background ratio sufficiently to allow a monochromator to be used to select both the excitation and the emission wavelength. In this way, the problem of scattered light can be virtually eliminated. Pulsed dye-lasers are likely to fulfil this need for high intensity excitation sources, provided that the requirement for a reasonably high repetition rate can be met. Of course, with high power excitation sources, one must be wary of the increased likelihood of permanent photochemical changes in the sample.

Even at the present level of development of single photon counting decay spectroscopy, it has been possible, in some cases, to select the emission wavelength and the excitation wavelength by means of monochromators. In the
study of excited state charge-transfer complexes (Exciplexes, Chapter IV) there is adequate fluorescence intensity for this to be done. Preliminary studies have revealed that "twin monochromator" lifetime experiments are feasible even when observing weak emission from low pressures of aromatic vapours (Chapter VI). This area of research is likely to prove most fruitful.
CHAPTER III

ANALYSIS OF FLUORESCENCE DECAY CURVES

When the single photon technique is used, the data which is collected is produced by an exciting pulse of finite width and consists of a sum of counts due to photon emission from an excited species and counts due to random background. From this data it is necessary to evaluate the nature and rate of the decay process which would arise if excitation was initiated with a delta pulse and there was no background.

In many cases, the lifetime to be measured is long when compared with the excitation pulse. Provided that random background has been removed, a function describing the decay may be postulated and its validity tested by comparing how closely it fits the experimental points.

Pulse methods for lifetime measurements have the important advantage over indirect techniques that fluorescence emission is observed directly as a function of time. It is therefore possible to determine accurately the errors involved in estimating the decay process and thus be able to reject a hypothesized function if the error incurred is too large.
Where the finite duration of the excitation pulse introduces a distortion, this must be accounted for by our hypothesis, but the essence of the procedure of decay analysis remains the same.

It will be shown that random background can be removed without biasing the results.

1. DATA HANDLING

Single photon counting data are read from the memory of the multichannel analyser to a teletype which produces both typed copy and punched paper tape. The paper tape is used as input for a program run on a CDC 3600 computer which translates the data from ASCII code to BCD and stores the data on disc. On-line display consoles, which allow interruptive access to the computer, are used for editing the data, for preparing programmes and for execution of jobs.

Initially, a semi-logarithmic plot of the data is obtained on a 12" chart and this may be inspected for any obvious read-in errors. Where the decay is clearly exponential, a straight line fit may be made to the semi-log plot to obtain an initial estimate of the lifetime. For non-exponential decays, one must have some a priori knowledge of the process initiating the decay before a meaningful analysis can be carried out. The procedure chosen is used to analyse the decay data and results are obtained both in graphical form and as printed output.
2. REMOVAL OF BACKGROUND

When the signal to noise ratio of the experiment is low, random background contributes significantly towards the number of counts recorded in each channel of the multi-channel analyser. It is therefore necessary to remove the background and to do so without introducing any bias in the results. We are required to prove that simple subtraction of the mean background from the observed decay curve is an acceptable and rigorous procedure.

The experiment constitutes exciting the sample at time zero with a flash of light. The sample subsequently emits \( N \) photons where \( N \) is a random variable with probability distribution

\[
P(N=n) = p_n, \quad n = 0, 1, 2, \ldots
\]

(III.1)

The photons are emitted with time lags \( T_j (j=1, 2, \ldots, N) \) which are independent, identically distributed random variables with common distribution

\[
P(T_j \leq t) = \Phi(t)
\]

(III.2)

and density function

\[
\frac{d\Phi(t)}{dt} = I(t)
\]

(III.3)

In addition, there is a background emission of photons\(^\dagger\)

\(^\dagger\) The background is of course not due to photon emission but it is recorded as if it were and therefore may be treated as such for the purposes of this argument.
which follow a Poisson distribution with parameter $\lambda$.

The experiment involves making repeated measurements of photon emission over a time interval $(0, K)$, but only those measurements are recorded where exactly one photon is observed in $(0, K)$. Let $u$ be the time delay that is recorded (and which may be due to either fluorescence or background) and let $f(t)$ be its density function. We need to find an expression for $f(t)$.

The event whereby exactly one photon is recorded in $(0, K)$ and which lies in $(t, t + dt)$ can occur in two ways.

(i) The event is due to background emission. With the condition that $N$ is known, we can write the probability of this event as

$$P_1 = \lambda e^{-\lambda t} \left( 1 - \Phi(K) \right) dt$$

(III.4)

(ii) The event is due to fluorescence emission from the sample and no background emission occurs in $(0, K)$. The probability of this event, conditional on $N$ being known and $N > 0$ is

$$P_2 = NI(t) e^{-\lambda t} \left( 1 - \phi(K) \right) dt$$

(III.5)

The total probability is the sum $P_1 + P_2$. It follows that the probability of observing exactly one photon in $(0, K)$ can be obtained by integrating $P_1 + P_2$ with respect to $t$ between the limits $(0, K)$. 


\[ \int_{0}^{K} (P_1 + P_2) \, dt = \lambda e^{-\lambda K} \left\{ I - \Phi(K) \right\}^N + N\Phi(K) e^{-\lambda K} \left\{ I - \Phi(K) \right\}^{N-1} \]

(III.6)

Given that \( N \) is known and writing \( I - \Phi(K) = \Theta(K) \)

\[ f_N(t) \, dt = (P_1 + P_2) / \int_{0}^{K} (P_1 + P_2) \, dt \]

\[ = \frac{NI(t)\Theta(K)^{N-1} e^{-\lambda K} dt + \lambda \Theta(K)^N e^{-\lambda K} dt}{N\Phi(K)\Theta(K)^{N-1} e^{-\lambda K} + \lambda \Theta(K)^N e^{-\lambda K}} \]

(III.7a)

Thus \( f_N(t) = \frac{NI(t) + \lambda \Theta(K)}{N\Phi(K) + \lambda \Theta(K)} \)

(III.7b)

Finally, by removing the conditioning on \( N \),

\[ f(t) = \sum_{n=0}^{\infty} f_N(t)P_n = \sum_{n=0}^{\infty} f_n(t)P_n \]

and the required density function \( f(t) \) is obtained.

\[ f(t) = \sum_{n=0}^{\infty} \left\{ \frac{nI(t) + \lambda \Theta(K)}{n\Phi(K) + \lambda \Theta(K)} \right\} P_n \]

(III.7c)

Equation (III.7c) can be written in the form

\[ f(t) = C_1 I(t) + C_2 \]

(III.8)

where

\[ C_1 = \sum_{n=0}^{\infty} \left\{ \frac{n}{n\Phi(K) + \lambda \Theta(K)} \right\} P_n \]

(III.9)

and

\[ C_2 = \sum_{n=0}^{\infty} \left\{ \frac{\lambda \Theta(K)}{n\Phi(K) + \lambda \Theta(K)} \right\} P_n \]

(III.10)

Thus it is perfectly legitimate to subtract the background component \( C_2 \) provided that an accurate estimate of its magnitude can be obtained. This is done as follows.
The single photon counting apparatus is set up with suitable delay of the stop pulse so that the time profile of the decay curve is recorded in channels 20-128 (for a 128 channel memory). Channels 1-19 then correspond to the "tail" of the decay curve arising as a result of the previous excitation flash (i.e. the flash occurring immediately prior to the one which currently caused a start pulse). However, at a flash repetition rate of $\sim 10\text{kHz}$ and a TAC range of say $10^{-6}\text{s}$, the probability of the events recorded in channels 1-19 being due to fluorescence emission would be exceedingly small. This is obvious since, in general, the fluorescence is likely to have a mean lifetime of less than $10^{-6}\text{s}$. The time between successive excitation flashes would then correspond to 100 or more mean lifetimes, thus ensuring that the fluorescence emission occurring just prior to an excitation flash would be negligible.

With reference to equation (III.8), this means that $I(t)=0$ for channels 1-19 and the observed density function in this region is in fact an estimate of $C_2$, the background emission. The mean number of counts per channel for channels 1-19 is taken to be the mean background and can be subtracted from the decay curve. We thus obtain a probability density which is directly proportional to $f(t)$. 
3. EXPOENTIAL AND NON-EXPONENTIAL DECAY

Like radioactive decay, the decay of molecular luminescence is a random process which in many cases leads to an expression of the form

\[ A e^{-t/\tau} = I(t) \]  \hspace{1cm} (III.11)

\( A \) is a constant for a particular measurement of the fluorescence decay curve, \( I(t) \) and \( \tau \) is the mean lifetime.

If the excitation pulse can be considered to be a close approximation to a delta pulse, we can treat the probability density function \( I(k) \), \( k = 1, 2, \ldots, n \) as being an undistorted estimate of \( I(t) \). \( n \) is the number of data points (MCA channels). For each \( k \), \( I(k) \) represents a single estimate of the mean of a Poisson distribution of counts for that channel. For the Poisson distribution, the mean equals the variance, \( \sigma_k^2 \). The estimated value of the weighted average of the individual variances of each data point is a measure of the uncertainty in the data. We call this estimated uncertainty, SSQP (Sum of Squares of Poisson error). The weighting factor for each data point \( I(k) \) is the inverse of the variance.

\[
SSQP = \frac{1}{n} \sum_{k=1}^{n} \left\{ \frac{1}{\sigma_k^2} \cdot \sigma_k^2 \right\} = \frac{n}{\sum_{k=1}^{n} \left\{ \frac{1}{I(k)} \right\}} \hspace{1cm} (III.12)
\]

The generally accepted procedure for fitting a theoretical expression to a set of data is the method of
least squares. Margulies (1968) has emphasised the
distinction between the problem when the functional form
of the data is known and when it is not known. In the
latter case, the number of parameters in the fitted
function must be no more than that indicated by the error
in the data. Although the least squares sum decreases as
the number of parameters is increased, the resulting fit
is not necessarily a better representation of the data.

Let $I^0(k)$ be the function fitted to the data for a
particular choice of the parameters $A, \tau$ which have been
found to minimise the least squares sum. The sum is
c caracterised by the weighted mean variance of the fit,
$SSQR$, of $I^0$ to the original data $I$,

$$SSQR = \frac{1}{n - r - 1} \sum_{k=1}^{n} \left\{ \frac{1}{I(k)} \left[ I(k) - I^0(k) \right]^2 \right\}$$

(III.13)

The factor $v = n - r - 1$ is the number of degrees
of freedom left after fitting $n$ data points with $r$
parameters. The most complex theoretical model which can
be justified by the data is that for which $SSQR$ is not
statistically significantly different from $SSQP$. The
statistic $\chi^2$ may be used to estimate the "goodness of fit"
by comparing $SSQR/SSQP$ with the reduced chi-square $\chi^2_v$.

$$\chi^2_v = \frac{\chi^2}{v} = \frac{SSQR}{SSQP}$$

If the fitted function is a good approximation to the
data, then the value of the reduced chi-square should be
approximately unity. Using the accepted 5% level of
significance, this means that for 80-100 data points $\chi^2_v$ must be less than 1.6.

The application of this reasoning may be illustrated in terms of real experimental data. Figure III.1 shows two examples of fluorescence decay curves obtained by exciting the first singlet state of phenanthrene and of naphthalene-$d_8$ in the vapour phase at pressures below 0.1Torr. The fluorescence decay of phenanthrene is found to follow essentially a single exponential whereas naphthalene-$d_8$ shows non-exponential behaviour.

The results obtained for fitting a single exponential (equation III.11) are summarised in Table III.1. It is readily seen that for phenanthrene, we cannot justify introducing any further complexity in our hypothesized function since $SSQR = SSQP$. However, for naphthalene-$d_8$, $SSQR >> SSQP$ and it is justifiable to increase the number of parameters in the function.

| TABLE III.1 |
| Results obtained for fitting a single exponential |
| A | $\tau$(ns) | SSQR | SSQP | $SSQR/SSQP$ |
| phenanthrene | 4942.3 | 55.5 | 335 | 292 | 1.15 |
| naphthalene-$d_8$ | 3629.7 | 206.7 | 3600 | 316 | 11.4 |
Fig.III.1  Fluorescence decay curves for a) phenanthrene and b) naphthalene-d₈ in the vapour phase. The decay of naphthalene-d₈ deviates from a single exponential.

Fig.III.2  a) Typical non-exponential decay curve resulting from the fluorescence of benzene-d₆ (0.5 Torr) excited to a single vibronic level with 253.5nm radiation.

b) Schematic $\chi^2$ error contours obtained when fitting a sum of exponentials.
A sum of two exponentials suggests itself as being a likely choice\(^\dagger\) and is written in the form

\[
I(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2}
\]

(III.14)

where \(\tau_1, \tau_2\) are the lifetimes of the two decay components weighted by the constants \(A_1, A_2\).

It is at this point that the problem becomes exceedingly difficult. For other than perfect (error-free) data, resolution of multi-exponential curves results in a correlation between the various parameters. This is illustrated in Figure III.2. For a given error in the data, the corresponding contour delineates a family of solutions which are equally acceptable. At best, we can indicate a possible range of values which \(\lambda_1, \lambda_2\) may assume. The minimum value, for which the sum of squares deviation is least (corresponding to near perfect data) is not necessarily the most probable and indeed may be highly improbable.

\(^\dagger\) The physical basis for the choice of a sum of exponentials lies in the assumption that two distinct states, each with its own characteristic lifetime, are contributing to the emission process. Rate constants \(\lambda_1, \lambda_2\) are commonly used instead of the inverse lifetimes \(1/\tau_1, 1/\tau_2\).
4. NUMERICAL METHODS FOR FITTING EXPONENTIALS

The fitting of a single exponential to decay data is a straightforward procedure involving the minimisation of a function of the two variables, $A, \tau$. Any numerical procedure will suffice. It was found convenient to use a simplex method which depends on the comparison of function values at the $(n+1)$ vertices of a general simplex, where $n$ is the number of parameters (Nelder & Mead 1965). The vertex with the highest value is reflected in the hyperplane of the remaining vertices. The simplex adapts itself to the local landscape by expanding or contracting and converges onto the final minimum. No assumptions are made about the surface except that it is continuous and has a unique minimum in the area of the search.

When the curvature of the landscape is rapidly changing, the method is superior to minimisation techniques using gradients or quadratic forms. Conversely, in the neighbourhood of a minimum, it may not be as efficient in final rapid convergence.

This method is readily extended to the case of a sum of exponentials which involves minimising a function of four parameters. However, the results obtained are indicative of the difficulty encountered in analysing a sum of two exponentials. Table III.2 has been compiled from three independent calculations of the four parameters, $A_1$, $\tau_1$, $A_2$, and $\tau_2$. 
A₈, τ₁, τ₂ for the fluorescence decay of naphthalene-d₈, shown above in Figure III.1. All calculations were performed using the simplex method with the same stopping criterion for final convergence, the only difference being that the starting estimates for the four parameters differed slightly for each calculation.

**TABLE III.2**

<table>
<thead>
<tr>
<th>Calculation</th>
<th>A₁</th>
<th>T₁</th>
<th>A₂</th>
<th>T₂</th>
<th>SSQR</th>
<th>SSQP</th>
<th>SSQR/SSQP</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1519</td>
<td>97.2</td>
<td>2371</td>
<td>267.5</td>
<td>357</td>
<td>316</td>
<td>1.13</td>
</tr>
<tr>
<td>2</td>
<td>2445</td>
<td>132.3</td>
<td>1400</td>
<td>336.6</td>
<td>329</td>
<td>316</td>
<td>1.04</td>
</tr>
<tr>
<td>3</td>
<td>1722</td>
<td>104.8</td>
<td>2165</td>
<td>279.2</td>
<td>365</td>
<td>316</td>
<td>1.16</td>
</tr>
</tbody>
</table>

In each case, SSQR ≈ SSQP, which leads to the conclusion that all three calculations lead to acceptable estimates of A₁, A₂, T₁, T₂. It would require a deeper insight into the mechanism of decay before the solution with most physical significance could be chosen.

An alternative and more suitable procedure for fitting sums of exponentials makes use of the maximum likelihood technique (Fisher, 1950). An iterative method which incorporates Poisson statistics has been described by Orth, Falk & Jones (1968). The concept of a "mixture" of exponentials is more appropriate from a computational point of view and in contrast to equation (III.14), takes
the form:

$$I(t) = \left( \frac{A_1}{\tau_1} \right) e^{-t/\tau_1} + \left( \frac{A_2}{\tau_2} \right) e^{-t/\tau_2} \quad (III.15)$$

Lee & Jones (1971) have established that the degree of correlation between $A$ and $\tau$ is reduced if this expression (III.15) is used. However, it does not reduce the correlation between $A_1$ and $A_2$ or $\tau_1$ and $\tau_2$. Thus, although the maximum likelihood technique is computationally superior to the simplex method (the amount of computer time is less by a factor of $\sim 6$), with real data which contains error, a family of acceptable solutions must still be obtained.

Isenberg and Dyson (1969) applied the method of moments to analyse multi-exponential decays and claimed that systems with relatively closely spaced decay constants could be analysed. However, they admitted that such a method could only yield successful results if the precision of the data was exceedingly good. In a number of cases they obtained three components from noisy data that was, in fact, composed of a two component decay. This serves to emphasise the point made above that an increase in the number of parameters will always yield a better fit but may not necessarily lead to the correct solution.

It is of interest to examine the converse situation whereby a non-exponential fluorescence decay curve, known to be composed of a sum of many exponentials, is analysed in terms of a sum of only two exponentials. A mixture of fifty exponentials was computed using lifetimes ranging
from 100 to 250ns. The pre-exponential factors $A_\ell$, were at first weighted equally and later varied according to whether the shorter or longer lifetimes were required to dominate. An example of a curve simulated in this manner is illustrated in Figure III.3. Using the simplex method for parameter estimation, a curve made up from 50 exponentials was analysed in terms of a sum of two exponentials (equation III.14). The results are summarised in Table III.3.

Since the simulated curve does not contain statistical error, it is meaningless to compare SSQR and SSQP (which, according to equations (III.12) and (III.13), are 0.97 and 2098 respectively). However, it is apparent from Table III.3 that the sum of two exponentials is an extremely good fit to a curve which is in fact composed of a sum of fifty exponentials.

This exercise demonstrates conclusively that without an established physical basis for fitting a particular choice of a sum of exponentials, the rate parameters one obtains are of little significance. When the data being analysed contain statistical error, it is virtually impossible to establish the number of exponentials which make up the decay curve. In the light of these results, it is clear that observed non-exponential behaviour should not simply be "analysed", as was attempted by Isenberg & Dyson (1969). The physical reasons for non-exponentiality must be known before proceeding with an analysis of the experimental decay curve.
Fig. III.3 Decay curve composed of a sum of 50 exponentials. Lifetimes range from 100 to 250 ns in equal increments. Pre-exponential weightings are equal.

TABLE III.3 Comparison between data points of simulated decay curve formed from a sum of 50 exponentials and data points of curve fitted using a sum of 2 exponentials. \( k \) represents channel number.

<table>
<thead>
<tr>
<th>( k )</th>
<th>Simulated</th>
<th>Fitted</th>
<th>( k )</th>
<th>Simulated</th>
<th>Fitted</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>25651</td>
<td>25648</td>
<td>65</td>
<td>5664</td>
<td>5664</td>
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<tr>
<td>15</td>
<td>21582</td>
<td>21583</td>
<td>70</td>
<td>5135</td>
<td>5135</td>
</tr>
<tr>
<td>20</td>
<td>19472</td>
<td>19474</td>
<td>75</td>
<td>4364</td>
<td>4364</td>
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</tr>
<tr>
<td>35</td>
<td>12537</td>
<td>12536</td>
<td>90</td>
<td>3057</td>
<td>3058</td>
</tr>
<tr>
<td>40</td>
<td>11338</td>
<td>11337</td>
<td>95</td>
<td>2603</td>
<td>2604</td>
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<tr>
<td>45</td>
<td>9598</td>
<td>9597</td>
<td>100</td>
<td>2364</td>
<td>2365</td>
</tr>
<tr>
<td>50</td>
<td>8688</td>
<td>8687</td>
<td>105</td>
<td>2014</td>
<td>2015</td>
</tr>
<tr>
<td>55</td>
<td>7365</td>
<td>7364</td>
<td>110</td>
<td>1830</td>
<td>1831</td>
</tr>
<tr>
<td>60</td>
<td>6673</td>
<td>6672</td>
<td>115</td>
<td>1561</td>
<td>1561</td>
</tr>
</tbody>
</table>
The simulated curve of Figure III.3 is of further interest since it shows that a sum of a large number of exponentials, even with widely differing parameters, can give rise to a curve which very nearly follows a single exponential. This observation will be alluded to in the discussion concerning the fluorescence decay of phenanthrene vapour (Section V.7).

5. THE DECONVOLUTION PROBLEM

In measuring short lifetime fluorescence, one has to contend with the distortion of decay curves due to the finite duration of the excitation pulse. The deconvolution problem encountered here is akin to problems met in other spectroscopic situations, for example, the application of slit width corrections, the decomposition of overlapping absorption bands and finite energy-spread corrections in mass spectrometry.

The correction of errors in spectrometric data due to the finite resolving power of real spectrometers has been examined by Khidir & Decius (1962). It was concluded that, although an exact formal solution could in many cases be found for the problem, this solution proved to be without direct value since it was excessively sensitive to errors in the experimental data. When resorting to deconvolution to improve resolution in data containing errors, it can possibly occur that apparent structure is spuriously
generated in a spectrum that is inherently diffuse. Care must be exercised in applying a deconvolution technique to separate overlapping and close-lying peaks.

The need to deconvolute physical data distorted by instrumental response has prompted discussion by several authors (Morrison 1963; Dotti 1967; Jones & Misell 1967; Moore 1968). Their findings produce the agreeable impression that resolution has been improved by deconvolution and additional information wrung from experimental observation. However, this information must be paid for by the insertion of *a priori* conditions into the deconvolution procedure, without which the improved resolution can be misleading or even false. Because each type of experimental result produces its information in a different form, there is probably no uniquely satisfying manner of deconvolution. In fluorescence decay spectroscopy involving photon counting, the errors are well known and this forms a basis for the discussion which follows.

The true fluorescence decay curve $I(t)$ for an excited species is that obtained by excitation with a delta function light pulse. In practice, excitation pulses have finite widths and it is necessary to determine the true time dependence $I(t)$ from an observed fluorescence decay curve $f(t)$ and the excitation pulse $P(t)$.

The excitation pulse $P(t)$ is assumed to be that intensity distribution collected in the $n$ channels of a multichannel analyser or sampling oscilloscope. However, there can be no distinction made between the following two
cases: (a) Where the pulse height distribution in the \( n \) data channels is a true representation of the intensity distribution, within a pulse, over the time interval of data collection. (b) The pulse height distribution represents the frequency distribution of many shorter pulses of equal intensity, whose occurrences in time are spread over the interval of observation.

Since the experiment involves collection of a large number of pulses (usually \( >10^6 \) for sum of all channels) the two cases are treated as being equivalent and could only be distinguished by an experiment involving a single observation of one pulse.

Consider an observation time divided into \( n \) discrete channels provided by a multichannel analyser or sampling oscilloscope. That part of the excitation pulse in a particular channel, \( P(k-j+1) \) can be considered to approximate a delta-pulse which contributes an amount \( P(k-j+1) I(j) \) to the fluorescence in channel \( k \), where \( I(j) \) is the true response, \( j \) channels after a delta pulse. Whereas each delta pulse produces a true fluorescence response, the sum of such pulses, describing the actual intensity distribution with respect to time of the relevant section of the lamp pulse, produces the observed time dependence \( f(k) \) in channel \( k \). The measured fluorescence intensity in a channel \( k \) is given by

\[
f(k) = P(k) I(1) + P(k-1) I(2) + \ldots + P(k-j+1) I(j) + \ldots + P(1) I(k).
\] (III.16)
A point for point convolution of a true response and an excitation pulse can be performed by evaluating equation (III.16) for \( k = 1, 2, \ldots, n \).

This can be expressed by the convolution sum:

\[
f(k) = \sum_{j=1}^{k} P(k-j+1) I(j) \quad (k = 1, 2, \ldots, n).
\] (III.17)

The ideal experiment would involve data collection in an infinite number of channels during the interval of observation, and we would be able to express the convolution of the functions \( P(t) \) and \( I(t) \) in terms of the convolution integral:

\[
f(t) = \int_{\infty}^{t} P(t-t') I(t') dt'.
\] (III.18)

The convolution integral is a special case of a Volterra integral equation of the first kind and can be written in the form:

\[
f(t) = \int_{0}^{t} P(t,t') I(t') dt
\] (III.19)

where the kernel \( P(t,t') = 0 \) if \( t' > t \) or \( t < 0 \).

The difficulty in solving equation (III.19) numerically can be appreciated by considering \( P(t,t'), f(t) \) as step functions (which they are in an experiment involving \( n \) channels): i.e.

\[
P(t-t') = P_{rs}(r-1 < t < r, s-1 < t' < s)
\]
\[
f(t) = f_{r}(r-1 < t < r).
\]
\((r, s = 1, 2, \ldots, n)\).
Then equation (III.19) is represented by

\[ f_r = \sum_{s=1}^{r} P_{rs} \int_{s-1}^{g} I(t') dt' \quad (r-1 < t < r) \quad (III.20) \]

from which it cannot be concluded that \( I(t') \) is necessarily a step function. It can however be concluded that by setting

\[ \int_{s-1}^{g} I(t') dt' = i_s \]

equation (III.20) then becomes

\[ f_r = \sum_{s=1}^{r} P_{rs} i_s \quad (r = 1, 2, \ldots, n). \quad (III.21) \]

Hence the system (III.20) possesses an intrinsic difficulty: even if the determinant of \( P_{rs} \) is non-zero and if (III.21) which is inherently the same expression as the convolution sum of equation (III.17) possesses a unique solution, the system (III.20) will possess infinitely many solutions \( I(t') \) since only the \( i_s \) which are the mean values of \( I(t') \) in the successive intervals \((0,1), (1,2), \ldots, (n-1,n)\), are determined uniquely.

Therefore, although equation (III.17) can be solved explicitly as a system of linear equations using the deconvolution recurrence relation:

\[ I(k) = \left\{ \frac{\bar{f}(k) - \sum_{j=1}^{k} P(k-j+2) I(j-1)}{P(1)} \right\} / P(1) \]

\( (k = 1, 2, \ldots, n) \quad (III.22) \]

the solution will be highly sensitive to small errors in the data, leading to tremendous oscillations in the calculated \( I(k) \). As the number of points used to describe
the functions is increased, the solutions using (III.22) first become more accurate, but eventually get worse, leading to physically meaningless solutions.

6. METHODS OF SOLUTION

Of the variety of methods proposed for the numerical solution of the convolution integral, the majority involve an initial curve fitting technique with the common aim to find a smooth approximation to the observed (distorted) data. In fact, it has been stated categorically (Dromey & Morrison 1970) that smoothing or noise removal is an imperative prerequisite for satisfactory deconvolution. Numerical methods involving matrix inversion and treatment in terms of a constrained linear system have also been proposed (Phillips 1962; Twomey 1963; Strand and Westwater 1968). In these, smoothing criteria are imposed upon the solution, but the errors involved remain somewhat undefined.

In the study of ionization efficiency curves, electron beams are not mono-energetic so that fine structure is often obscured. Deconvolution is used to retrieve some resolution but random scatter in the experimental points prevents further increasing the effective resolution (Morrison 1963). The particular nature of this problem has led to the use of Fourier transforms and similar techniques for the numerical solution of the convolution integral equation. This method is suitable since the form of the observed functions is such that they smoothly
approach zero at both extremities, and so are ideal for approximation with Fourier series (Figure III.4).

Deconvolution of fluorescence decay data has been investigated by Munro & Ramsay (1968). The authors suggest that the most appropriate method is an analytic procedure based on the use of Fourier transforms. However, in fluorescence lifetime measurements, it is possible to measure only a finite portion of the decay curve which, in theory, extends in time to infinity. Thus it is often necessary to deal with data which is truncated at one end, for example, when a discontinuity occurs where observation ceases (Figure III.4). In some cases, the excitation pulse is itself discontinuous at one extremity due to a rising tail emission (refer to Section II.5). This situation does not favour treatment in terms of Fourier series. Furthermore, the heavy smoothing required with such an approach may not be justifiable as regards extracting a meaningful physical interpretation from a fluorescence decay curve. This point can be illustrated by recalling the case of fitting a sum of exponentials to decay data (Section III.3). For a given error in the data, a family of solutions is obtained, all of which are equally acceptable. Any attempt at smoothing or noise removal in this instance would simply not be justified and could significantly alter the family of acceptable solutions.
Fig. III.4.

a) Typical ionisation efficiency curve and apparatus function from molecular beam experiments.

b) Typical exciting pulse and fluorescence decay curve using photon counting. Decay curve is for the fluorescence of the pyrene-diethylaniline exciplex.
7. A FORMAL SOLUTION

For error free data, it is an acceptable hypothesis that the expected value of an observed count (in a channel of the MCA) is that obtained from a convolution of the true count with the distorting pulse. The solution for the true function $I(k)$ is obtained by minimising the norm of the residual, that is by setting

$$\frac{\partial}{\partial I(\nu)} \left[ \sum_{k=1}^{n} \{ f(k) - \sum_{j=1}^{k} P(k-j+2) I(j) \}^2 \right] = 0$$

(III.23)

which yields a set of $n$ symmetric secular equations:

$$\sum_{\mu=1}^{n} \sum_{j=1}^{n} \left\{ P(j-\nu+1) P(j-\mu+1) \right\} I(\mu) =$$

$$\sum_{k=1}^{n-\nu+1} P(k) f(k+\nu-1).$$

If the solution obtained is reconvoluted with the pulse $P(k)$, the original function $f(k)$ will be retrieved, and the sum of squares deviation of the reconvoluted curve from the original data will be due only to any round off error introduced during computation. Figure III.5 shows a pictorial representation in the form of a contour map of the weighted sum of squares deviation (SSQR) of the reconvoluted curve from the original data.

It must be emphasized that such a treatment is suitable only for perfect data for which the expectation value of the norm of the residual in equation (III.23) is zero. An
Fig. III.5

(i) For perfect (error free) data, the expectation value of the norm of the residual in equation (III.23) is zero. By solving the set of n symmetric secular equations and calculating the goodness of fit, the least squares solution corresponding to $SSQR=0$ is obtained.

(ii) In general, the data contains experimental error, and instead of a unique solution, a family of solutions is obtained for a given error. Every member of the family, for which $SSQR^2 < SSQP$, is an equally acceptable solution.
extension of this approach to experimental data containing statistical errors invalidates this assumption and necessitates a restatement of the problem. In general, the observed function \( f(t) \) will not be known accurately, and we should restate equation (III.18) in the form

\[
\int_0^t P(t-t') I(t') \, dt' = f(t) + e(t)
\]  

(III.24)

where \( e(t) \) is the error present in observing \( f(t) \). In fluorescent lifetime measurements involving photon counting, the nature of errors is well established and so \( e(t) \) can be estimated in the following manner.

The observed function \( f(k) \) is a single sample from a population of curves which would have been obtained in repetitive experiments if the pulse introduced no statistical error in this curve. Then the weighted mean variance of the distribution of which \( f(k) \) is a single sample is

\[
\frac{1}{n} \sum_{k=1}^n \frac{1}{\bar{f}(k)}.
\]  

(III.25)

If the pulse does introduce additional error this can be estimated and included. The final error expected in \( I(k) \) will then also have this value, SSQP. Having obtained \( I(k) \) this is now reconvoluted with the pulse \( P(k) \) to obtain a reconvoluted curve \( f^0(k) \). The weighted mean variance of the fit of \( f^0(k) \) to the original data \( f(k) \) is given by
SSQR = \frac{\sum_{k=1}^{n} \left\{ \frac{1}{f(k)} \left[ f(k) - f^0(k) \right]^2 \right\}}{\sum_{k=1}^{n} \frac{1}{f(k)}} \quad (III.26)

since from equation (III.13), \( n-r-1 = n \) for 120 data points and two or four parameters, \( r \).

In terms of numerical approximation, the solution of equation (III.24) presents the same difficulty as equation (III.19). However, instead of a unique solution of (III.24) a family \( F \) of solutions is obtained for a given error \( e(t) \), and the real problem then is to choose from the family \( F \), the true solution \( I(t) \). In Figure III.5 the family of solutions for which \( SSQR = SSQP \) is shown as a contour line, the shaded portion representing a schematic for the probability distribution for the value of \( SSQP \). As all solutions are \textit{a priori} equally probable, it is necessary to inject some physical information in order to make a selection. It is at this point that the methods and needs of particular experiments differ from one another.

If the functional form of \( I(t) \) is known, a least squares fit could be used to find a best fit to \( I(t) \). However, if we do not assume \( I(t) \) to possess a known functional form, and if we wish to impose no more restriction on our result other than it should have an amount of error \( SSQP \) and contain \textit{a minimum} of information consistent with this error, any additional information is then probably wrong and the smoothest member of this
family should be selected. This is in effect applying Occam's razor. A conditional solution of this type has been developed by Phillips (1962) and of various smoothness conditions, minimisation of the norm of the second derivative of $I(t)$ is chosen. Further, the error $e(t)$ is assumed to be an arbitrary function except for a condition on the size of $e(t)$. Utilizing the method of Lagrangian multipliers, $I(t)$ is the solution which satisfies (III.24) and minimises the expression:

$$\gamma \int_0^t [I''(t')]^2 dt' + \int_0^t [e(t')]^2 dt'. \quad (III.27)$$

In this manner, for each value of $\gamma$, the undetermined multiplier, a solution $I(t)$ is obtained, and with it, an error $E$ defined by $E^2 = \int_0^t [e(t')]^2 dt'$. (The method is described below in full). The value of $\gamma$ chosen is that for which the calculated error $E$ has the desired magnitude. In attempting to rationalize the errors one could also have chosen the methods of Twomey (1963) or Strand & Westwater (1968).

The numerical method

The integral equation (III.24) is replaced by the linear system

---

† William of Occam (1300-1349), "Entia non runt multiplicanda praeter necessitatem".
\[
\sum_{i=0}^{n} k_{j,i} r_i = f_j + e_j \quad (j = 0, 1, \ldots, n)
\]  

(III.28)

where \( \langle k_{j,i} \rangle \) is the pulse matrix obtained from the excitation pulse vector, \( p(t) \); \( r \) is the unknown true fluorescence response vector, \( f \) is the observed fluorescence response and \( e \) is the minimum error consistent with the data.

The total error \( E \) in the observed data is defined by

\[
\sum_{j=0}^{n} e_j^2 = E^2
\]  

(III.29)

where \( E \) is constant.

The solution \( r^* = (r_0, r_1, \ldots, r_n) \) of equation (III.28) is chosen to be that which satisfies the condition:

\[
\sum_{i=0}^{n} (r_{i+1} - 2r_i + r_{i-1})^2 = \min_{r \in R} \sum_{i=0}^{n} (r_{i+1} - 2r_i + r_{i-1})^2
\]  

(III.30)

where \( R \) is the set of vectors satisfying (III.28) and (III.29); \( r \) is assumed to be zero outside the interval of observation, i.e. \( r_{-1} = r_{n+1} = 0 \). Utilizing the method of Lagrangian multipliers, conditions (III.29) and (III.30) are replaced by the single condition that \( r^* \) is the vector satisfying (III.28) that minimises the expression

\[
\gamma \sum_{i=0}^{n} (r_{i+1} - 2r_i + r_{i-1})^2 + \sum_{i=0}^{n} e_i^2
\]  

(III.31)
where $\gamma$ is a given positive constant. For $\gamma = 0$ the problem is reduced to that of solving equation (III.17) by the method given in equation (III.23). Let $K \equiv (k_{ji})$ denote the excitation pulse matrix (recalling that $k_{ji} = 0$ if $i > j$) and let $K^{-1} \equiv (a_{ji})$.

It can be shown (Phillips 1962) that the equations required to solve for $r^*$ and for $e$, the calculated error which corresponds to a particular $\gamma$, are:

$$r^* = (K + \gamma L)^{-1}f$$  \hspace{1cm} (III.32)

$$e = -\gamma L r^*$$  \hspace{1cm} (III.33)

where $L = (\lambda_{kk})$

and

$$\lambda_{lk} = a_{k+2,l} - 4a_{k-1,l} + 6a_{k-1,l} - 4a_{k+1,l} - a_{k+2,l}$$  \hspace{1cm} (k, l = 0, 1, \ldots, n).

The terms with negative coefficients or coefficients greater than $n$ are defined according to:

$$a_{-2,l} = a_{0,l} \quad a_{n+1,l} = 0$$
$$a_{-1,l} = 0 \quad a_{n+2,l} = -a_{n,l}$$

By iterating the parameter $\gamma$, a solution $r^*$ of the equations (III.32) and (III.33) is obtained for various values of $\gamma$, the larger the magnitude of $\gamma$, the greater the amount of smoothing.

Since the total error in the observed data is $E^2$, the value of $\gamma$ chosen is that which gives the calculated error $e$ the desired order of magnitude.
8. PRACTICAL APPLICATION

The fluorescence decay of hexafluoroacetone gas at a high enough pressure to be thermally equilibrated (>200Torr) is exponential over several orders of magnitude in intensity and has a mean lifetime of 84ns (Halpern & Ware 1970). When excited by a fast air lamp, (~4ns fwhm) this decay represents an ideal \( I(t) \).

To provide a distorting pulse, \( P(t) \), the air lamp was collected on a time scale which had been expanded by a factor of twenty, thus producing a broad \( P(t) \).

\( I(t) \) and \( P(t) \) were then convoluted using equations (III.17) to obtain \( f(t) \) as the simulated observed function (see Figure III.6).

Deconvolution was carried out using the method described above. Solutions for \( I(t) \) were obtained for various values of the smoothing parameter \( \gamma \) and in each case the error \( E \) corresponding to that value of \( \gamma \) was calculated and compared with the estimate of the Poisson error in the data, SSQP.

The advantage in this approach lay in the ability to compare the calculated \( I(t) \) with the original data and to check for any systematic deviations introduced by the method.

\[ \sum_{j=0}^{n} e_j^2 = E^2. \]
Fig. III.6  a) True fluorescence decay $I(t)$.  
b) Excitation pulse $P(t)$  
c) Fluorescence response curve $f(t)$ from convolution of $I(t)$ and $P(t)$.  

$P(t)$ and $f(t)$ have been scaled down for purposes of illustration.

Fig. III.7  Solutions $I(t)$ obtained for various values of the smoothing parameter $\gamma$.  
a) $\gamma = 0.5$  
b) $\gamma = 5.0$  
c) $\gamma = 50$  
d) Solution obtained using the method of least squares (equation III.23).
Figure III.7 shows the results obtained for some values of $\gamma$. For $\gamma = 0$, the solution obtained corresponds to the exact matrix inversion technique, where the solution is oscillatory. It becomes immediately apparent that the choice of $\gamma$ (see Figure III.7c) for which the error $E$ is of the same order as SSQP, does not represent the best solution.

Some spurious structure has been produced in the solution, which increases as $\gamma$ is further increased. It was found that even for small errors in the data, the method introduced unwanted structure in the solution $I(t)$ and, with data containing large statistical error, there were no values of $\gamma$ for which physically sensible results could be obtained.

The explanation lies in the inherent nature of the method, which constrains the solution to be non-oscillatory (by minimization of the second derivative) yet contain an error which is only limited in its summed magnitude. Thus, a slowly varying modulation will satisfy both conditions and yield the solutions shown above. Though mathematically acceptable, this is not consistent with the true physical situation where the error is randomly distributed and is therefore a high frequency component.

Values calculated for SSQR corresponding to various $\gamma$ are shown in Table III.4. It can be seen that owing to the non-arbitrary distribution of the error $E$ inserted
in the solution, the expected increase in SSQR does not eventuate as the parameter $\gamma$ is increased.

**TABLE III.4**

<table>
<thead>
<tr>
<th>$\gamma$</th>
<th>$E \times 10^4$</th>
<th>SSQR $\times 10^6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.225</td>
<td>0.628</td>
</tr>
<tr>
<td>0.5</td>
<td>0.154</td>
<td>0.686</td>
</tr>
<tr>
<td>5.0</td>
<td>0.837</td>
<td>0.212</td>
</tr>
<tr>
<td>10.0</td>
<td>0.725</td>
<td>0.058</td>
</tr>
<tr>
<td>15.0</td>
<td>0.825</td>
<td>0.046</td>
</tr>
<tr>
<td>50.0</td>
<td>1.376</td>
<td>0.158</td>
</tr>
</tbody>
</table>

It thus becomes difficult to justify the choice of $\gamma$ for which the most acceptable solution is obtained, and furthermore, when the nature of the true function is not known, there is no way in which the $\gamma$ corresponding to the most acceptable solution can be chosen.

9. **CONVOLUTING AND FITTING WITH THE NULL HYPOTHESIS**

Rather than deconvolution, it is felt that an *a priori* theory should be directly postulated to define the true decay curve and then tested to determine its validity, which is, after all, the accepted method of testing a theory.
The simplest analytical function for \( I(t) \), for example a single exponential (equation (III.11)), is convoluted (equation (III.17)) with the pulse. Appropriate starting values for the parameters \( A, \tau \) are chosen and the least squares sum is minimised with respect to \( A, \tau \).

The null hypothesis, in the statistical sense is then applied to see if the fit to the observed function \( f(t) \), given by the ratio \( \text{SSQR/SSQP} \), is so poor as to invalidate the hypothesized function. If so, further complexity must be introduced until this is no longer the case.

For exceedingly short decays, it is a case of the decay lifetime distorting the pulse and the lower limit of time measurement is theoretically set only by the precision of the data. In practice it has been possible to measure lifetimes reproducibly down to as short as 0.5ns. The spread of transit time of the photomultiplier tube introduces considerable uncertainty for lifetimes shorter than 0.5ns.

In measuring lifetimes of such short duration, the ideal experiment would involve measuring the fluorescence decay curve and the excitation pulse simultaneously. This is necessary because flash lamp characteristics, which are a function of gas purity, electrode environment and temperature, change with time. Collecting the lamp before or after collecting the decay curve may often produce a spurious result, as is evident from the data presented in Table III.5. The lifetime of azulene vapour (refer to
Section V.10 determined using pulse data collected before collecting the decay curve, varies by as much as 30% from the correct value of 2.1 ns.

**TABLE III.5**

<table>
<thead>
<tr>
<th>Measurement</th>
<th>λex(nm)</th>
<th>τ(ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>337.1</td>
<td>2.0</td>
</tr>
<tr>
<td>2</td>
<td>337.1</td>
<td>1.6</td>
</tr>
<tr>
<td>3</td>
<td>337.1</td>
<td>2.3</td>
</tr>
<tr>
<td>4</td>
<td>337.1</td>
<td>2.9</td>
</tr>
</tbody>
</table>

To measure both pulse and decay curves simultaneously, one would need two separate detection systems. However, a substantial improvement can be obtained by collecting the pulse and decay curves in separate halves of the MCA memory and alternating from one to the other several times during a run. (The pulse is collected by substituting a mirror in place of the sample). If this procedure is used, the results are quite satisfactory (Table III.6).
TABLE III.6

Variation of measured lifetime of azulene vapour when pulse and decay curves are collected by alternating from one to the other several times.

<table>
<thead>
<tr>
<th>Measurement</th>
<th>λex(nm)</th>
<th>τ(ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>337.1</td>
<td>2.09</td>
</tr>
<tr>
<td>2</td>
<td>337.1</td>
<td>2.12</td>
</tr>
<tr>
<td>3</td>
<td>337.1</td>
<td>2.14</td>
</tr>
<tr>
<td>4</td>
<td>337.1</td>
<td>2.01</td>
</tr>
</tbody>
</table>

Since convolution involves integration, no restrictions need be imposed on the nature of the response and pulse curves. For the example cited above in Figure III.4, arbitrary truncation of the data is desirable to examine in more detail an initial part of the decay curve and is perfectly acceptable.

Furthermore, the confidence limits that are chosen in accepting or rejecting a solution must be stated explicitly and can be established according to the needs of an experiment.

To ensure rejecting a theory which may be wrong, one does not proceed to the function of increased complexity unless the error in fitting is larger than acceptable at given confidence limits.
To ensure accepting a theory which may be correct, one can continue to functions of increasing complexity until the error in fitting is smaller than acceptable at given confidence limits.

In relation to Figure III.5 this means, for the former strategy, approaching the probability distribution in a direction of decreasing error (from the top) and stopping at a given level on the usual side of the error distribution. For the latter strategy, one would continue through the most probable contour to the low error confidence level of the distribution.
CHAPTER IV

EXCIPLEXES

The transfer of electronic excitation energy between molecules or groups of molecules has long been of interest to workers in many areas of physics, chemistry and biology. In particular, it has been revealed that in many photochemical processes, the sharing of electronic excitation energy by two or more molecules is a primary step in the reaction mechanism. Early studies of molecular complexes laid foundations for intensive investigations in this area of research.

The formation of molecular complexes from aromatic entities which are themselves otherwise stable is a widely established phenomenon. Complex formation is usually accompanied by a new and characteristic absorption band. The concept of donor-acceptor interaction was developed by Mulliken (1952 a,b) and extended by McGlynn (1958) to give a satisfactory account of molecular complexing. This theoretical framework invoked a "charge transfer transition" which referred to the intermolecular process whereby an electron was partially or wholly transferred from one component of the complex to the other. The properties of
ground state molecular complexes have been comprehensively reviewed by Briegleb (1961) and by Mulliken & Person (1962).

Excimer formation was discovered by Förster & Kasper (1954). The fluorescence spectrum of pyrene in solution was found to undergo a concentration dependent change whilst no accompanying change could be observed in the absorption spectrum. This phenomenon was interpreted as being due to the association of an electronically excited pyrene molecule with another pyrene molecule in the ground state. The term excimer was attributed to this excited state dimer which, unlike the Mulliken charge transfer complex, was unstable in the ground state. However, the importance of charge-transfer states in the wavefunction of the excimer was soon recognized by Ferguson (1958). The excimer can be considered to be a single excited species in which the electrons of the two molecules are mutually coupled by exchange. Since this description does not require close resonance of the energy levels of the participating molecules, it was not surprising that Leonhardt & Weller (1963) produced experimental evidence for the formation of excited state molecular complexes involving molecules of different electronic structure. Whilst investigating fluorescence quenching of aromatic hydrocarbons (A) by typical electron donors (D), it was found that a charge transfer complex formed in the excited state (an exciplex) provided a path for the quenching of fluorescence. The intensity of the fluorescence spectrum of perylene was found to diminish as increasing amounts of dimethylaniline were added and
simultaneously, a broad, structureless emission approximately 5000 cm\(^{-1}\) lower in energy appeared. Subsequently, the role of exciplex formation in fluorescence quenching has been extensively investigated.

1. CHARGE TRANSFER CHARACTER OF EXCIPLLEXES.

The charge transfer nature of exciplexes can be indirectly demonstrated by flash photolysis studies. Transient absorption spectra due to the radical ions A\(^{-}\) and D\(^{+}\) have been observed (Leonhardt & Weller 1963; Mataga & Ezumi 1967; Knibbe, Rehm & Weller 1968; Koizumi & Yamashita 1968).

Direct estimations of exciplex dipole moments have generally been obtained by measuring the energy of the exciplex emission maximum as a function of the dielectric constant of the solvent (Knibbe & Weller 1967; Knibbe, Rehm & Weller 1968). Electron affinity and ionisation potential data are needed in this method of estimating the charge transfer character of exciplexes. The results are therefore likely to be unreliable since, not only is there a large scatter in the published values of electron affinities and ionisation potentials (Blaunstein & Christophorou 1971), but as well their usage cannot be justified in an experimental environment which differs in terms of solvent and in the involvement of excited states.

Selinger & McDonald (1972) have examined the behaviour of exciplexes in polar solvents and analysed the effect of
solvent viscosity as well as dielectric constant. They have shown that the quenching of the primarily excited species is independent of solvent polarity but decreases as usual with increasing viscosity. By measuring the dependence of the ratio of exciplex : monomer emission intensities on solvent polarity in solvents of similar viscosity, a measure of the degree to which charge has been transferred can be obtained. This result is independent of the values of electron affinities and ionization potentials.

2. MECHANISM OF EXCIPLEX FORMATION.

Studies by Weller and then Mataga have shown that exciplexes are formed between many different substituted aromatic hydrocarbons and between aromatic hydrocarbons and amines. The species with the highest value of the sum of electron affinity and ionisation potential is assumed to be the electron acceptor. Amines are generally electron donors and the hydrocarbons are acceptors. Knibbe & Weller (1967) have shown that exciplexes may be formed by exciting the electron donor (D) in some cases and the acceptor (A) in others. They use a classification based on the absorption spectra of the donor and the acceptor. I. Where the acceptor absorbs at lower energy than the donor, the acceptor is the initially excited species.
The following mechanism has been suggested for donor-acceptor pairs such as diethylaniline-pyrene, diethylaniline-perylene and diethylaniline-anthracene.

\[ D + A^* \xrightarrow{k_a} (AD)^* \xleftarrow{k_d} A \]

\[ A + h\nu \rightarrow A \quad A + D + h\nu' \rightarrow A + D \]

II. Where the acceptor molecule absorbs at higher energy than the donor, as in the case of naphthalene-diethylaniline, biphenyl-diethylaniline, an alternative mechanism is assumed to operate:

\[ D^* + A \xrightarrow{k_a} (AD)^* \xleftarrow{k_d} A \]

\[ D + h\nu \rightarrow D \quad A + D + h\nu' \rightarrow A + D \]

\[ k_e \quad k_q \quad k'_e \quad k'_q \]

† \( k_e \) and \( k'_e \) are the radiative transition probabilities for \( A^* \) and exciplex respectively; \( k_q \) and \( k'_q \) are the corresponding unimolecular non-radiative transition probabilities; \( k_a \) and \( k_d \) are the associative (bimolecular) and dissociative rate parameters.
In polar solvents, solvated ion-pair formation may also contribute towards non-radiative deactivation of the exciplex. However, the discussion to follow will be restricted to non-polar solvents so that this mode of deactivation can be neglected.

The description proposed by Weller suggested that particular donor-acceptor pairs could be classified according to whether an exciplex was formed via mechanism (I) or mechanism (II). In fact, there is no apparent reason why a given donor-acceptor pair should not form an exciplex as a result of both (I) and (II).

McDonald & Selinger (1971) established by selectively exciting either A or D that it was possible to form an exciplex via excitation of either species in a given donor-acceptor pair. Each species must be selectively excited in the presence of a suitable concentration of the other. This condition is easily fulfilled in the long wavelength region where only one species absorbs. At shorter wavelengths, there is competitive absorption and in many cases it is not possible to excite the second species selectively whilst having a sufficient concentration of the other to produce exciplex emission. Three donor-acceptor pairs were found to be amenable to selective excitation: diethylaniline-naphthalene, diethylaniline-biphenyl and naphthalene-l-cyanonaphthalene.

The fluorescence spectra obtained for the naphthalene-diethylaniline exciplex are shown in Figure IV.1. In each case the fluorescence of the primarily excited species is
Fig. IV.2 Fluorescence decay curves showing the effect of selective excitation on the build up of exciplex fluorescence intensity for donor-acceptor pairs:

a) naphthalene-diethylaniline,  
b) 1-cyanonaphthalene-naphthalene,  
c) biphenyl-diethylaniline. Calibration is 0.63 ns/channel

* denotes initially excited species.
quenched in accordance with the Stern-Volmer relation.

Two questions immediately arise from these results and can be stated as follows:

(a) Is it in fact the same exciplex which is formed by excitation of A and by excitation of D? It is not immediately obvious from the nature of the exciplex emission (Figure IV.1) that this is necessarily the case.

(b) Is it possible to exclude the alternative mechanism whereby energy transfer to the longer wavelength absorbing species is a primary step prior to the formation of exciplex? The quenching experiments can give no information regarding the time scale of this possible process.

Question (a) can be answered by determining the fluorescence lifetime \(1/(k_\epsilon^r + k_\delta^r)\) of the exciplex emission for both cases of the acceptor or donor being excited selectively. It is necessary therefore that both the excitation and emission bandpass be small. Using the photon counting lifetime apparatus, it was found that both the exciting light and the fluorescence emission could be selected using monochromators. The discussion of question (b) is better left until the time dependent studies have been presented.
3. TIME DEPENDENT STUDIES OF EXCIPEX FORMATION

Experimental

Fluorescence was excited using the low pressure nanosecond flash lamp (Section II.5) through a Bausch & Lomb double grating monochromator. The exciting radiation had a bandwidth of 2nm. The emission was viewed at 45° by a Phillips 56DUVP/03 photomultiplier through a second monochromator (Bausch & Lomb "high intensity" type with variable slits). Decay measurements were carried out at 23°C.

Samples were prepared using spectroscopic grade solvents and held in a suprasil cell. Naphthalene was purified by zone refining and recrystallisation; biphenyl was treated with KMnO$_4$, sublimed and zone refined; 1-cyanonaphthalene was recrystallised and sublimed under vacuum. Diethylaniline was refluxed with acetic anhydride and distilled; it was stored under nitrogen in the dark.

Solutions were deoxygenated by prolonged bubbling with high purity dry nitrogen. This method was found satisfactory, although it has previously found criticism. The measured lifetime of naphthalene using this method of deoxygenation was found to agree with measurements of other workers (Aladekomo & Birks 1965; Mataga, Tomura & Nishimura 1965), who effected removal of oxygen by freeze-thaw cycles. The long lifetime of naphthalene in cyclohexane solution (119ns) ensures that the measured lifetime is a critical test
of the efficiency of the process used for deoxygenation.

For higher temperature studies, the sample cell was surrounded by a water jacket in the form of a clear silica dewar containing distilled water. Temperature control was maintained by means of an immersion heater and thermostat.

Results

Fluorescence decay curves for the naphthalene-diethylaniline, 1-cyanonaphthalene-naphthalene and biphenyl-diethylaniline exciplex systems are shown in Figure (P. 87) IV.2. The outstanding feature of these results is that the overall time dependence of the exciplex fluorescence depends upon the excitation wavelength and thus depends on which species is initially excited. In each case, the shorter wavelength excitation gives rise to an initial build-up in the exciplex emission intensity, followed by subsequent decay. Lower energy excitation does not result in a long build-up. The kinetic scheme proposed for exciplex formation leads to a description of the time dependence which predicts the initial build-up of the emission. Analogous to the case of the excimer, the differential equations expressing the concentrations of \( A^* \) (or \( D^* \)) and \((AD^*)\) in terms of the rate parameters are:

\[
\frac{d[A^*]}{dt} = -n[A^*] + k_d [AD^*] \quad \text{(IV.1)}
\]
\[
\frac{d[AD^*]}{dt} = -n'[AD^*] + k_a [A^*][D] \quad \text{(IV.2)}
\]

where \( n = \kappa_e + \kappa_q + k_a[D] \) and \( n' = \kappa'_e + \kappa'_q + k'_d \).
Fig. IV.1 a) Fluorescence spectrum of diethylamine (0.09M in cyclohexane) with different concentrations of naphthalene. Excitation at 316nm.

Fig. IV.1 b) Fluorescence spectrum of naphthalene (0.17M in cyclohexane) with different concentrations of diethylamine. Excitation at 285nm.
The equations may be solved to give the normalised intensities $I, I'$ of the monomer and exciplex fluorescence emission as a function of time.

\begin{align*}
I(t) &= \frac{k_e e}{\lambda_2 - \lambda_1} \left\{ (\lambda_2 - n)e^{-\lambda_1 t} + (n - \lambda_1)e^{-\lambda_2 t} \right\} \quad \text{(IV.3)} \\
I'(t) &= \frac{k'k_a[D]}{\lambda_2 - \lambda_1} \left\{ e^{-\lambda_1 t} - e^{-\lambda_2 t} \right\} \quad \text{(IV.4)}
\end{align*}

where $\lambda_{1,2} = \frac{h}{n+n'} \pm \sqrt{(n-n')^2 + 4k_a k_d[D]}$ \quad \text{(IV.5)}

The form of equation (IV.4) is such that at time $t = 0$ (the time at which the system is initially excited by the pulse) the intensity of exciplex emission is also zero. The expression consists of a difference of two exponentials and the intensity function shows a build-up to a maximum followed by a decay. The maximum in exciplex emission intensity can be obtained by differentiating equation (IV.4) and setting the derivative to zero, thus obtaining

\begin{equation}
t_{\text{max}} = \frac{\ln (\lambda_2/\lambda_1)}{\lambda_2 - \lambda_1} \quad \text{(IV.6)}
\end{equation}

Bearing in mind that this mechanism proposes that exciplex formation occurs as a result of a collisional encounter between the excited and unexcited species, we may turn once more to the data presented in Figure IV.2.

For the naphthalene-diethylaniline exciplex, excitation at 285nm of a solution of $2 \times 10^{-1}$M naphthalene (N) and $3 \times 10^{-3}$M diethylaniline (DEA) in cyclohexane selectively promotes naphthalene to its first excited state. The formation of exciplex results from a collision between N* and DEA. The intensity of exciplex emission
reaches a maximum 36ns after the excitation flash. A solution of $2 \times 10^{-3}$ M naphthalene and $2 \times 10^{-2}$ M diethylaniline excited at 316nm ensures selective excitation of diethylaniline so that in this case, exciplex formation involves a collision between DEA* and N. The observed fluorescence decay curve shows only a small time delay (the finite width of the excitation pulse is partly responsible for the build-up).

Similar results are observed for the 1-cyanonaphthalene-naphthalene exciplex. Where naphthalene is the excited species, the time delay is found to be 34ns. If 1-cyanonaphthalene (CNN) is excited, a much shorter (10ns) time delay is observed. For the system, biphenyl (B) - diethylaniline, a time delay of 8ns is observed for exciplex formation involving B* and DEA, which is considerably shorter than for the delays involving N* in the previous two systems. A small time delay is again observed when diethylaniline is the initially excited species. The results are summarised in Table IV.1, together with the measured lifetime of monomer fluorescence for each of the molecules studied.

It can be seen that there is a correlation between the observed (monomer) lifetime of the initially excited species and the magnitude of the time delay in the fluorescence decay curve of the exciplex. This may be intuitively understood if we consider the diffusion process involved in the formation of an exciplex.
TABLE IV.1

<table>
<thead>
<tr>
<th></th>
<th>$\tau^*$ (ns)</th>
<th>$\lambda_{ex}$ (nm)</th>
<th>Time delay (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphthalene (*) 0.18 M Diethylaniline 0.003 M</td>
<td>119</td>
<td>285</td>
<td>36±2</td>
</tr>
<tr>
<td>Diethylaniline (*) 0.02 M Naphthalene 0.002 M</td>
<td>3.4</td>
<td>316</td>
<td>≈2</td>
</tr>
<tr>
<td>Naphthalene (*) 0.05 M 1-Cyanonaphthalene 0.0016 M</td>
<td>119</td>
<td>255</td>
<td>34±2</td>
</tr>
<tr>
<td>1-Cyanonaphthalene (*) 0.001 M Naphthalene 0.006 M</td>
<td>17</td>
<td>316</td>
<td>10±1</td>
</tr>
<tr>
<td>Biphenyl (*) 0.15 M Diethylaniline 0.005 M</td>
<td>15</td>
<td>240</td>
<td>8±1</td>
</tr>
<tr>
<td>Diethylaniline (*) 0.014 M Biphenyl 0.051 M</td>
<td>3.4</td>
<td>316</td>
<td>≈2</td>
</tr>
</tbody>
</table>

(*) denotes initially excited species

$\tau^*$ is the observed lifetime of the initially excited species measured in cyclohexane (10$^{-4}$ M)

$\lambda_{ex}$ is the wavelength of excitation.

If exciplex formation is to occur, it must do so before the initially excited species is deactivated by some competing process (emission or non-radiative decay). Thus the mean lifetime of the initially excited species (say A*) places a lower limit on the concentration of D needed to form a given concentration of exciplex and an upper limit on the time at which the concentration of exciplex reaches a maximum. The factors determining the time delay are apparent from equation (IV.6) above and include the concentration of the unexcited species, the rates of formation and dissociation of the excited complex, and...
the rates of deactivation of both the initially excited species and the exciplex. A full quantitative comparison between experiment and theory must await evaluation of all the rate parameters in equations (IV.1) - (IV.6), measured for these experimental conditions.

4. THE POSSIBILITY OF ENERGY TRANSFER AS A PRIMARY STEP

It was postulated above, (question (b)), that, if the initially excited species in a given donor-acceptor pair absorbs at higher energy than the unexcited species, energy transfer may occur prior to exciplex formation.

If we consider the results obtained with naphthalene-diethylaniline, when naphthalene is selectively excited, there is a delay of \( \sim 36 \text{ ns} \) before the exciplex emission maximum is reached. We can therefore exclude the possibility of rapid \( (>10^9 \text{s}^{-1}) \) long-range (resonance) transfer of energy to diethylaniline since exciplex formation would then necessarily have to occur within the mean lifetime of diethylaniline. A delay of 36ns could not be possible.

However, one cannot eliminate the possibility that energy transfer occurs within the collision complex immediately prior to electron transfer.

5. EXCIPLLEX DECAY TIMES

Assuming the mechanism of formation to be analogous to the excimer case, the time dependence of exciplex
fluorescence emission can be represented by equation (IV.4). The decay time, $\tau$ of the initially excited species and the decay time, $\tau'$ of the exciplex are defined by the relationships

$$\tau = \frac{1}{k_e + k_q} \quad \text{(IV.7)}$$

$$\tau' = \frac{1}{k_e' + k_q'} \quad \text{(IV.8)}$$

The decay parameters, $\lambda_1$ and $\lambda_2$ from equation (IV.5), define respectively the overall rate of depletion of exciplex and of monomer. They include the contributions due to $k_a$ and $k_d$. Use of a mixture of exponentials (equation (IV.4)) to analyse the exciplex fluorescence decay curve would give the decay parameters $\lambda_1, \lambda_2$ and not the pure lifetimes. Without knowing the values of $k_a$ and $k_d$, the exciplex decay time cannot be obtained from such an analysis. However, it is possible to define conditions under which the decay parameters, $\lambda_1$ and $\lambda_2$ become good approximations to $1/\tau'$ and $1/\tau$ respectively. This may be seen from the following discussion.

The proposal is to define two regions which can be characterized by the relative rate of dissociation ($k_d$) versus rate of deactivation ($k'_e + k'_q$). Cohen & Selinger (1969) made such a comparison for the general case of fluorescence quenching via the formation of a quench complex.

An $\alpha$ region is defined by the condition $k_d >> k'_e + k'_q$ so that a quasi-equilibrium between $A^* + D$ and $(AD)^*$ is maintained in the excited state. The equilibrium is not
influenced by the rates of deactivation.

β conditions prevail when $k_d << k_e' + k_q'$. In this case, a complex, once it is formed, will deactivate rather than dissociate.

The experimental parameters which influence the relative rates of dissociation and deactivation are viscosity, temperature, the nature of $A$ (i.e. the magnitude of $\Delta H^*$, the enthalpy for exciplex formation) for a given $D$, and the concentrations.

To determine whether α or β conditions prevail, a small amount of additional quenching for the complex may be added. The additional quenching can be provided by oxygen, this procedure being known as the "oxygen test". Under α conditions, $k_d >> k_e' + k_q' + k_{O_2}$ and so the ratio $I'/I$, given by equation (IV.9), is not affected.

$$\frac{I'}{I} = \frac{k_e'}{k_e} \cdot \frac{k_a[A]}{k_e' + k_q' + k_d} \quad \text{(IV.9)}$$

Under β conditions, $k_d << k_e' + k_q'$ and $I'/I$ is inversely proportional to $k_e' + k_q' + k_{O_2}$ and is therefore reduced by the addition of oxygen.

We may turn once more to the definition of the decay parameters $\lambda_1$ and $\lambda_2$ given by equation (IV.5). It is easily shown that for β conditions, equation (IV.5) simplifies to yield

$$\lambda_1 = k_e' + k_q' = \frac{1}{\tau'} \quad \text{(IV.10)}$$

$$\lambda_2 = k_e + k_q = \frac{1}{\tau} \quad \text{(IV.11)}$$

Thus when β conditions prevail, the whole decay curve corresponding to exciplex emission can be analysed in
terms of the decay parameters $\lambda_1$, $\lambda_2$ which will enable the exciplex lifetime to be obtained. Cohen & Selinger (1969) have pointed out that the dependence of $I'/I$ on the addition of oxygen is a necessary but not sufficient criterion for $\beta$ conditions. This is apparent since, if the relative rates of deactivation and dissociation are roughly equal, i.e. $k'_e + k'_q \approx k_d$, $I'/I$ will depend on $[O_2]$ even though it will not be strictly proportional to $1/(k'_e + k'_q + k'_O_2)$. $\beta$ conditions are defined according to the strict inequality $k_d \ll k'_e + k'_q$ and it is this condition which must be met rather than the observation of a "positive" result when the oxygen test is applied. The temperature dependence of $I'/I$ reveals that, at $23^\circ$C, only the biphenyl-diethylaniline exciplex is well in the $\beta$ region (McDonald & Selinger 1971). The naphthalene-diethylaniline and 1-cyanonaphthalene-naphthalene exciplexes are not strictly in $\alpha$ or in $\beta$ conditions at $23^\circ$C. Thus it must be conceded that the "lifetimes" of the naphthalene-diethylaniline and 1-cyanonaphthalene-naphthalene exciplexes, when measured at room temperature, in fact correspond to a measure of the decay parameter $\lambda_1$ and not to the true lifetime $\tau'$. For the biphenyl-diethylaniline exciplex, the correct value for $\tau'$ are obtained at $23^\circ$C.

It is not obvious from the decay curves in Figure IV.2 whether the actual decay time of the exciplex is the same for selective excitation of either A or D. This is partly because the plots of intensity versus time are on a linear scale (to best illustrate the build-up) but also due
to the fact that the build-up is not the same for all curves. To obtain the exciplex decay time (either $\tau'$ or $1/\lambda_1$, depending on whether or not $k_d << k'_d + k'_\text{e}$) it would be necessary to analyse the decay curve in terms of two exponentials (equation IV.4). However, Birks, Dyson & Munro (1963) have shown that it is sufficient to fit a single exponential to the "tail" emission (the emission occurring considerably later than the initial build-up). It is necessary, therefore, to collect the decay curve using a longer time scale than is shown in Figure IV.2 and to analyse the later section of the decay. Decay times obtained in this manner are summarised in Table IV.2.

**TABLE IV.2.**

Exciplex Decay Times in Cyclohexane for Selective Excitation of either Donor or Acceptor. Asterisk denotes initially excited species

<table>
<thead>
<tr>
<th>Donor</th>
<th>Acceptor</th>
<th>Excitation Wavelength (nm)</th>
<th>Decay time (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>diethylaniline*</td>
<td>naphthalene</td>
<td>316</td>
<td>27.4</td>
</tr>
<tr>
<td>diethylaniline</td>
<td>naphthalene*</td>
<td>285</td>
<td>27.0</td>
</tr>
<tr>
<td>diethylaniline*</td>
<td>biphenyl</td>
<td>316</td>
<td>18.0</td>
</tr>
<tr>
<td>diethylaniline</td>
<td>biphenyl*</td>
<td>240</td>
<td>18.1</td>
</tr>
<tr>
<td>naphthalene*</td>
<td>1-cyanonaphthalene</td>
<td>255</td>
<td>26.0</td>
</tr>
<tr>
<td>naphthalene</td>
<td>1-cyanonaphthalene*</td>
<td>316</td>
<td>26.3</td>
</tr>
</tbody>
</table>

Within the limits of experimental error, the decay times are independent of whether the donor or acceptor is
the initially excited species. It should be noted that even if the decay time is not the true lifetime, the observation that it does not change when one or other species is excited remains a sufficient answer to question (a) proposed above (section IV.2). Namely, the same exciplex is formed when either the donor or the acceptor is the primarily excited species.

Variation in time delay

Under β conditions, the time delay has been shown to be a measure of $k_a$ for the pyrene excimer in solutions of different viscosities (Speed & Selinger 1969). Similar results have been observed for exciplexes (Knight 1968; Knight, Speed & Selinger 1969). As the conditions are changed from β to α, the time delay is correspondingly reduced. Under strictly α conditions, the associative and dissociative rates, $k_a, k_d$ are much faster than the rates of deactivation of the exciplex. The delay under α conditions is very short in comparison with the exciplex lifetime and it is not observed on the time scale over which the exciplex lifetime is normally measured. This is so for the naphthalene excimer at room temperature. By increasing the temperature, the naphthalene*—diethylaniline exciplex can be forced into the α region and the delay is found to shorten progressively until at ~45°C it becomes too short to measure. A similar behaviour is observed for the naphthalene*—1-cyanonaphthalene
exciplex at 50°C. In contrast, the biphenyl*-diethylaniline exciplex still exhibits a delay of ~5ns when the temperature is raised to 70°C. (The latter system is the only one which lies well in the β region at 23°C). With respect to time delay, the distinction between α and β regions is only a matter of degree. True α conditions are said to prevail when there is no measurable time delay.

When there is a measurable time delay, the β condition $k_d < k' + k_q$ applies although the ratio $k_d/(k' + k_q)$ continues to decrease with decreasing temperature or increasing solvent viscosity. There is no definitive point at which one can say that $k_d << k' + k_q$ since the time delay simply increases until the associative rate, which also depends on viscosity, becomes too small for exciplex formation to be detected.
In past years, the study of emission spectra of polyatomic molecules has been performed principally in condensed phases, namely in solutions, in rigid glasses and in solid matrices. These investigations have provided a vast range of experimental data from which the following broad generalisations concerning emission from condensed media can be made.

Radiative transitions from states higher than the lowest excited state of a given multiplicity are not often observed. Non-radiative relaxation to lower states tends to overwhelm any radiative process so that the quantum yield of emission is too low to be observed with current techniques. Azulene and certain azulene derivatives are a rare exception to this rule (Beer & Longuet-Higgins 1955; Viswanath & Kasha 1956; Binsch, Heilbronner, Jankow & Schmidt 1967).

Spectral characteristics of emission are independent of which (bound) excited state, of a given multiplicity, is initially excited. As a general rule, quantum yields of
emission are less than unity.

The observed rate of radiative decay is found to be exponential with a mean lifetime $\tau$, this usually being smaller than the radiative lifetime $\tau_r$ calculated from the oscillator strength of absorption. The observed mean lifetime is expressed in the form

$$\tau = 1/(k_r + k_{nr})$$  \hspace{1cm} (V.1)

where $k_{nr}$ is the sum of all unimolecular non-radiative decay processes and $k_r$ is the reciprocal of the radiative lifetime $\tau_r$.

The fluorescence quantum yield $Y$ may be defined in terms of $k_r$ and $k_{nr}$

$$Y = k_r/(k_r + k_{nr}) = \tau/\tau_r$$  \hspace{1cm} (V.2)

from which one obtains the overall non-radiative decay rate $k_{nr}$ in terms of the observed lifetime and quantum yield

$$k_{nr} = 1/\tau_{nr} = (1-Y)/\tau$$  \hspace{1cm} (V.3)

The radiative lifetime $\tau_r$ can be estimated from the integrated intensity of the appropriate absorption transition using the relation derived by Strickler & Berg (1962). For strongly allowed, broad band transitions, the calculated radiative lifetime is normally in reasonable agreement with the experimental value obtained from the observed lifetime and quantum yield (using equation (V.2.)) In many instances, however, the assumptions inherent in the Strickler & Berg relationship are invalid and this leads to a poor estimate of the radiative lifetime.
The phenomenon of non-radiative decay has attracted a great deal of theoretical interest since the concept of a "radiationless transition" was first introduced by Zener (1932). The principal theoretical discussions regarding radiationless processes in condensed phases have been reviewed by Henry & Kasha (1968). At that stage it appeared that experiment and theory, at least on a qualitative basis, were in close accord.

The past bias towards the study of molecular emission spectra in condensed phases has been due mainly to experimental convenience. In addition, solid matrices have provided the only means by which molecules may be studied in a fixed, known orientation. At temperatures near absolute zero (at which the majority of materials are solid) spectra are considerably simplified since sequence structure is virtually eliminated. Furthermore, condensed phases are the natural media in which the effect of environmental perturbations may be determined.

The need for complementary information concerning molecules which are not subject to any environmental influence has provided motivation for the study of emission from gaseous systems. Other than providing conditions which allow environmental complications to be circumvented, gas phase studies enable the emissive properties of higher vibrational states of an excited electronic state to be probed.
Until the beginning of the last decade, experimental limitations have attenuated progress in the investigation of gas phase luminescence. The low vapour pressure and consequent low optical density of many materials precluded any study whatsoever. However, with the advent of improved excitation sources in the form of high pressure xenon and xenon mercury arcs, high intensity nanosecond flash lamps, and lasers, such research is now possible. Improved spectral and temporal response characteristics of photomultiplier tubes, together with new signal averaging and single photon techniques have enabled detection of exceedingly weak emission. In particular, investigation of the luminescence properties of very low pressures of gases has yielded information concerning the behaviour of a molecule which is essentially isolated during its excited state lifetime.

1. RADIATIONLESS TRANSITIONS IN ISOLATED MOLECULES

Earlier theories of radiationless transitions were based on the implicit assumption that the coupling between the molecule and its surroundings was essential for the occurrence of a radiationless process. Gouterman (1962) treated radiationless transitions by analogy with radiative transitions but restricted discussion to the case of a solute molecule embedded in a crystalline solvent of another. The force field set up by the phonons of the solvent provided the necessary perturbation for a
radiationless transition. Although qualitatively successful, the theory was of restricted use.

The representation of radiationless processes in terms of the time evolution of an initially prepared state of the solute, which is coupled to a set of nearly degenerate non-stationary states of the system (solute + solvent) was introduced by Robinson & Frosch (1962, 1963). The system Hamiltonian is defined as $H_0 + H'$ where $H'$ is the perturbation which causes the zero order states to be non-stationary. $H'$ arises from coulombic interactions among the electrons and nuclei of the system. Together with the investigations of Ross and co-workers (Hunt, McCoy & Ross, 1962; Byrne, McCoy & Ross 1965), the contention arose that the rate determining step for radiationless transitions is an intramolecular process. The medium provides a manifold of states approximately degenerate with the excited state and a sink for vibrational relaxation processes.

Sufficient experimental evidence has now been gathered from gas phase emission studies to demonstrate conclusively that radiationless processes can take place in an isolated molecule. For example, the quantum yield of benzene is found to be independent of pressure at pressures below 0.1Torr, the limiting value being $Y = 0.34$ (Kistiakowsky & Parmenter 1965; Anderson & Kistiakowsky 1968; Douglas & Mathews 1968). Formation of benzene in its triplet state accounts for a major part of the non-radiative decay (Ishikawa & Noyes 1962; Cundall & Davies 1966) and identifies the process of intersystem
crossing (radiationless transition between electronic states of unlike multiplicity). Under normal experimental conditions, no fluorescence corresponding to emission from the second excited singlet state could be observed from naphthalene vapour at low pressure (Stockburger 1962; Watts & Strickler 1966). The emission arising as a result of excitation into the second singlet state, although diffuse, resembles that arising from the first singlet state and corresponds to emission from highly excited vibrational levels of $S_1$. The process of internal conversion (radiationless transition between states of the same multiplicity) is considered to be responsible for the lack of $S_2$ emission.

It is apparent that the overall behaviour of isolated molecules differs little from the behaviour of molecules in condensed phases. The mechanisms which are responsible for intersystem crossing and internal conversion (collectively termed *electronic relaxation*) must also be instrumental in determining relaxation phenomena in dense media.

Recent theoretical discussions led by Siebrand (1966), Lin (1966), Robinson (1967), Bixon & Jortner (1968, 1969), and Rhodes, Henry & Kasha (1969) have added considerable insight to the mechanism of electronic relaxation. However, within the last three years, experimental studies have provided remarkably intricate details concerning the character of individual vibronic levels of isolated molecules. Theories of electronic relaxation have been forced to
consider a range of observations far more subtle than those presented in Kasha's earlier reviews (Kasha 1966; Henry & Kasha 1968). Some of the most recent of these experimental studies will be summarised since a clear perspective of these works is essential if one is to correctly interpret the fluorescence decay studies presented in this thesis.

2. FLUORESCENCE OF AROMATIC VAPOURS AT LOW PRESSURE

In 1969, Parmenter & Schuyler presented the results of an elegant experiment in which they had obtained fluorescence spectra from single vibrational levels of the first excited singlet state of benzene vapour. The concept of resonance fluorescence is well known in atomic spectroscopy and it may be inferred that emission from individual rotational levels of a molecule is the analogous case in molecular spectroscopy. However, in large molecules, rotational levels are often not optically separable and the rotational band contour as a whole is attributed to a certain vibronic level. Resonance fluorescence refers to emission from a vibronic level which is populated in the primary step of excitation.

The essential conditions for the occurrence of resonance fluorescence from single vibronic levels are:

(i) the spectral bandwidth of the exciting radiation must be sufficiently narrow to ensure that only a single vibronic level is populated;

(ii) the initially excited vibronic level
must not be deactivated by collisions;

(iii) vibrational rearrangement does not take place within the lifetime of the excited state.

Condition (ii) may be fulfilled at sufficiently low vapour pressures. Assuming a collision diameter of $7.4 \times 10^{-8} \text{cm}$ for naphthalene (Mack 1925), the Kinetic theory predicts that a single molecule will undergo $\sim 1.1 \times 10^6$ collisions per second at $23^\circ \text{C}$ and $0.07\text{Torr}$ vapour pressure. One may use the Poisson distribution to calculate the probability that $0, 1, 2, \ldots$ collisions occur within a given time $T$. These values are tabulated below for $T = 200\text{ns}$ and for $T = 500\text{ns}$.

**TABLE V.1a.**

<table>
<thead>
<tr>
<th>Number of Collisions</th>
<th>Probability that $n$ collisions take place within time $T$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T = 200\text{ns}$</td>
</tr>
<tr>
<td>0</td>
<td>0.803</td>
</tr>
<tr>
<td>1</td>
<td>0.177</td>
</tr>
<tr>
<td>2</td>
<td>0.019</td>
</tr>
<tr>
<td>3</td>
<td>0.001</td>
</tr>
</tbody>
</table>

*Vapour pressures are calculated from data given in the Handbook of Chemistry and Physics (1967).*
The mean fluorescence lifetime of a particular vibronic level of naphthalene (measured at 0.07Torr) is 270ns (Section V.5). From Table V.1ait would appear that there is a significant probability that one collision will occur within 200ns after a naphthalene molecule is initially excited. However, the fluorescence spectrum obtained by exciting this vibronic level (at 0.07Torr) indicates that collisions do not play a significant role and resonance fluorescence can be obtained (Blondeau & Stockburger 1971 a,b). It is obvious that the shorter the mean fluorescence lifetime of the excited species, the smaller the probability of collisional perturbation of the excited state.

Condition (i) is not only dependent on the available instrumental resolution but depends also on the absorption spectrum of the molecule concerned. Stockburger (1972) has adopted a crude classification of aromatic molecules according to the properties of the first singlet absorption spectrum.

I) Main absorption bands are resolved with little or no underlying sequence background (benzene).

II) Main bands are resolved but sequence background exists (toluene, aniline, naphthalene).

III) Single bands are not resolved, spectra are diffuse (molecules the size of tetracene).

Class I. So far, it would seem that benzene is the only molecule which satisfies the criteria in class I. Parmentier & Schuyler (1969, 1970 a,b) have made a detailed study of fluorescence from single vibronic levels of benzene.
vapour and have determined quantum yields for the three levels $0^0$, $6^1$, $6^{1*1}$ respectively.† Excitation can be truly limited to a single vibronic level and no indications of intramolecular vibrational redistribution exist in the fluorescence spectra.

Class II. Blondeau & Stockburger (1971 b) have obtained (approximately) single vibronic level spectra from naphthalene by irradiating well resolved absorption bands, namely the levels $8(b_{1g})^1$ and $8(b_{1g})^27(a_g)^1$. †† The spectra exhibit

† The notation for vibronic levels of benzene follows that of Callomon, Dunn & Mills (1966). The normal mode numbering is after Wilson (1934).

†† For naphthalene, the normal mode numbering of Hollas (1962) will be used to distinguish between vibrations of a particular symmetry class. The symmetry of the first excited state of naphthalene is designated as $^1B_{2u}$ and the second excited singlet, $^1B_{2u}$. This notation follows Pariser (1956) and corresponds to choosing the long molecular axis to coincide with the $x$-direction, the short axis with the $y$-direction. The $z$-axis is perpendicular to the molecular plane. The frequently occurring vibration $v_8$ of $b_{1g}$ symmetry, in this notation, corresponds to $8(b_{3g})$ in the notation used by Blondeau & Stockburger (1971 a,b).
discrete structure which can be correlated with the vibronic activity seen in absorption. However, there is also a diffuse background intensity which appears to be related to the unresolved sequence background on which the discrete absorption is built up. In principle, this behaviour would not alter even if extremely narrow excitation bandwidth could be used. It must be emphasised, however, that these resonance fluorescence spectra are considerably less congested than the equilibrated fluorescence (emission which occurs from a Boltzmann distribution of levels when the overall pressure is raised). Blondeau & Stockburger used a 35cm⁻¹ bandwidth for excitation, and pointed out that sequence bands near the main transition were also excited. It is obvious from the spectra that they have been successful in restricting their excitation to populating a very narrow selection of levels.

Sequence bands are "hot" bands and so they serve to populate vibronic levels much higher in energy than does the main absorption band. Where the higher levels give rise to only a diffuse background, this may simply be subtracted from the spectrum if quantum yields are to be determined. In measuring fluorescence lifetimes, excitation of sequence bands may introduce shorter components in the fluorescence decay curve and one must correct for this (if possible) when determining the lifetime of the desired level. Such measures are discussed below in Section V.5.
Resonance fluorescence spectra corresponding to class II have also been recorded for toluene, $p$, $m$ and $o$-xylene and aniline (Blondeau & Stockburger 1971 a). An interesting extension of the work concerning aniline (and some deuterated analogues) by Quack & Stockburger (1972) reveals the occurrence of intense bands due to the strongly anharmonic inversion vibration ("umbrella mode") of the NH$_2$ group. From the spectra, it was possible to determine a one-dimensional double-minimum potential function for this mode.

**Class III.** The causes of diffuseness, as seen in the vapour spectra of polyatomic molecules, have been categorically treated by Byrne & Ross (1971). Trivial diffuseness, a temperature dependent overcrowding of individually sharp lines, is responsible for the sequence background seen in naphthalene. In larger molecules, this overcrowding can become severe, and sharp features will not be seen at the temperatures needed to maintain sufficient vapour pressure for an absorption experiment. Anthracene and phenanthrene are the largest cyclic aromatic molecules in which fine structure has been observed (Byrne & Ross 1965; Craig & Gordon 1965).

However, it must be remembered that the observation of sharp features in the absorption spectrum is not alone a sufficient criterion to enable excitation to a pure single vibronic level. Individually sharp bands may still carry a significant fraction of intensity due to overlap from nearby bands. Here the importance of rotational band contours must not be overlooked. A summary of assigned rotational contours
in cyclic molecules has been compiled by Ross (1971) and in many instances the band contours of an individual absorption band can be found to extend over 30 cm\(^{-1}\) or more. Fortunately, there is still a wide range of large molecules, of which naphthalene and azulene are typical examples, where the band contours have features sharp enough and are sufficiently well separated to permit the selection of individual vibronic bands (McHugh & Ross 1970).

Although a high extinction coefficient may enable the absorption spectrum to be easily measured at lower temperatures, where sequence congestion is minimised, the quantum efficiency may be so low as to preclude detection of the emission spectrum unless the vapour pressure is raised. An increase in temperature to obtain increased vapour pressure, and hence optical density, must also increase sequence congestion. A practical difficulty often arises whereby most of the intensity of a vibronic band is contained in the rotational envelope - the necessity for narrow bandpass excitation centred on the band head to avoid closely-lying sequence bands results in much of the available absorption intensity being unusable.

Intrinsic diffuseness, as a result of electronic relaxation, is exemplified in the spectra of many well-studied polyatomic molecules. In such cases, it is meaningless to speak of fluorescence originating from single vibronic levels. This phenomenon is discussed at some length by Byrne & Ross (1971).
Closely allied with electronic relaxation as a cause of diffuseness in absorption spectra, the process of intramolecular vibrational redistribution (anharmonicity) may give rise to poorly structured emission (Condition (iii) above). The distinction between electronic relaxation and anharmonicity is based on the premise that discrete electronic states can be defined. Anharmonicity is a process which redistributes vibrational energy among a quasi-continuum of levels within the same electronic manifold. Electronic relaxation distributes energy among a dissipative continuum of levels belong to another electronic state whose origin lies well below in energy. Neporent (1951) was among the first to introduce the idea that energy redistribution occurs on a time scale which is competitive with radiative decay. However, Byrne & Ross (1971) have advocated that anharmonicities present in analysed spectra of aromatic molecules, as judged from variations in sequence patterns, are rarely greater than $1 \text{cm}^{-1}$ and, as such, may not be the ubiquitous explanation for diffuse emission. Neporent and others (Neporent 1950; Neporent & Mirumyants 1960; Stevens 1956) studied gas-phase emission spectra under collision-free conditions and found an equivalence between thermal energy (temperature) and excess photon energy (energy of excitation). Rapid energy redistribution still remains a popular explanation. Significantly, broad bandpass excitation was used. At the present level of development of single vibronic level fluorescence spectroscopy, it is often difficult to distinguish whether the congestion in emission spectra
arises as a result of anharmonicity or simply as a result of exciting a host of upper vibronic levels during the absorption act. In many large molecules, emission spectra are found to be diffuse unless excitation coincides exactly with the 0-0 band, eg. anthracene (Haebig 1968), indazole and isoquinoline (Logan & Ross 1968). It is an unexplored point as to whether exceedingly narrow band excitation into a 1-0 band, which lies reasonably well separated from sequence structure, still gives rise to diffuse emission.

3. SINGLE VIBRONIC LEVEL LIFETIMES

In measuring the dependence upon wavelength of fluorescence lifetimes, one is not only faced with the problems met in continuous irradiation emission studies of vapours, but one must also provide a method for timing the rate of emission. The art of fluorescence decay spectroscopy at its present embryonic stage has been outlined in Chapter II. The measurement of single vibronic level lifetimes of large molecules has, in the past, proved to be an elusive task. It is pertinent to note that the first direct measurement of lifetimes of single vibronic levels of an isolated large molecule was reported less than two years ago (Selinger & Ware, 1970 a).

In earlier pioneering work, Schlag & von Weyssenhoff (1969) studied the fluorescence lifetime of β-naphthylamine (0.5Torr pressure) as a function of excitation energy. From their results, the authors attempted to draw conclusions concerning the behaviour of individual vibronic states, but this interpretation must be treated with some
reserve. An excitation bandpass of 250-450 cm\(^{-1}\) was used, which, when compared with the complexity of the absorption spectrum, makes their claim to having obtained "a direct timed measurement of the relaxation from individual vibronic levels" highly optimistic. Their observations did prove, however, that the lifetime of \(\beta\)-naphthylamine decreases from \(\sim 14\) ns to \(\sim 2\) ns as the excitation energy is increased from 0 to \(\sim 11,000\) cm\(^{-1}\) above the origin of the first singlet.

**Benzene**

Nishikawa & Ludwig (1970) have studied the time dependence of the fluorescence of benzene vapour as a function of pressure and as a function of excitation wavelength. At the lowest pressure used (3 Torr), fast collisional deactivation of the initially excited state would be still highly probable. However, the results obtained at a pressure of 3 Torr revealed that collisional equilibration was incomplete. When exciting the 253 nm radiation (\(\pm 1\) nm), the fluorescence decay curve showed non-exponential behaviour with an initial component which was shorter than the decay observed for longer wavelength excitation. At higher pressures the lifetime was independent of excitation wavelength. The lower pressure data corresponds to emission from a considerable number of states which are populated as a result of partial collisional equilibration. Emission from those states which are energetically in the vicinity of the initially excited
level gives rise to the shorter (average) component. The two level scheme naively used by the authors to extract a "long" and "short" decay component certainly cannot be accepted as being justified. At higher pressures, collisional deactivation causes the emission to originate from a Boltzmann population of levels and thus the lifetime is invariant with excitation energy.

The lifetime of three single vibronic levels of benzene and benzene-$d_6$ were measured at a pressure of 0.1Torr by Selinger & Ware (1970a,b). Being somewhat in the nature of a preliminary excursion, a relatively wide excitation bandpass of $\sim$300cm$^{-1}$ was used. However, the authors argued that in benzene, for strong band heads, this bandpass ensured that $\geq$90% of the excited molecules would reach the desired vibronic level (Radle & Beck 1940). Although true for the $6^1_0$ transition, this claim cannot be conceded for the $6^1_01^1_0$ and $6^0_1$ transitions. With a 300cm$^{-1}$ excitation bandpass, excitation of the $6^0_1$ transition overlaps the $6^1_2$ and $6^1_01^0_1$ transitions. States of higher energy are populated and their contribution towards the total emission produces an overall shorter lifetime. Gelbart, Spears, Freed, Jortner & Rice (1970) determined lifetimes of these same states using 20-40cm$^{-1}$ excitation bandpass. Their values for the $6^0_1$ ($0^0$ state) and $6^1_01^1_0$ transitions are 11% and 5% longer respectively than those of Selinger & Ware.

Ware, Selinger, Parmenter & Schuyler (1970) combined lifetimes with quantum yield determinations and found absolute rate constants for radiative and non-radiative
decay for the levels, $0^0$, $6^1$ and $6^1l^1$. Both rate constants showed sensitivity to which vibrational state of the molecule was excited. The rate of radiative decay was roughly consistent with predictions based on the Herzberg-Teller theory of vibronically induced transitions (Herzberg & Teller 1933; Albrecht 1960). The non-radiative rate was compared with the theoretical rate of intersystem crossing $(^1B_{\delta u} \rightarrow ^3B_{\delta u})$ derived using the familiar Golden Rule formula,

$$k_{i\delta c} = (4\pi^2/\hbar) \beta^2 \rho F$$

(V.4)

where $\beta$ is the electronic matrix element for coupling of the two electronic states, $\rho$ is the density of vibronic states in the triplet manifold and $F$ is an average Franck-Condon factor for the initial singlet level and final triplet levels. $\beta$ was assumed to be a constant for the three levels and a satisfactory correspondence between the experimental and theoretical rates led the authors to conclude that all vibronic levels of the $^1B_{\delta u}$ state lie within the statistical limit\(^+\) or "\(\omega\)" limit in the terminology used by Robinson (1967).

\(^+\) The term "statistical limit" classifies large molecules in which the density of vibronic states is extremely high. Intramolecular electronic relaxation occurs and is essentially independent of external perturbations. (Refer to Jortner, Rice & Hochstrasser, 1969).
Spears & Rice (1971) have made a more comprehensive study of the lifetimes and quantum yields of 22 vibronic states of benzene under collision-free conditions. The high sensitivity of their single photon counting apparatus enabled them to use an excitation bandpass of 15-40cm$^{-1}$ which, for most of the 22 levels, ensured that excitation was limited to a virtually pure single vibronic state. A commendable feature of their study was their attempt to estimate the fraction of molecules which would be excited into the desired vibronic level. In this manner, even if some overlapping bands were excited, the lifetimes of pure vibronic states could be established within well defined bounds. Since benzene appears at present to be the only aromatic molecule belonging to Class I, this procedure must necessarily be followed for lifetime studies of other aromatics and large molecules which lie in Class II.

Spears and Rice find that the non-radiative lifetime decreases as the vibrational energy of the prepared state increases but the principal variation is with the number of quanta of a vibration, not simply the energy. The behaviour of C$_6$D$_6$ and C$_6$H$_5$F has been found to follow a similar pattern (Abramson, Spears & Rice, 1972).

**Naphthalene**

The principal aim of the work to be presented in this chapter was to study the fluorescence decay from individual vibronic levels of naphthalene vapour and to extend such
studies to other large molecules of Class II. During the course of this research, other workers have reported lifetime measurements of naphthalene vapour at low pressure but none have succeeded in achieving the desired aim of exciting pure single vibronic levels.

Laor & Ludwig (1971) measured fluorescence lifetimes of naphthalene vapour, at a pressure of 0.07Torr, as a function of excitation wavelength, and referred to the excitation bandpass they used as "narrow band excitation". Such a description serves to emphasize what gross inadequacies there have been in fluorescence decay spectroscopy, even in recent years. The bandwidth they used was, in fact, \( \sim 600 \text{cm}^{-1} \). However, despite this limitation, the results proved to be of some interest in that the lifetime was found to shorten drastically as the excitation energy was varied over a range of 14,000cm\(^{-1}\). For excitation at 308nm, the lifetime was measured as 180ns, whereas at 215nm, it had shortened to 2ns. The inverse lifetime, \( 1/\tau \), was found to vary linearly with energy when excitation probed the first and second excited singlet states. When exciting into the third singlet, the dependence of \( 1/\tau \) upon excitation energy appeared to be roughly exponential, a qualitatively similar observation to that obtained for \( \beta \)-naphthylamine (Schlag & von Weyssenhoff 1969).

In a subsequent communication, Hsieh, Laor & Ludwig (1971) reported revised lifetimes for the first excited singlet state of naphthalene using improved instrumentation.
They were able to reduce the excitation bandwidth to ~100 cm\(^{-1}\) and found that the decay rate, \(1/\tau\), no longer showed a linear dependence on excitation energy. Instead, fluctuation of the decay rate with excitation energy was observed. This behaviour could be partially reconciled if \(1/\tau\) was plotted against energy above the origin of the \(7B_{3u}\) state rather than against excitation energy. (They were exciting sequence bands in some cases.) The erratic variation was no longer apparent. The authors attributed the remaining small deviations to uncertainties in their data and concluded that no experimental evidence could be found for a dependence of the relaxation rates on the nature of the vibrations involved. However, with a 100 cm\(^{-1}\) bandpass, many sequence members are excited (see section V.4) and the choice of a value for energy of the level or levels reached in the upper state must be somewhat arbitrary. An attempt was made to repeat these measurements using a 35 cm\(^{-1}\) bandpass but the uncertainty of their monochromator setting was of the order of ±12 cm\(^{-1}\). The only significant additional finding was that there appeared to be some degree of non-exponentiality in the decay curves. The limited time range of their instrument prevented further investigation of this feature and no explanation was offered.

Hsieh et al initially set out to combine lifetime measurements with the quantum yield measurements of Uy & Lim (1970). However, since the latter were determined using a bandpass of ~120 cm\(^{-1}\), the values of \(k_r\) and \(k_{nr}\) obtainable from such data would be exceedingly
difficult (if not impossible) to interpret in terms of rates of relaxation of individual vibronic states. Blondeau & Stockburger (1971 b) have justifiably criticized the attempts made by Uy & Lim (1970) to derive conclusions regarding the behaviour of individual vibronic levels from the "structure" observed in the energy dependence of quantum yield when such broad bandpasses are used. Hsieh et al are in agreement with this point of view and, furthermore, they suggest that any "fluctuations" in the energy dependence of $1/\tau$ or $Y$ are more than likely due to excitation of combinations of sequence bands. In view of this, they also consider that the results of von Weyssenhoff & Kraus (1971) for aniline vapour should be reinterpreted. Hsieh et al conclude their communication with a somewhat pessimistic submission that for molecules as complex as naphthalene, excitation to individual vibronic levels is likely to be an almost impossible task.

The most recent communication concerning lifetimes of naphthalene vapour optimistically purports to having very nearly satisfied the criteria for single vibronic level studies. Schlag, Schneider & Chandler (1971) report lifetimes of sixteen levels of naphthalene measured with a bandpass of $20\text{cm}^{-1}$, at a pressure of 0.1Torr. It is unfortunate, however, that as a result of using a phase-shift method (albeit modified to incorporate single photon detection) the lifetime measurements suffer from considerable systematic error which lies well outside the ±15% figure.
of precision quoted by the authors. In Chapter II of this thesis, it was stressed that, when using the phase-shift method, a correction for scattered light must be included and the correct choice of decay law must be used to analyse the results. If this is not done, the results are likely to be grossly in error.

Schlag et al state that other than for the origin and one nearby sequence band, the error introduced by scattered light may be neglected. For the origin, their measured value is 84ns, although after including a correction for scattered light they suggest that a value of 200±50ns may be more appropriate. From this, one would suspect that for other levels too the scattered light may not be negligible. However, a more serious criticism of this study is that an excitation bandpass of ~20cm⁻¹ does not probe one single vibronic level. Such a criticism is all the more pertinent when using the phase-shift technique. Emission from a few higher levels, populated when sequence bands are excited, leads to a faster initial component in the decay curve (Section V.5). A direct timing technique enables the fast component to be observed and the appropriate decay law used for analysis, whereas the phase method presents its data in a form that does not enable direct observation of the nature of the decay curve. Schlag et al interpreted their phase-shift data assuming a single-exponential decay law. This was, at the time, justified since the non-exponentiality reported
by Hsieh, Laor & Ludwig (1971) was by no means conclusive. It remains, however, that the lifetimes determined in this way each represent only an inseparable average lifetime for the group of levels which are excited when using a 20cm$^{-1}$ bandpass. Nevertheless, the decay rate does show a significant dependence upon the (approximate) vibronic energy content, although any quantitative interpretation based on these results is likely to be incorrect.

The difficulties involved in obtaining accurate measurements of single vibronic level lifetimes for a molecule such as naphthalene can now be clearly appreciated. The lack of accurate experimental results concerning rates of radiative and non-radiative relaxation of vibronic states has frustrated attempts made towards obtaining a detailed theoretical understanding of these processes. Much of the lively controversy among different theoretical schools of thought at present is only remotely concerned with application to experimental observations. There is a compelling need for careful studies of other molecules, comparable with the detailed investigation of benzene by Spears & Rice (1971), if the present gap between theory and experiment is to be bridged.

At the risk of being repetitive, it was established above that bandpass inadequacies can lead to serious errors when one attempts to determine lifetimes of single vibronic levels. The absorption spectrum of naphthalene vapour is considerably more complex than that of benzene and in the course of this research considerable attention
has been paid to its intricacies before undertaking lifetime studies. The approach that has been pursued will now be discussed.

4. OPTICAL SELECTION OF VIBRONIC STATES OF NAPHTHALENE

The $^1B_{2u} - ^1A_g$ transition between the ground and first excited singlet state of naphthalene is well known both in the vapour and in the crystal. McClure (1954) studied the absorption spectrum of naphthalene in durene at 20K and showed that the pure electronic transition between the ground and the first excited singlet state is polarized parallel to the longer in-plane axis. The stronger bands of the system are all short axis polarized as is the $^1B_{2u} - ^1A_g$ transition to the second singlet excited state. These strong bands are due to transitions in which an odd number of quanta of $b_{1g}$ symmetry are involved and which derive their intensity through vibronic coupling with the $^1B_{2u}$ state.

Vibrational analysis of the vapour absorption spectrum was performed by Craig, Hollas, Redies & Wait (1961). By using inferences drawn from rotational contours, they confirmed McClure's assignment of the first excited state and identified most of the fundamental frequencies appearing in the spectrum.

To assist in discussion, a low resolution absorption spectrum of the $^1B_{3u} + ^1A_g$ transition of naphthalene vapour measured at 23°C (vapour pressure 0.07Torr) is
shown in Figure V.1. The spectrum was obtained with a resolution of 0.1 nm by means of a Cary 14 double beam spectrophotometer fitted with a 1 m gas cell. It is of interest to note that the only published spectrum of naphthalene vapour, which shows the overall features of the $^1B_{3u}$ absorption, is that measured by Henri & de Laszlo in 1924.

Portions of the vapour spectrum, photographed at high resolution, are shown in Plate 2. The photographs are reproduced, with grateful acknowledgment, from prints of spectra taken by Craig, Hollas, Redies & Wait (1961).

The low resolution spectrum consists of a series of band groups, each of which has a similar vibrational substructure. Each principal band head has associated with it sequence bands which lie to longer wavelength. The strongest group of the system, corresponding to the $8(b_{1g})^7$ transition, is shown in Plate 2a. The two more prominent sequences, with intervals of 10 cm$^{-1}$ and 55 cm$^{-1}$, occur with up to four or five members. The weak 6 cm$^{-1}$ sequence does not appear with more than one member under the conditions of temperature and path length used by Craig et al.

Hollas (1962) assigned the 10 cm$^{-1}$ sequence to a $b_{2u}$ vibration with frequencies 171 cm$^{-1}$ and 181 cm$^{-1}$ in the excited and ground state respectively. The 55 cm$^{-1}$ sequence was attributed to a $b_{3g}$ vibration with frequencies 195 cm$^{-1}$ and 140 cm$^{-1}$. There appears to still be some doubt concerning the 6 cm$^{-1}$ sequence although it is certain that it
Fig. V.1 Low resolution vapour absorption spectrum of the $^1B_{3u} - ^1A_g$ transition in naphthalene. A Cary 14 double beam spectrophotometer fitted with a 1m gas cell was used to record the spectrum. The resolution was 0.1nm and the vapour pressure 0.07 Torr corresponding to a cell temperature of 23°C. The vertical scale is in absorbance units x10.
PLATE 2

High resolution spectra of naphthalene vapour.

a) The double headed 438+0 band group near 32 458 cm\(^{-1}\) showing the strong sequence bands separated by 10 cm\(^{-1}\), the weak 6 cm\(^{-1}\) sequence and the first member of the long 55 cm\(^{-1}\) sequence.

b) The single headed 0+0 band group near 32 020 cm\(^{-1}\). The diffuse background, caused by overlapping sequence structure is of considerably greater relative intensity than in a).

c) The perturbed double headed 0+506 hot band group near 31 514 cm\(^{-1}\).
is indeed a sequence member and not part of the rotational structure (Innes, Parkin, Ervin, Hollas & Ross 1965).

In contrast to benzene, the vibrational structure in naphthalene does not consist of one, two and three quantum additions of fundamentals. Transitions to vibronic states involving only $a_g$ and $b_{1g}$ fundamentals in single quanta occur (there are three exceptions, $0+2\times987$, $0+438+2\times987$ and $0+2\times1435$, but these are very weak). Hence, the dependence of lifetime on the number of quanta of excess vibrational energy cannot be tested in naphthalene as it was in benzene (Spears & Rice 1971).

Table V.1b summarises the vibrational frequencies and assignments which are relevant to this investigation of single vibronic level lifetimes. Information concerning naphthalene-$d_8$ has also been included.

TABLE V.1b

Vibrational frequencies (cm$^{-1}$) and assignments in naphthalene-$h_8$ and $-d_8$ vapour

<table>
<thead>
<tr>
<th></th>
<th>$-h_8$</th>
<th>Assignment</th>
<th>$-d_8$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i)</td>
<td>ground state</td>
<td>506</td>
<td>8($b_{1g}$)</td>
</tr>
<tr>
<td>(ii)</td>
<td>excited state</td>
<td>438</td>
<td>8($b_{1g}$)</td>
</tr>
<tr>
<td></td>
<td>($^1B_{3u}$)</td>
<td>501</td>
<td>9($a_g$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>702</td>
<td>8($a_g$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>911</td>
<td>7($b_{1g}$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>987</td>
<td>7($a_g$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1389</td>
<td>5($a_g$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1435</td>
<td>4($a_g$)</td>
</tr>
</tbody>
</table>
In order to select single vibronic levels in naphthalene, it is clear that the bandpass must be sufficiently narrow to restrict excitation to the principal band head. The practical problem is to maintain satisfactory signal-to-background ratio whilst retaining the required resolution. The 10 cm\(^{-1}\) sequence is of critical importance, since the first member is normally quite prominent. Blondeau & Stockburger (1971 b), in using a 35 cm\(^{-1}\) bandpass, would have excited at least two members of this sequence. Schlag, Schneider & Chandler (1971) obtained an excitation spectrum which proved, unfortunately, that their bandpass of 20 cm\(^{-1}\) could not resolve the 10 cm\(^{-1}\) sequence. It is essential that the bandpass used for excitation be sufficiently narrow to ensure that the 6 cm\(^{-1}\) and the first of the 10 cm\(^{-1}\) sequence members contribute only to a small proportion of the excited species. In the absence of intensity limitations, this criterion could be readily met with the monochromator used in this work to perform optical selection (see Section V.5). For most of the levels studied, the narrowest bandpass which gave a satisfactory signal-to-noise ratio, when using a deuterium-filled nanosecond flash lamp, was 12 cm\(^{-1}\). The strong 8(\(b_{ig}\))\(^{1}\) transition in naphthalene-h\(_{g}\) allowed the bandpass to be reduced to 6 cm\(^{-1}\) without significantly affecting the signal-to-noise ratio.

By superimposing a triangular slit function over the relevant part of the absorption spectrum, one can obtain an estimate of the percentage of 6 cm\(^{-1}\) and 10 cm\(^{-1}\) sequence bands which are simultaneously excited. The slit function
is centred on the main band maximum. For the \(8(b_{1g})^1\) transition, it can be expected that, with a bandpass of \(6\text{cm}^{-1}\), 95% of the excited molecules would reach the desired vibronic level. A significant feature of the resonance fluorescence spectrum of naphthalene is that a diffuse background emission, corresponding to unresolved sequence bands, lies beneath the discrete emission bands (Section V.2). From the spectrum in Figure V.1, it can be seen that in absorption, the intensity of the unresolved background increases with increasing energy. At higher energies, the continuous background must be partly due to the onset of the much stronger \(1B_{8u} \leftarrow 1A_g\) transition. It is only the low-lying \(8(b_{1g})^1\) band which stands noticeably well clear of the background. However, it is instructive to examine the high resolution spectra so as to obtain a better picture of the structure of each band head. Spectra taken at low resolution can often be misleading as regards intensity distributions when there are many close lying bands. A photoelectric tracing of the \(8(b_{1g})^1\) band, photographed at high resolution by Hollas & Thakur (1971), is shown in Plate 3a. The double headed structure is characteristic of the type \(B\) bands which correspond to the vibronically induced transitions of \(b_{1g}\) symmetry. Type \(A\) bands, showing a single intense peak, are characteristic of the electronically allowed part of the \(1B_{8u} \leftarrow 1A_g\) system (Plate 3b). The principal feature to note is that the high energy side of either type of band is relatively free from any complications due to the
Plate 3a. Rotational band contours for the $8(b_{1g})_0^1 \approx 44_0^1$ band of naphthalene.

a) Observed band with overlapping sequence bands
b) Computed type B band with additional type B bands to simulate the sequence bands
c) A single computed type B band.
Plate 3b. Rotational band contours for the $0^0_0$ band of naphthalene.

a) Observed band with overlapping sequence bands
b) Computed type A band with additional type A bands to simulate the sequence bands
c) A single computed type A band
d) A single computed type C band
sequence or rotational envelope of any strong preceding band. Nevertheless, it is apparent from the photographic spectra (Plate 2) that for weak transitions such as the origin, the unresolved background is of appreciable relative intensity and must be taken into consideration.

With a 12cm\(^{-1}\) bandpass, it is estimated that for transitions other than \(8(b_{lg})^I_0\), less than 5\% of the emission intensity stems from excitation of the weak 6cm\(^{-1}\) sequence band and less than 10\% stems from the 10cm\(^{-1}\) sequence band. Some further improvement can be had by offsetting the monochromator setting so that it is actually centred slightly higher in energy than the band maximum. Such a procedure is limited to only slight offsetting since it leads to a correspondingly poorer signal-to-background ratio. A compromise was reached which normally allowed the monochromator to be centred \(\sim 2-3\) cm\(^{-1}\) to the higher energy side of the band maximum.

At first sight it would appear that the small percentage of sequence levels which are excited when using a 12cm\(^{-1}\) bandpass would lead to errors in the fluorescence lifetime. This would certainly be the case if the phase method were used. However, in Section V.5 it will be shown that emission resulting from excitation of the 6cm\(^{-1}\) and 10cm\(^{-1}\) sequence bands and from the unresolved background contributes only a very low amplitude, short lifetime component to the decay curve. This can be dealt with easily.
The absorption spectrum of naphthalene-\textit{d}_8, measured under the same conditions as naphthalene-\textit{h}_8, is shown in Figure V.2. Due to ground state sequence forming vibrations being of lower frequency in the deuterated species, the unresolved background is of even greater intensity in naphthalene-\textit{d}_8. The \(a_g\) and \(b_{1g}\) band heads are thus not nearly so prominent as in naphthalene-\textit{h}_8 and many are obscured towards the high energy end of the spectrum. Again, the \(8(b_{1g})_0^1\) transition is most outstanding, whereas the origin band is only just discernible.

In naphthalene-\textit{d}_8 the hot band \(8(b_{1g})_0^0\), which lies at 315.97nm, 490cm\(^{-1}\) below the origin, coincides almost exactly with the 315.89nm line of the air-filled nanosecond flash lamp. The intensity of this air line is some orders of magnitude greater than the deuterium lamp at the corresponding wavelength. Consequently, a bandpass as narrow as 6cm\(^{-1}\) may be used, whilst still retaining satisfactory signal-to-noise ratio. In fact, it was possible to reduce the bandpass to 3cm\(^{-1}\). Such a luxury proved to be unnecessary since, apart from being a factor of four more time consuming, the results were indistinguishable from those obtained with a 6cm\(^{-1}\) bandpass. Although the coincidence in wavelength is not exact, it is an experimentally perfect situation, since the air line maximum lies slightly higher in energy than the 490-0 band head. Moreover, the \(\Delta v=1\) sequence bands of the 1-0 315.89nm air line are degraded to higher energy (see
Fig. V.2 Low resolution vapour absorption spectrum of the $^1B_{3u} - ^1A_g$ transition in naphthalene-d$_8$. A Cary 14 double beam spectrophotometer fitted with a 1m gas cell was used to record the spectrum. The resolution was 0.1nm and the vapour pressure 0.07 Torr corresponding to a cell temperature of 23°C. The vertical scale is in absorbance units x10.
Figure II.7b, which shows the similar 0+0 band at 337.09 nm) whereas the 8(b_1g)^0 band in naphthalene-d_8 is degraded to lower energy (refer to the analogous 506+0 band in naphthalene-h_8 shown in Plate 2c). We can thus be assured that, in this case a pure single vibronic level, the zero vibrational level, is excited.

It is extremely fortunate that this coincidence exists since it affords a means of determining with confidence the lifetime of the vibrationless state of naphthalene-d_8. The weak origin band lies amongst considerable congestion so that the lifetime measured by measuring the 0_0^0 transition cannot be relied upon due to the very large amplitude of unresolved (short lifetime) background emission. The analogous 506+0 hot band in naphthalene-h_8 cannot be utilized in the same manner as the 490+0 band in naphthalene-d_8 since to date no coincident exciting line has been found. The deuterium flash lamp (which provides a continuum) does not offer sufficient intensity.

5. LIFETIMES OF SINGLE VIBRONIC LEVELS OF THE ISOLATED NAPHTHALENE MOLECULE

The preceding section described the measures taken to establish the best compromise between signal-to-background ratio and resolution. It is now necessary to demonstrate that the decay curves obtained by exciting with a 12 cm^{-1} bandpass allow the lifetime of a pure single vibronic level to be assigned with some degree of confidence.
It will be instructive to examine some preliminary results obtained using an excitation bandpass of 2nm ($\sim 200\text{cm}^{-1}$) and then to observe the effect of reducing the spectral bandpass.

The single-photon technique for lifetime measurements has been discussed in depth (Chapter II) but some aspects of experimentation which pertain to vapour phase studies will be described.

**Experimental**

The naphthalene used was scintillation grade material supplied by Eastman Ltd. It was purified by zone refining and recrystallized from spectroquality alcohol. The purity was checked by recording the emission spectrum of the crystal.

Octadeuteronaphthalene was obtained from Merck, Sharp & Dohme (Canada) and used as received. The isotopic purity was stated as better than 99.5%. Chemical purity was checked by recording the crystal emission spectrum and was found to be satisfactory.

The vacuum system used for evacuating the sample cell was constructed using Westglass greaseless 'O'-ring stopcocks. A three-stage mercury diffusion pump, isolated from the line by a liquid nitrogen trap, enabled rapid pumping down to $10^{-5}\text{Torr}$. To ascertain whether traces of mercury affected the results, tests were carried out using a line fitted with greased stopcocks and a silicone-oil diffusion pump. Lifetime measurements were found to be
independent of which line was used.

The sample cell consisted of a 30\,mm diameter all-quartz Rayleigh horn with a straight cylindrical section 150\,mm in length. The excitation window was situated at one end of the cylindrical section whilst the other end was shaped into a curved, tapered, closed horn. The viewing window, at right angles to the excitation window, was joined so that its centre lay \( \approx 25\,\text{mm} \) from the front of the horn. Both windows were of polished suprasil. The horn, apart from the windows, was painted black to minimise scattered light. A filler tube of pyrex was joined via a graded seal to the rear section of the horn. The filler tube could be connected to the vacuum line using an 'O'-ring fitting.

To fill the horn, a small crystal of naphthalene was introduced, the horn evacuated for \( \approx 30\) minutes and then sealed off at a constriction in the filler tube. This procedure was found to be more satisfactory than using a stopcock to seal the horn, since there was no possibility of leakage and the problem of oxygen quenching could be totally eliminated. No photochemical products were detectable, even after prolonged irradiation with the nanosecond flash lamp. Nevertheless, the sample was regularly changed by opening the horn and repeating the filling procedure. The empty cell gave no extraneous fluorescence. Scattered excitation light was filtered out using a 1\,cm path length of an aqueous solution of 0.5g/dm\(^3\) potassium hydrogen phthalate (Kasha 1948).
Room temperature was normally less than 23°C and found to be constant to within ±0.5°C during the time taken for a lifetime measurement. The vapour in the cell was thus at a corresponding pressure of 0.07Torr.

The nanosecond flash lamp, mounted with micrometer adjustment on a Hilger optical bench, was operated with a spark gap of 10mm and charging capacitance of 11pF (the flash lamp circuit is shown in Figure II.4). The lamp was gated at a repetition rate of 11kHz and, with an applied anode voltage of 9kV, drew an average d.c. current of 2mA. Under these conditions the deuterium lamp had a pulse width of 5ns and the air lamp, 6.5ns. Even for the shortest lifetime measured (96ns), a convolution and fitting procedure to correct for the finite width of the pulse was not necessary.

Light from the flash lamp was collected with a 40mm diameter 75mm focal length suprasil lens and then focussed on to the entrance slit of a 0.75m Czerny-Turner (Spex 1700-III) monochromator. A 1200 line/mm grating, blazed at 500nm was used in the second order. Monochromator settings were checked with known lines of a low pressure mercury arc and calibrated accordingly. Light leaving the exit slit was collimated and passed into the Rayleigh horn. The fluorescence was collected at right angles with a 50mm focal length lens and viewed by a Phillips 56DUVP/03 photomultiplier cooled to -20°C and operated at a cathode voltage of 2400V. The entire exit optics were enclosed in a completely light-tight box.
Typical count rates were of the order of $2s^{-1}$ for the weaker transitions and $25s^{-1}$ for the $0\leftrightarrow490$ air-excited transition in naphthalene-$d_8$. In some cases it was necessary to collect the decay curve for up to 48 hours in order to obtain the desired precision. During such long counting periods, regular attention to the lamp electrodes was necessary to sustain optimum performance (refer to Section II.5).

Preliminary results were obtained using a 0.25m Bausch & Lomb double grating monochromator for excitation. The bandpass could be set at 2nm, 0.5nm and 0.2nm although the poor dispersion and hence narrow slitwidth enabled only the 2nm and 0.5nm settings to be used with any success.

Preliminary results using low resolution

When a bandpass of 2nm ($\sim200\text{cm}^{-1}$) is used, at least three members of the $55\text{cm}^{-1}$ sequence are excited, as well as a host of $10\text{cm}^{-1}$ sequence members. Moreover, considerable overlap occurs with other transitions. The decay curves would be expected to display non-exponentiality and this is indeed found to be the case.

Typical decay curves obtained by exciting naphthalene-$h_8$ and naphthalene-$d_8$ with a $200\text{cm}^{-1}$ bandpass are shown in Figure V.3. Deviation from a single exponential is apparent. The decay curve obtained by exciting in the region of the $0\leftrightarrow490$ band with a $50\text{cm}^{-1}$ bandpass is compared with the strictly exponential decay of hexafluoroacetone.
Fig. V.3a Fluorescence decay curve for naphthalene-$\text{H}_8$
Excitation: 301.6 nm
Bandpass: 2 nm
6.35 ns/channel

Fig. V.3b Fluorescence decay curve for naphthalene-$\text{d}_8$
Excitation: 290.6 nm
6.35 ns/channel
Bandpass: 2 nm
Fig. V.4a. Fluorescence decay from the vibrationless state of naphthalene-d$_8$ obtained by exciting the 0-490 band with 315.9 nm radiation. Non-exponentiality is apparent for this bandpass of 0.5 nm. 13.03 ns/channel

Fig. V.4b. The pure single exponential decay of hexafluoroacetone vapour at 100 Torr
Excitation: 315.9 nm
Bandpass: 0.5 nm
5.03 ns/channel
Although physically unjustifiable, a naive two-exponential fit to the decay curves was used and the decay components obtained in this way are summarized in Table V.2.

**TABLE V.2.**

Lifetimes of naphthalene and naphthalene-$d_8$ using low resolution excitation. $\tau_1$, $\tau_2$ are decay components (ns) obtained by fitting a sum of two exponentials

<table>
<thead>
<tr>
<th>$\lambda_{ex}$ (nm)</th>
<th>$\tau_1$</th>
<th>$\tau_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>naphthalene-$d_8$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>290.6</td>
<td>91</td>
<td>130</td>
</tr>
<tr>
<td>294.4</td>
<td>97</td>
<td>133</td>
</tr>
<tr>
<td>299.5</td>
<td>117</td>
<td>147</td>
</tr>
<tr>
<td>307.1</td>
<td>176</td>
<td>268</td>
</tr>
<tr>
<td>315.9</td>
<td>213</td>
<td>378</td>
</tr>
<tr>
<td>naphthalene-$h_8$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>301.6</td>
<td>119</td>
<td>172</td>
</tr>
<tr>
<td>303.6</td>
<td>139</td>
<td>199</td>
</tr>
<tr>
<td>308.1</td>
<td>208</td>
<td>270</td>
</tr>
</tbody>
</table>

Lifetimes of pure single vibronic levels

Excitation wavelengths were chosen using the data of Craig, Hollas, Redies & Wait (1961) for naphthalene-$h_8$ and the data of Craig & Hollas (1961) for naphthalene-$d_8$.

To demonstrate the consistency of the overall experimental
procedure, ten independent determinations of the lifetime of the $8(b_{1g})^1$ state of naphthalene-$h_g$ were carried out. The standard deviation was found to be 0.8%. If one includes the calibration accuracy of $\pm 2\%$, the precision of measurement can be stated as being better than 3%.

To examine the effect of reducing the excitation band-pass, the decay curve of the $8(b_{1g})^1$ state of naphthalene-$h_g$ was determined for various settings of the monochromator slitwidth. Decay curves $35\text{cm}^{-1}$ and $6\text{cm}^{-1}$ bandpass are shown in Figure V.5. Excitation with a $35\text{cm}^{-1}$ bandpass (the same as that used by Blondeau & Stockburger (1971 b) for single vibronic level fluorescence studies) results in a decay curve which exhibits an initial shorter lifetime section followed by an essentially pure exponential decay. When the excitation bandpass is reduced to $6\text{cm}^{-1}$, a strictly exponential decay curve with no initial short component is obtained. The outstanding result, however, is that a computer fit to the exponential section of the $35\text{cm}^{-1}$ curve gives a lifetime of $262\text{ns}$, in close accord with the value of $270\text{ns}$ obtained from the $6\text{cm}^{-1}$ curve. This finding would only be possible if the short lifetime component did not carry much intensity, a contention which is consistent with the estimates obtained for the purity of the initially prepared state. For all but one of the levels studied, more than 80% of the excited molecules are expected to be initially in the desired vibronic state. Other levels studied in naphthalene-$h_g$ also show the same trend towards pure exponential decay as the bandpass is
Fig. V.5a. Fluorescence decay from $8(b_{1g})^1$ state of naphthalene-$h_8$. With a 35 cm$^{-1}$ bandpass there is a shorter lived component which arises due to excitation of sequence bands. Excitation: 308.09 nm 13.03 ns/channel

Fig. V.5b. When the bandpass is reduced to 6 cm$^{-1}$, the decay from the $8(b_{1g})^1$ state follows a single exponential.
Fig. V.6a. Fluorescence decay from the $8(\alpha_g)^1$ state of naphthalene-$h_8$. Excitation: 305.60 nm
Bandpass: 12 cm$^{-1}$
6.35 ns/channel

Fig. V.6b. Fluorescence decay from the $8(\beta_g)^{14}(\alpha_g)^1$ state of naphthalene-$h_8$. Excitation: 295.05 nm
Bandpass: 12 cm$^{-1}$
6.35 ns/channel
reduced. In Figure V.6, decay curves for the two transitions $8(a_g^1)^0$ and $8(b_g^1)^0 4(a_g^1)^0$ are illustrated. Both these bands lie in a fairly congested region of the absorption spectrum (see Figure V.1) and consequently a small percentage of short lifetime component remains even when the bandpass is reduced to $12\text{cm}^{-1}$. Both transitions are weak and any further reduction of bandpass gave too poor a ratio of signal-to-background.

The final estimates quoted for the lifetimes of pure vibronic states in naphthalene-$h_8$ have been calculated by fitting a single exponential to the latter section of the decay curves. It was pointed out in Section III.4 that analysis of a decay curve in terms of a sum of two exponentials produces a family of acceptable solutions for a given error in the data. Furthermore, there is no real justification for fitting two exponentials to the decay curves for naphthalene-$h_8$ since the parentage of the short lifetime "component" is not known. It has been shown that less than 15% of the emission intensity stems from unwanted discrete states (populated via the $10\text{cm}^{-1}$ and $6\text{cm}^{-1}$ sequence bands) but the remaining intensity of the short lifetime component must be due to the unresolved background.

A small degree of uncertainty still remains in estimating the lifetime of a pure vibronic state. This concerns the possibility that the lifetimes of other states populated during the excitation step are not vastly different from that of the principal level. If there is a sufficient number of these, the decay curve as a whole will remain
apparently exponential although the lifetime will be a weighted sum of the lifetimes of the mixture of states (refer to Section III.4). In this instance, if the undesired levels are sequence-members, and if their lifetimes are shorter than that of the desired level, the observed lifetime will be correspondingly shortened. It can be expected that, for the higher states in naphthalene-\(h_8\), such an uncertainty is present. A necessary qualification, however, is that if the intensity due to the unidentified levels is derived from states with lifetimes substantially different from the principal level, this would show up as distinct non-exponentiality in the decay curve. Since this is not the case, the observed lifetime is unlikely to be more than \(\sim 15\%\) shorter than that of the pure state, even for the unfavourably situated higher states.

With these considerations in mind, the lifetimes of pure vibronic states of naphthalene-\(h_8\) are presented in Table V.3. The origin band has not been included, since, for the reasons outlined in Section V.4 together with those above, the measured value of \(\sim 300\text{ns}\) is unlikely to be correct. The dependence of lifetime on excess energy above the \(^7B_{3u}\) origin is illustrated in Figure V.7.

In naphthalene-\(d_8\), the sequence intervals corresponding to those shown in Plate 2 for naphthalene-\(h_8\) are 49\(\text{cm}^{-1}\), 9\(\text{cm}^{-1}\) and 5\(\text{cm}^{-1}\). The absorption spectrum shown in Figure V.2 illustrates the increased sequence congestion in comparison with naphthalene-\(h_8\). When attempting to excite a single vibronic level in naphthalene-\(d_8\), contribution to
Fig. V.7 Overall decay rate (inverse of observed lifetime) as a function of energy above the $^1B_{3u}$ origin in naphthalene-$h_8$. Error bars indicate estimated range within which the lifetime of the pure vibronic state is expected to lie.

The dotted lines are indicative only of the relationship between the levels shown.

Symmetries of fundamental frequencies are given below.

\[
\begin{array}{cccccccc}
438 & 501 & 702 & 911 & 987 & 1389 & 1435 \\
b_{1g} & a_g & a_g & b_{1g} & a_g & a_g & a_g
\end{array}
\]
**TABLE V.3.**

Lifetimes of single vibronic levels of the $^1B_{3u}$ state of naphthalene-$h_g$

<table>
<thead>
<tr>
<th>Vibronic State</th>
<th>Energy above origin of $^1B_{3u}$ state (cm$^{-1}$)</th>
<th>Excitation wavelength (nm)</th>
<th>Excitation bandpass (cm$^{-1}$)</th>
<th>% of other$^a$ transitions overlapped</th>
<th>Observed$^b$ lifetime (ns)</th>
<th>Estimated range$^c$ of lifetime of pure vibronic state (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$8(b_{1g})^1$</td>
<td>438</td>
<td>308.09</td>
<td>6</td>
<td>5</td>
<td>270</td>
<td>265 - 275</td>
</tr>
<tr>
<td>$8(a_g)^1$</td>
<td>702</td>
<td>305.60</td>
<td>12</td>
<td>15</td>
<td>174</td>
<td>171 - 177</td>
</tr>
<tr>
<td>$7(b_{1g})^1$</td>
<td>911</td>
<td>303.66</td>
<td>10</td>
<td>10</td>
<td>218</td>
<td>212 - 224</td>
</tr>
<tr>
<td>$8(b_{1g})^18(a_g)^1$</td>
<td>1140</td>
<td>301.58</td>
<td>12</td>
<td>12</td>
<td>162</td>
<td>158 - 166</td>
</tr>
<tr>
<td>$5(a_g)^1$</td>
<td>1389</td>
<td>299.31</td>
<td>12</td>
<td>15</td>
<td>148</td>
<td>143 - 153</td>
</tr>
<tr>
<td>$8(b_{1g})^17(a_g)^1$</td>
<td>1425</td>
<td>298.99</td>
<td>12</td>
<td>10</td>
<td>203</td>
<td>199 - 207</td>
</tr>
<tr>
<td>$8(b_{1g})^19(a_g)^18(a_g)^1$</td>
<td>1641</td>
<td>297.10</td>
<td>12</td>
<td>15</td>
<td>136</td>
<td>131 - 141</td>
</tr>
<tr>
<td>$8(b_{1g})^14(a_g)^1$</td>
<td>1873</td>
<td>295.05</td>
<td>12</td>
<td>15</td>
<td>118</td>
<td>116 - 125</td>
</tr>
<tr>
<td>$8(b_{1g})^18(a_g)^17(a_g)^1$</td>
<td>2127</td>
<td>292.86</td>
<td>12</td>
<td>20</td>
<td>96</td>
<td>93 - 100</td>
</tr>
</tbody>
</table>

$^a$ Estimated from absorption spectrum and intensity of short lifetime component in the decay curve

$^b$ Precision of measurement is better than 3%

$^c$ Based on degree of precision in data and % of other transitions overlapped.
the emission from unresolved background is likely to be greater than for naphthalene-\(h_8\) and consequently the uncertainty in the lifetime will be greater. Non-exponentiality is apparent in the decay curve for the \(8(b_{1g})^19(a_g)^1\) level (Figure V.8a). For states other than the vibrationless state and the \(8(b_{1g})^2\) state, the lifetimes quoted may be in error by as much as 20%. The true lifetime of the pure state would be expected to be longer.

In contrast to naphthalene-\(h_8\), the lifetime of the vibrationless state of naphthalene-\(d_8\) can be confidently assigned. The facility to probe the vibrationless state is provided by the fortuitous coincidence of the 0-490 hot band with the 315.9nm line of the air flash lamp (see Section V.4). The observed lifetime is 485 ±10ns. Figure V.8b illustrates the pure exponential decay curve obtained for the vibrationless state. The lifetime of the \(8(b_{1g})^1\) state of naphthalene-\(d_8\) is also accurately known since the \(8(b_{1g})^1\) transition lies in a clear region of the spectrum. A comparison between the lifetimes of the \(8(b_{1g})^1\) state for naphthalene-\(h_8\) and -\(d_8\) yields the ratio \(\tau_{d_8}/\tau_{h_8} = 1.15\). Assuming that the lifetime of the 0 state is also longer by \(~15\%\) in naphthalene-\(d_8\), the lifetime of the vibrationless state of naphthalene-\(h_8\) is estimated as being \(~420\)ns.

The results for naphthalene-\(d_8\) are summarised in Table V.4 and the energy dependence of the inverse lifetime shown in Figure V.9.
Fig. V.8a  Fluorescence decay from the vibrationless state of naphthalene-\textsubscript{d8}.
Excitation: 315.97nm
Bandpass: 6cm\textsuperscript{-1}
26.87ns/channel

Fig. V.8b  Fluorescence decay from the $8(b_{1g})^{1}g(a_{g})^{1}$ state of naphthalene-\textsubscript{d8}.
Excitation: 302.62nm
Bandpass: 12cm\textsuperscript{-1}
6.35ns/channel
Fig. V. 9 Overall decay rate (inverse of observed lifetime) as a function of energy above the $^1B_{3u}$ origin in naphthalene-$d_8$.

Error bars indicate estimated range within which the lifetime of the pure vibronic state is expected to lie. However, there is some added uncertainty for transitions other than 0+490 and 422+0 (see text).

Dotted lines indicate only the relationship between the levels shown.

Symmetries of fundamental frequencies are given below.

<table>
<thead>
<tr>
<th>Energy (cm$^{-1}$)</th>
<th>Symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>490,422</td>
<td>$b_{1g}$</td>
</tr>
<tr>
<td>484</td>
<td>$a_g$</td>
</tr>
<tr>
<td>638</td>
<td>$a_g$</td>
</tr>
<tr>
<td>1283</td>
<td>$a_g$</td>
</tr>
<tr>
<td>1411</td>
<td>$a_g$</td>
</tr>
</tbody>
</table>
TABLE V.4
Lifetimes of single vibronic levels of the $^1B_{3u}$ state of naphthalene-\textit{d}_8

<table>
<thead>
<tr>
<th>Vibronic State</th>
<th>Energy above origin of $^1B_{3u}$ state (cm$^{-1}$)</th>
<th>Excitation wavelength (nm)</th>
<th>Excitation bandpass (cm$^{-1}$)</th>
<th>% of other$^a$ transitions overlapped</th>
<th>Observed$^b$ lifetime (ns)</th>
<th>Estimated range$^c$ of lifetime of pure vibronic state (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>315.97</td>
<td>6</td>
<td>&lt;5</td>
<td>485</td>
<td>480 - 490</td>
</tr>
<tr>
<td>$8(b_{1g})^1$</td>
<td>422</td>
<td>307.12</td>
<td>10</td>
<td>15</td>
<td>310</td>
<td>298 - 322</td>
</tr>
<tr>
<td>$8(b_{1g})^29(a_g)^1$</td>
<td>906</td>
<td>302.62</td>
<td>10</td>
<td>25</td>
<td>145</td>
<td>138 - 160$^d$</td>
</tr>
<tr>
<td>$8(b_{1g})^28(a_g)^1$</td>
<td>1058</td>
<td>301.24</td>
<td>12</td>
<td>20</td>
<td>158</td>
<td>153 - 164$^d$</td>
</tr>
<tr>
<td>$5(a_g)$</td>
<td>1283</td>
<td>299.21</td>
<td>12</td>
<td>20</td>
<td>164</td>
<td>159 - 170$^d$</td>
</tr>
<tr>
<td>$4(a_g)$</td>
<td>1411</td>
<td>298.07</td>
<td>12</td>
<td>20</td>
<td>142</td>
<td>138 - 149$^d$</td>
</tr>
<tr>
<td>$8(b_{1g})4(a_g)$</td>
<td>1832</td>
<td>294.38</td>
<td>12</td>
<td>20</td>
<td>135</td>
<td>130 - 142$^d$</td>
</tr>
</tbody>
</table>

$^a$ Estimated from absorption spectrum and intensity of short lifetime component in decay curve.

$^b$ Precision of measurement is better than 3%.

$^c$ Based on degree of precision in data and % of other transitions overlapped.

$^d$ These values may be subject to some uncertainty beyond the estimated range (see text).
6. DISCUSSION - NAPHTHALENE

The arguments to follow are to be principally concerned with the lifetimes of single vibronic levels of naphthalene-$h_8$. Although the lifetimes of the $0^0$ and $8(b_{1g}^0)^2$ states of naphthalene-$d_8$ compare in reliability with the results obtained for naphthalene-$h_8$, one cannot attach sufficient credibility to the observed lifetimes of the remaining levels of the deuterated species.

It is of interest to compare the results obtained in this study with those of previous workers. In Table V.5, the lifetimes obtained by Hsieh, Laor & Ludwig (1971) and by Schlag, Schneider & Chandler (1971) are reproduced, together with some of the results previously shown in Table V.3. A full comparison is hindered by the fact that Hsieh et al chose vibronic regions of the spectrum which were roughly equally spaced with respect to energy above the origin, whilst Schlag et al attempted to probe successive members of the 55cm$^{-1}$ sequence. The levels chosen in the present work correspond to progression band heads involving $b_{1g}$ and $a_g$ fundamentals only, since these transitions are most amenable to fine optical selection.
TABLE V.5

Comparison between lifetime studies of the \(^{1}B_{3u}\) state of the isolated naphthalene molecule

<table>
<thead>
<tr>
<th>Vibronic state</th>
<th>Hsieh et al (35cm(^{-1}))^a</th>
<th>Lifetime (ns) Schlag et al (20cm(^{-1}))^a</th>
<th>Present study (12cm(^{-1}))^a</th>
</tr>
</thead>
<tbody>
<tr>
<td>0^0</td>
<td>250</td>
<td>200^a</td>
<td>420^d</td>
</tr>
<tr>
<td>8(b_1g)^1</td>
<td>215</td>
<td>211</td>
<td>270^e</td>
</tr>
<tr>
<td>8(a_g)^1</td>
<td>-</td>
<td>106</td>
<td>174</td>
</tr>
<tr>
<td>7(b_1g)^1</td>
<td>-</td>
<td>92</td>
<td>218^f</td>
</tr>
<tr>
<td>8(b_1g)^18(a_g)^1</td>
<td>158^b</td>
<td>75</td>
<td>162</td>
</tr>
<tr>
<td>8(b_1g)^17(a_g)^1</td>
<td>135</td>
<td>109</td>
<td>203</td>
</tr>
</tbody>
</table>

^a Excitation bandpass

^b The authors obtained this value from the tail of the decay curve

^c Includes a correction for scattered light and is accurate to only \(\pm 25\%\)

^d Estimated value by comparison with naphthalene-d\(_8\) (see text)

^e Result obtained with 6cm\(^{-1}\) bandpass

^f Result obtained with 10cm\(^{-1}\) bandpass.
The only agreement among any of the three sets of results in Table V.5 is for the $8(b_{1g})^18(a_g)^1$ level. For this level, Hsieh et al calculated the lifetime from the tail of the decay curve and obtained a value of 158ns. This compares favourably with the value of 162ns determined in the present study. The figure of 75ns quoted by Schlag et al is indicative of inaccuracies involved in phase methods. For all other levels, the lifetimes of Hsieh et al are shorter than those obtained in the present study. This is due to the inadequate resolution of their excitation as well as due to the limited time range of their instrument which prevents deviation from exponential behaviour to be seen easily. There are also qualitative differences in the three sets of results. For example, Hsieh et al find the lifetime of the $8(b_{1g})^18(a_g)^1$ state to be longer than that of the $8(b_{1g})^17(a_g)^1$ state. Schlag et al are in agreement with the present work in that the reverse order is found for these two levels. However, detailed comparisons between previous studies and the lifetimes measured in the course of this research are unlikely to prove beneficial. The evidence presented in Sections V.4 and V.5 strongly favours acceptance of the present data.

Quantum Yields

Before one can proceed to discuss the details of the dependence of decay rate on vibronic energy content, it is necessary to realise that a proper account of the relative rates of the radiative and non-radiative decay
would require measurements of quantum yields.

Parmenter & Schuyler (1970 b) first determined absolute quantum yields from several specific vibronic levels in benzene. These measurements confirmed that the quantum yield was not constant for all vibronic levels. Indeed, the relative quantum yield measurements of Spears & Rice (1971) showed that in benzene, the variation in yield can be quite dramatic. For example, the yield of the $0^1$ state is 0.22 whereas the yield of the $6^15^2$ state, 2070 cm$^{-1}$ higher in energy, is 0.06.

Comparable studies of quantum yields of single vibronic levels in naphthalene have not yet been reported. Although Blondeau & Stockburger (1971 b) succeeded in obtaining resonance fluorescence spectra from naphthalene vapour, they did not determine fluorescence quantum yields. The dearth of information is understandable since, apart from the notorious difficulties involved in obtaining accurate quantum yields, it is considerably more difficult to achieve single vibronic level excitation in naphthalene than in benzene. Consequent inaccuracies arising as a result of both poor optical selection and insufficient emission intensity are likely to be prevalent. Uy & Lim (1970) have studied the quantum yield of fluorescence from various vibronic regions (selected with 100 cm$^{-1}$ resolution) in naphthalene-$h_8$ and $-d_8$ at a pressure of $\sim$0.1 Torr. The quantum yield is found to depend on which vibronic region is excited. A subsequent communication by
the same authors (Lim & Uy 1972) describes the quantum yield studies for naphthalene-hg using a 5nm bandpass ($\nu 600\text{cm}^{-1}$).

Of considerable concern is the large discrepancy between these results and those obtained under identical conditions, (0.1Torr pressure, 25°C, 5nm excitation bandpass) by Formosinho & Porter (1972). The yields measured by Lim & Uy are appreciably less than those of Formosinho & Porter. The two sets of results differ by a factor of $\sqrt{3}$ at 250nm and a factor of $\sqrt{4.5}$ at 310nm.

The zero-point vibrational level of $^1B_{3u}$ naphthalene

The lifetime of the vibrationless state of naphthalene-d$_8$ is 485ns. An estimate of 420ns is obtained for the lifetime of the $0^0$ state of naphthalene-h$_8$ by assuming that isotopic substitution has the same effect on the lifetime of the vibrationless state as it does on the $8(b_{1g})^1$ state.

From the integrated intensity of the $^1B_{3u} \rightarrow ^1A_g$ absorption, as estimated from the vapour spectrum of Figure V.1, one obtains a radiative lifetime for the $0^0$ level of 550ns. Various estimates of $\tau_n$ for naphthalene have appeared in the literature, all based on solution spectra. A recent value of 630ns, obtained from the observed lifetime and quantum yield in cyclohexane (Mataga, Tomura & Nishimura 1965) is comparable. The uncertainties are determined, not by considerations of slitwidth effects (in the vapour spectrum) or dielectric
corrections (solution) but simply by the uncertainty concerning how much of the intensity of the $^1B_{2u}+^1A_g$ transition underlies the high frequency end of the $^1B_{2u}+^1A_g$ transition and how much of the latter underlies the former. The above estimate of 550ns should probably be interpreted as 500-650ns. The integrated intensity from which this figure is derived is a thermal average over populated ground state levels. It is, however, dominated by transitions from $0^+_g$ and $0^+_g + \text{inactive}$ vibrations, and the estimate given should be close to that obtained from the idealization of a vapour at zero Kelvin.

There is a question whether the principal decay channels from $0^0$ (e.g. $0^0 \rightarrow 8(b_{1g})^1$) have the same probabilities as the principal excitation channels (e.g. $8(b_{1g})^1+0_0$). From studies of the temperature dependence of the absorption, it has been stated that their probabilities are equal to within 10% (Passerini & Ross 1954). There is no information on the minor channels.

One is thus led to conclude that the quantum yield of the zero point level of naphthalene is fairly high: at the very least: $420(\text{obs})/650$ (high estimate from absorption) = 0.65. Formosinho & Porter (1972) obtain a value of 0.92 for the quantum yield when irradiation is at $310\pm2.5\text{nm}$. The yield deduced from the lifetime measurement is not grossly inconsistent with this result. In contrast, Lim & Uy (1972) obtain a value of 0.21 when irradiating at $308\pm2.5\text{nm}$. This figure appears to be wrong. However, both workers used broad band excitation and the
quantum yields are not representative of the properties of a single level.

Without further confirmation of the value of 0.92 for the quantum yield of low vibrational levels of naphthalene, it is difficult to accept Formosinho & Porter's suggestion that the lowest vibrational level belongs to the intermediate case. Robinson (1967) argued that benzene may be an example of a large molecule for which certain states lie in the statistical limit, but the lowest vibrational level represents the intermediate case. The recent work of Ware, Selinger, Parmenter & Schuyler (1970) and Spears & Rice (1971) contradicts this proposal for benzene, and it seems highly probable that naphthalene, which has many more vibrational degrees of freedom, would also lie in the statistical limit. The theoretical justification for the occurrence of radiationless transitions in isolated molecules is that the density of intramolecular vibrational states is sufficiently large in the region of the optically prepared state. The energy gap between the $^2B_{3u}$ state and the lowest triplet ($^3B_{2u}$) state in naphthalene is $\sim 10,000 \text{cm}^{-1}$ (Ferguson, Iredale & Taylor 1954). Calculations by Bixon & Jortner (1968) show that naphthalene certainly meets the requirements for intramolecular coupling to a dissipative quasi-continuum provided by the density of triplet states.
Before engaging in a discussion concerning the factors which affect the non-radiative decay of single vibronic levels of the isolated $^1B_{3u}$ naphthalene molecule, it is necessary and instructive to examine the behaviour of the radiative lifetime as expected from the Herzberg-Teller theory of vibronic coupling. In particular, consider the zero vibrational level of the $^1B_{3u}$ state and the level containing one quantum of the $8(b_{1g})$ vibration. A simplified diagram of the energy levels in naphthalene is shown in Figure V.10.

The point to be made now is that the radiative lifetime of $8(b_{1g})^1$ should be, in this simplification, three times shorter than that of the zero point level, $0^0$. This conclusion is embedded, not very obviously, in a treatment of the temperature-dependence of the absorption intensity of benzene, by Albrecht (1960), but is there obscured by the need for thermal averaging and by the fact that the vibronically active vibrations are doubly degenerate. In the case of benzene, the radiative lifetimes of the $6^1$ and $0^0$ levels are in the ratio 1:2, as used by Selinger & Ware (1970 b) and Spears & Rice (1971). For a non-degenerate vibration, a simple proof, entirely consistent with the Herzberg-Teller argument, is as follows. Consider the crude adiabatic levels (cf. Nitzan & Jortner 1971) of Figure V.10. The notation for wavefunctions has
Fig. V.10. Schematic representation of energy levels in naphthalene. Double-headed arrows denote coupling between states.
capital letters for electronic states and numbers for vibrational quanta of frequency $\nu_a$, say. Consider the initially prepared state $|M\nu_a\rangle$ to have $\nu_a$ quanta of $\nu_a$. The dominant vibronic coupling matrix elements between states $|M\rangle$ and $|N\rangle$ are of the form

$$<M|\left(\partial V/\partial Q\right)_{Q_a=0}|N\rangle|\nu_a|\nu_a+1>$$

$$<M|\left(\partial V/\partial Q\right)_{Q_a=0}|N\rangle|\nu_a|\nu_a-1>$$

where $|\nu_a\rangle$ is interpreted as the vibrational part of the wavefunction for the state $|M\nu_a\rangle$. In the harmonic approximation, the vibrational part can be written as

$$<\nu_a|Q|\nu_a+1>= (\nu_a+1)^{\frac{1}{2}}<\nu_a|Q|1>$$

$$<\nu_a|Q|\nu_a-1>= \nu_a^{\frac{1}{2}}<\nu_a|Q|1>$$

and the electronic part can be denoted by a constant, say $C$.

Figure V.10 indicates the unperturbed wavefunctions (on the left), and on the right the wavefunctions corrected to second order, where

$$\lambda = -C/(E_N^0 - E_M^0)$$

it being assumed that $(E_N^0 - E_M^0) >> \nu_a$. 

\[ \]
For the downward transitions shown, the only effective electronic matrix element is

$$<G|\mu^e|N> = \mu^e$$  \hspace{1cm} (V.8)

The $0^0 (\equiv |M0_a>)$ level has a single decay channel with transition moment $\lambda^m$. The $8(b_{1g})^1 (\equiv |M1_a>)$ level has two channels with moments $\lambda^m$ and $2\lambda^m$ (assuming $<1_a|1_a> = <0_a|0_a>$). The relative rates of radiative decay are thus as

$$\lambda^2 : (\lambda^2 + 2\lambda^2), = 1:3.$$

In a similar manner, for the two quantum level,

$8(b_{1g})^2 (\equiv |M2_a>)$ the ratio would be

$$\lambda^2 : (2\lambda^2 + 3\lambda^2) = 1:5.$$

The emission spectrum from $8(b_{1g})^1$ obtained by Blondeau & Stockburger (1971 b) confirms the above expectation qualitatively by showing the two emissive channels $8(b_{1g})^1 \rightarrow 0$ and $8(b_{1g})^1 \rightarrow 8(b_{1g})_2$ as having intensities in the ratio 1:2.1. The single vibronic level emission from the zero point level is not available.

The observed lifetimes of the $8(b_{1g})^1$ and $0^0$ levels, best obtained from the perdeutero compound, are in the ratio 310 : 485, i.e. 1:1.6.

The discrepancy between this figure and the
theoretical figure of 1 : 3 is not unexpected since the existence of parallel decay channels, common to both the $8(b_{1g})^1$ and $0^0$ states will reduce this ratio. These parallel channels are of two kinds:

(i) radiative - through other vibronic modes, for example $8(b_{1g})^1 \rightarrow 8(b_{1g})_1^1 7(b_{1g})_1^1$ and $0^0 \rightarrow 7(b_{1g})_1^1$.

From Blondeau & Stockburger's spectrum, the contribution from these processes can be estimated for the $8(b_{1g})^1$ state, and are possibly responsible for reducing the ratio of 1 : 3 down to at least 1 : 2.

(ii) non-radiative - the competing process of inter­system crossing must be considered and it is not inconceivable that this could account for the remaining parallel processes which bring the ratio 1 : 2 down to the experimentally observed value of 1 : 1.6.

The above arguments show that the lifetimes of the $0^0$ and $8(b_{1g})^1$ levels are consistent with expectations based on our present understanding of vibronic coupling in naphthalene. A full explanation has not yet been found for the behaviour of the other levels shown in Figure V.7, but undoubtedly it would be necessary to consider the radiationless processes in more detail. However, some difficulties can immediately be foreseen. The most recent and most successful theoretical study of the dependence of radiationless decay rates upon the initially selected vibronic state is that of Heller, Freed & Gelbart (1972). With benzene, they find satisfactory agreement between
experiment and theory for the relative rates of members of a progression in any one vibrational mode. By taking relative rates, the electronic factor, which is the most difficult part of the rate expression to calculate accurately, cancels out. With naphthalene, there are no obvious progressions in any mode and this procedure would not be possible.

From studies of the pressure dependence of naphthalene fluorescence, Formosinho & Porter (1972) concluded that the process of intersystem crossing is reversible when the vibrational excess of the excited molecule is high. Non-exponential decay is then to be expected. However, in the present study (which is concerned with excitation to levels <2200 cm\(^{-1}\) above the origin) the non-exponentiality in the initial part of the decay curves has been shown to depend on the excitation bandpass and therefore can be related to the effect of sequence congestion.
Three distinct systems are apparent in the vapour absorption system of phenanthrene in the range 350nm to 220nm. The first system, assigned to the species $^1A_1$, is of considerable interest because both symmetric and non-totally symmetric vibrations are found responsible for intensity stealing from stronger transitions at higher energy. Moreover, the intrinsic intensity of the $S_1\rightarrow S_0$ transition in phenanthrene is approximately equal to the vibronically induced component, whereas in benzene the ratio is zero and in naphthalene it is $\sim 0.1$ (Craig & Gordon 1965; Hochstrasser & Small 1966).

Craig & Gordon (1965) were the first to discern sharp features in the $^1A_1\rightarrow^1A_1$ vapour absorption spectrum. The spectrum was nevertheless found to be highly congested and even at high resolution, closely resembled the solution spectrum. The bulk of research concerning the first system has been confined to studies in condensed phases.

The second singlet system has only recently received detailed attention. Fischer (1969) observed the spectrum in mixed crystals at 4K and confirmed the assignment of $^1B_2$ for the second singlet state. The vibronic structure is quite different from the first system, most of the intensity being in the broad origin band at 33900cm$^{-1}$. 

7. FLUORESCENCE DECAY OF THE ISOLATED PHENANTHRENE MOLECULE:
The vibronically active $a_1$ vibrations seen in the $^1A_1$ system are absent in the second system, but vibronic coupling is seen through a $b_2$ vibration which allows interaction with a higher $A_1$ state, thought to be the third system. Fischer (1972) has also measured the room temperature vapour absorption spectrum for the $^1B_2 - ^1A_1$ transition at high resolution.

The low resolution double-beam vapour absorption spectra of phenanthrene-$h_{10}$ and $-d_{10}$ in the range 300-220nm are shown in Figure V.11. These spectra were recorded at 60°C and 10cm path length on a Cary 14 spectrometer.

The third singlet absorption system consists principally of two very strong, broad bands with maxima (for $-h_{10}$) at 242.2nm and 234.7nm, and is otherwise relatively featureless. The beginning of a fourth system is seen at 218nm.

Powell (1967) studied the lifetime of phenanthrene in the vapour phase at pressures above 20Torr. To attain this pressure, temperatures in excess of 200°C were necessary. A sampling oscilloscope technique was used to measure lifetimes and colour filters were suitably chosen so as to limit the excitation to either the first or second singlet state. Powell measured the lifetimes of the first and second excited singlet states as $50\pm2$ns and $45\pm2$ns respectively.

Lifetime studies of the isolated phenanthrene molecule have not previously been reported. The difficulty
Fig. V.11. Low resolution vapour absorption spectra of phenanthrene-\(h_{10}\) and \(-d_{10}\). Spectra were recorded at 60°C and 10cm path length using a Cary 14 double beam spectrophotometer at a resolution of 0.1nm.
in undertaking such a study is apparent when one considers that Craig & Gordon (1965) required a 50m path length and a temperature of 90°C for adequate vapour pressure to record the 1A↓←1A↓ absorption. The high sensitivity of the single photon technique has enabled the fluorescence decay of phenanthrene vapour to be observed in 1cm path at a temperature of 55°C, at which the saturated vapour pressure is 0.03Torr. In cyclohexane solution, the lifetime has been measured as 56ns (Amata, Burton, Helman, Ludwig & Rodemeyer (1968)). In the vapour, the longest lifetime observed in the present work was 67ns (for the perdeutero compound), from which it can be safely assumed that, at 0.03Torr, an excited phenanthrene molecule will be essentially isolated over several mean lifetimes (refer to section V.2).

Experimental

Phenanthrene and phenanthrene-d<sub>10</sub> (purified as described by Fischer (1969)) were kindly supplied by Dr. Fischer. The procedure for filling the Rayleigh horn with phenanthrene vapour was the same as that used for naphthalene (see Section V.5). The horn was contained in a double-walled insulated box which was heated by circulating hot water from a Colora Ultra-Thermostat controlled at 55°C. The box was fitted with suprasil windows and was designed to completely enclose the horn. In this way, the temperature could be kept uniform and so prevent.
crystallisation of phenanthrene on the horn windows. From the first singlet system, emission could only be detected when using the strong 315.9nm and 337.1nm lines of the air-filled flash lamp. For the second and higher absorption systems, the dependence of lifetime on excitation energy was studied using the deuterium filled flash lamp. The excitation wavelength was selected by means of a Bausch & Lomb double grating monochromator with a bandpass of 2.0nm. Scattered excitation light was eliminated by using a filter solution consisting of 0.2g/dm³ cyanine perchlorate (Kasha 1948) which has an absorption cutoff at 345nm. The detection system has been described in Chapter II. Count rates ranged from 15s⁻¹ to 150s⁻¹. In some cases, it was possible to reduce the excitation bandwidth to 0.5nm whilst still retaining acceptable signal-to-background ratio.

**Dependence of lifetime on excitation energy**

Although the first singlet absorption system of phenanthrene shows some sharp features, excitation with a 2.0nm bandpass does not even remotely approximate excitation to single vibronic levels. Furthermore, studies are limited to the wavelengths corresponding to the strong lines of the air-filled flash lamp. The second, third and fourth absorption systems are diffuse and the excitation bandpass used would correspond to populating a very large number of overlapping levels, including many sequence bands.
From the decay curves of phenanthrene-$h_{10}$ and $-d_{10}$ shown in Figure V.12 and Figure V.13, it can be seen that the fluorescence decay follows a single exponential. This has been observed for all regions of excitation. Such an observation is quite consistent with the likely physical situation whereby a large number of states are initially excited. As was shown in Section III.4, the weighted sum of exponentials corresponding to the decay from states with widely varying lifetimes can give rise to an apparent single exponential decay. The effect of this would be to smooth out what may have been large variations in the dependence on energy of lifetimes of particular states.

In naphthalene, such an effect was responsible for the observation of an apparent smooth decrease in lifetime with increasing excitation energy when a 5nm excitation bandpass was used (Laor & Ludwig 1971). However, the lifetime of phenanthrene does not decrease smoothly with energy. There are significant deviations from a simple linear dependence, these being more pronounced in phenanthrene-$h_{10}$.

The emission was observed in the region corresponding to $S_1+S_0$ fluorescence and estimates of the relative fluorescence yield showed that over the 14,000cm$^{-1}$ range of excitation energy, the yield did not vary by more than ±50%. (Relative yields were determined in a manner similar to that described by Spears & Rice 1971). Attempts to locate emission from higher electronic states were
Fig. V.12. Fluorescence decay curves for phenanthrene-$h_{10}$ vapour at a pressure of 0.03 Torr, 55°C.

Excitation: a) 337.1nm \((S_1+S_0)\)  
b) 283.8nm \((S_2+S_0)\)  
c) 234.7nm \((S_3+S_0)\)

Bandpass: 2nm  
3.16ns/channel (a, b)  
2.61ns/channel (c).
Fig. V.13. Fluorescence decay curves for phenanthrene-d_{10} vapour at a pressure of 0.03 Torr, 55°C.

Excitation:  
- a) 337.1nm \( (S^1 + S^0) \)  
- b) 283.2nm \( (S^2 + S^0) \)  
- c) 232.6nm \( (S^3 + S^0) \)

Bandpass: 2nm  
3.12ns/channel (a,b)  
2.61ns/channel (c)
Fig. V.14. Overall decay rate (inverse of observed lifetime) as a function of excitation energy for phenanthrene-$h_{10}$ and $-d_{10}$ vapour under collision-free conditions.
### TABLE V.6.

Lifetimes of the isolated phenanthrene-$h_{10}$ molecule as a function of excitation energy

| Excitation wavelength (nm) | Excitation energy (cm$^{-1}$) | Lifetime (ns) | Electronic state  
|---------------------------|-------------------------------|---------------|------------------
| 337.1                     | 29665                         | 58.0          | $S_1$            
| 315.9                     | 31656                         | 53.6          | $(1\,^1A_1 + 1\,^1A_1)$  
| 286.0                     | 34965                         | 43.0          |                 
| 283.8                     | 35236                         | 44.3          |                 
| 277.8                     | 35997                         | 40.5          |                 
| 277.0                     | 36101                         | 41.5          |                 
| 273.5                     | 36563                         | 41.8          | $S_2$            
| 271.0                     | 36900                         | 39.5          | $(1\,^1B_2 + 1\,^1A_1)$  
| 267.7                     | 37355                         | 46.7          |                 
| 262.0                     | 38168                         | 45.0          |                 
| 253.0                     | 39526                         | 35.5          |                 
| 248.1                     | 40306                         | 34.5          | $S_3$            
| 242.2                     | 41288                         | 39.8          | $(1\,^1A_1 + 1\,^1A_1^2)$  
| 234.7                     | 42608                         | 37.9          |                 
| 218.3                     | 45809                         | 26.0          | $S_4$            

$a$ Excitation bandpass of 2.0nm  
$b$ Precision of measurement is ±3%  
$c$ Reduction of excitation bandpass to 0.5nm gave $\tau = 44.6$ns  
$d$ Assignments for these states are not confirmed
<table>
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<tr>
<th>Excitation wavelength (nm)</th>
<th>Excitation energy (cm(^{-1}))</th>
<th>Lifetime (\tau) (ns)</th>
<th>Electronic state</th>
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<td>337.1</td>
<td>29665</td>
<td>67.0</td>
<td>(S_1)</td>
</tr>
<tr>
<td>315.9</td>
<td>31656</td>
<td>60.5</td>
<td>(1A_1+1A_1^)</td>
</tr>
<tr>
<td>285.0</td>
<td>35087</td>
<td>49.9</td>
<td>(S_2)</td>
</tr>
<tr>
<td>283.2</td>
<td>35311</td>
<td>49.6(^a)</td>
<td>(1B_2+1A_1)</td>
</tr>
<tr>
<td>282.7</td>
<td>35373</td>
<td>50.2</td>
<td></td>
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<tr>
<td>279.3</td>
<td>35804</td>
<td>49.0</td>
<td></td>
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<td>36630</td>
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<td>37665</td>
<td>44.4</td>
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<td>37908</td>
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<td></td>
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<td>39293</td>
<td>40.1</td>
<td></td>
</tr>
<tr>
<td>243.9</td>
<td>41000</td>
<td>37.7(^d)</td>
<td>(S_3)</td>
</tr>
<tr>
<td>241.7</td>
<td>41374</td>
<td>44.5(^a)</td>
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</tr>
<tr>
<td>234.5</td>
<td>42644</td>
<td>41.4</td>
<td>(1A_1+1A_1^?)</td>
</tr>
<tr>
<td>232.6</td>
<td>42992</td>
<td>35.1</td>
<td></td>
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<tr>
<td>227.0</td>
<td>44053</td>
<td>33.7(^d)</td>
<td>(S_4)</td>
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<tr>
<td>220.0</td>
<td>45455</td>
<td>31.5</td>
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\(^a\) Excitation bandpass of 2.0nm
\(^b\) Precision of measurement is ±3%
\(^c\) Reduction of bandpass to 0.5nm gave same lifetime
\(^d\) Assignment for these states are not confirmed.
unsuccessful.

The lifetime data for phenanthrene-$h_{10}$ and-$d_{10}$ is summarised in Tables V.6 and V.7. The dependence of decay rate on excitation energy is shown in Figure V.14.

8. DISCUSSION - PHENANTHRENE

The most significant feature of the dependence of the lifetime of phenanthrene on excitation energy is, that over a range of some $14000\text{cm}^{-1}$, the overall decay rate increases by a factor of only 2.5. This observation contrasts strongly with the results obtained for naphthalene, for which the decay rate increases by a factor of 5 over a range in energy of $2000\text{cm}^{-1}$ (Section V.5). With regard to phenanthrene, the interpretation would seem to be that the process of electronic relaxation is affected only to a small extent by increasing the energy of the initially prepared state. This is yet another feature, apart from the unusual vibronic coupling seen in the absorption spectra, which differentiates phenanthrene from benzene and naphthalene. In benzene, the lifetime shortens by a factor of 2.5 over a range in energy of $3000\text{cm}^{-1}$ and it is well known that no fluorescence can be observed from the isolated molecule when it is excited more than $3300\text{cm}^{-1}$ above the origin of the first singlet. Recent high resolution studies show that the emission cutoff in benzene is coincident with the energy at which absorption bands of the first system become visibly
diffuse. The evidence favours the possibility of a previously unidentified $\sigma-\pi^*$ state occurring at this energy (Callomon, Parkin & Lopez-Delgado 1972). In phenanthrene, no such complexity appears to be present.

The measured decay rates of phenanthrene decrease markedly when excitation encounters the peaks of the stronger bands of the absorption spectrum. A simple explanation for this observation is that in such regions a larger proportion of excitation reaches the longer lived low vibrational levels.

In the few cases where the bandpass was reduced to 0.5nm (see Tables, V.6, V.7), no significant change in the lifetime could be detected.
9. THE DEUTERIUM ISOTOPE EFFECT

The enhancement of the lifetime and quantum yield of phosphorescence in large polyatomic molecules as a result of deuteration has been well documented (Lim & Laposa 1964; Martin & Kalantar 1968). It is currently accepted that deuteration decreases the rate of intersystem crossing between the lowest triplet state and the ground state. There has been, in the past, little experimental evidence for a similar widespread effect in fluorescence (Laposa, Lim & Kellogg 1965). On the contrary, Sharf & Silbey (1970) have suggested that when higher triplet states are involved in intersystem crossing from the singlet state, deuteration can actually enhance the rate of non-radiative decay.

Lim & Bhattacharjee (1971) have observed the lifetime and quantum yield of fluorescence in condensed media to be less for anthracene-d_{10} than for anthracene-h_{10}. However, this so-called "inverse" deuterium isotope effect does not appear to be a common phenomenon. Indeed, a single measurement on anthracene-d_{10} vapour (10^{-4} Torr) gave a lifetime longer than that of anthracene-h_{10}. (The latter measurement was described in Section II.7).

The lifetime studies of naphthalene and phenanthrene vapour under no-collision conditions (Sections V.5, V.7) reveal that the deuterated species is usually longer lived. In particular, the lifetime of 8(b_{1g})^2 state of perdeutero naphthalene is 15% longer than that of naphthalene. In the few cases where the lifetime of the
deuterated species is found to be shorter, the effect of sequences is a more plausible explanation than an inverse isotope effect. These observations are consistent qualitatively with studies of the lifetime and quantum yield of benzene vapour which show that the rate of inter-system crossing from the $^1B_{2u}$ state in C$_6$H$_6$ is approximately twice that in C$_6$D$_6$ (Breuer & Lee 1969; Spears & Rice 1971; Abramson, Spears & Rice 1972).

Quantum yield measurements by Uy & Lim (1970) show that the yield for the $8(b_{1g})^1$ level of naphthalene is less for the deuterated species. However, there is some doubt concerning these measurements (see Section V.6). The effect of deuteration on the lifetime of this level would suggest that the interpretation of Uy & Lim in terms of an inverse isotope effect is not correct.

Azulene, which fluoresces from its second excited singlet state, provided the first recorded example of the enhancement of fluorescence yield as a result of deuteration, the effect being observed in solution and, even more strongly, in frozen solution (Johnson, Logan & Ross 1964). However, lifetime measurements are needed to confirm that it is indeed the non-radiative rate which is reduced upon deuteration. These measurements will now be discussed.
10. LIFETIMES OF AZULENE

Experimental

For the vapour phase measurements, the techniques used were similar to those described for naphthalene (Section V.5) and phenanthrene (Section V.7). Because of the short lifetime of azulene, it is critical that, when the decay curve is being measured, no scattered excitation light should be observed. This condition was achieved by using a Chance-Pilkington OVI glass filter to select the region of emission. By means of the method of convoluting and fitting (Section III.9), lifetimes were determined to within an accuracy of 5%. Lifetimes for the vapour phase were measured under collision-free conditions (0.02 Torr, 23°C). For solution and frozen solution, the emission was viewed at 45° through a Bausch & Lomb high intensity monochromator used with a 2 nm bandpass centred on the fluorescence maximum. For measurements at 77K, the samples were held in a clear silica dewar containing liquid nitrogen. The solutions were deoxygenated and sealed before use. Sources of azulene and azulene-\textsubscript{d8} have been described previously (Hunt & Ross 1959; Johnson, Logan & Ross 1964).

Results

The decay curves for azulene-\textsubscript{h8} and -\textsubscript{d8} at 0.02 Torr
vapour pressure are shown in Figure V.15. Table V.8 summarises the effect of deuteration on lifetime. Deuteration is seen to enhance the lifetime by a factor of \( \approx 1.5 \) for azulene in frozen solution and for the isolated molecule. In solution the ratio is somewhat less (1.3).

When excitation is at 337.1\text{nm}, the lifetime of the vapour is longer than in condensed media. The vapour lifetime decreases when higher energy excitation is used.

**TABLE V.8**

Lifetimes \( (\tau) \) for the singlet \( S_0(1\text{A}_1(\Sigma)) \) state of azulene-\( \text{h}_8 \) and -\( \text{d}_8 \)

<table>
<thead>
<tr>
<th>Phase</th>
<th>( \lambda_{\text{ex}} ) (nm)</th>
<th>( \tau(\text{h}_8) ) (ns)</th>
<th>( \tau(\text{d}_8) ) (ns)</th>
<th>( \tau(\text{d}_8)/\tau(\text{h}_8) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>vapour 0.02 Torr</td>
<td>296K</td>
<td>315.9(^a) 1.08</td>
<td>1.73</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>337.1(^a) 2.09</td>
<td>2.94</td>
<td>1.4</td>
</tr>
<tr>
<td>( 10^{-4}) M methylcyclohexane</td>
<td>296K</td>
<td>337.1(^b) 1.63</td>
<td>2.08</td>
<td>1.3</td>
</tr>
<tr>
<td>( 10^{-4}) M methylcyclohexane</td>
<td>77K</td>
<td>337.1(^b) 1.82</td>
<td>2.67</td>
<td>1.5</td>
</tr>
</tbody>
</table>

\(^a\) Excitation bandpass of 0.5nm  
\(^b\) Excitation bandpass of 0.2nm

11. DISCUSSION - AZULENE

Johnson, Logan & Ross (1964) did not determine absolute quantum yields so, from their results, one cannot draw
Fig. V.15. Fluorescence decay curves for azulene-$h_8$ (....) and azulene-$d_8$ (++++) vapour at a pressure of 0.02 Torr, 23°C.
Excitation pulse (———) at 337.1nm
Bandpass: 0.5nm
0.30ns/channel
quantitative conclusions concerning the rates of the radiationless processes. Rentzepis, Jortner & Jones (1970) observed the $S_2 \rightarrow S_1$ transition of azulene by means of high power, picosecond pulses from a mode-locked laser. The quantum yield of fluorescence of azulene-$d_8$ was found to be $\sim 20\%$ greater than that of azulene-$h_8$. A subsequent communication by Huppert, Jortner & Rentzepis (1972) reveals that the absolute yields determined in their previous study were in error by a factor of $10^2$, but the ratio $Y_{d_8}/Y_{h_8}$ is unlikely to have changed. The non-radiative processes competing with the $S_2 \rightarrow S_1$ fluorescence must be the same as those in competition with the $S_2 \rightarrow S_0$ fluorescence; thus the results obtained by Johnson, Logan & Ross are confirmed. If one uses a radiative lifetime calculated from the integrated absorption of $2.4 \times 10^{-8}$ s for azulene-$h_8$ (Mann, Platt & Klevens 1949) the radiationless rate is $5 \times 10^8$ s$^{-1}$ for azulene-$h_8$ and $3 \times 10^8$ s$^{-1}$ for azulene-$d_8$ (assuming an enhancement of quantum yield of $\sim 20\%$).

The enhancement by deuteration of the fluorescence lifetime and quantum yield of benzene vapour has been explained in terms of a decrease in the rate of intersystem crossing from $S_1 \rightarrow T_1$, it being agreed that the internal conversion process $S_1 \rightarrow S_0$ can be neglected because of the prohibitive $S_1 - S_0$ energy gap of $\sim 38000$ cm$^{-1}$. The $S_1 - T_1$ energy gap is $\sim 8600$ cm$^{-1}$. In azulene, $\Delta E(S_2 - T_1)$ has been estimated as $16000 \pm 1400$ cm$^{-1}$.
(Lamola, Herkstroeter, Dalton & Hammond 1965) and $\Delta E(S^0 - S_1)$ is $\sim 14000 \text{cm}^{-1}$. On the basis of energy gap, it would therefore seem most likely that the isotope effect in azulene is largely due to a reduction on deuteration of the C–H stretching contribution to the $S_2 \rightarrow S_1$ internal conversion process (Byrne, McCoy & Ross 1965). However, there remains a likelihood that deuteration affects the rate of intersystem crossing to triplet states higher than $T_1$.

Although the absorption spectrum of the $S_2 + S_0$ transition of azulene vapour is sharp, the bandpass used for the lifetime studies does not resolve individual vibronic levels. High resolution spectra taken by McCoy (1964) show that the 337.1nm air line excites both azulene and azulene-$d_8$ in a region corresponding to high sequence members. With respect to the absorption spectra, the excitation is at relatively lower energy (in terms of wavelength) for azulene-$d_8$, but it probes similar sequence members. For both the deuterated and undeuterated species, the initially prepared levels would be $\sim 1500 \text{cm}^{-1}$ above the origin. The lifetime of the isolated molecule is considerably shorter for excitation at 315.9nm than at 337.1nm (a factor of two). On a qualitative basis, azulene behaves similarly to naphthalene in that the decay rate increases quite rapidly over a relatively small range of energy.
CHAPTER VI

LIFETIME STUDIES WITH OPTICAL SELECTION OF EXCITATION AND EMISSION

This chapter deals with two experimental studies of vapour phase emission, each of which involves measuring decay curves with optical selection of both excitation and emission.

The first is a preliminary attempt to observe the fluorescence decay from a single vibronic level of naphthalene-\textsubscript{d}_8 which has been populated as a result of vibrational relaxation. Such an experiment requires narrow-band excitation to select a single vibronic level and further, it requires the emission from some other level, reached as a result of collisional deactivation, to be resolved.

The second part of this chapter describes a study carried out in collaboration with A.R. Lacey. The vapour absorption spectrum of dibenzofuran was reported to consist of two sharp systems (Pinkham & Wait 1968). This spectrum has been re-examined and, in conjunction with
studies of the vapour emission, reveals that the data of Pinkham & Wait are incorrect.

1. VIBRATIONAL RELAXATION IN NAPHTHALENE-d₈

Vibrational energy exchange has been the subject of many studies, the majority of which have been concerned with small molecules using ultrasonic techniques (Cottrell & McCoubrey 1961; Stevens 1967). The pressure dependence of fluorescence emission from large molecules, whose spectra are diffuse, also received early attention (Neporent 1939, 1947; Terenin, Vartanyanan & Neporent 1939).

The information obtainable from acoustic studies is limited, most molecules showing only a single relaxation time. The study of structureless fluorescence spectra likewise yields little information concerning details of the many available pathways of vibrational relaxation in a polyatomic molecule.

Vibrational relaxation in NO has been studied by flash techniques (Basco, Callear & Norrish 1962) and by the observation of the pressure dependence of fluorescence after monochromatic excitation to a specified rovibronic state (Broida & Carrington 1963). Other diatomics have also been subject to detailed investigation. For large polyatomic molecules, the studies of Kistiakowsky & Parmenter (1965), Logan (1966) and Logan, Buduls & Ross (1968) on benzene stand alone as attempts to trace
vibrational relaxation by monitoring the change in a structured fluorescence spectrum as the pressure is varied. From these studies and, more recently, from the studies of Kemper & Stockburger (1970), it can be concluded that there are two measurable processes of vibrational relaxation:

A. The collision-induced decay of the initially excited level. This process can be described by a Stern Volmer relationship. Only a few collisions are needed to deactivate the initially prepared state.

B. The stepwise energy transfer as a result of many more collisions, leading finally to the equilibrated fluorescence spectrum.

Naphthalene can be expected to behave in a similar manner to benzene, but the study by Stockburger (1962) did not yield this kind of information: the 253.7nm mercury line used for excitation gives rise to diffuse emission in naphthalene.

The analysis of time-dependent and steady-state experiments yield the same information although each kind of experiment presents the results in a different manner. The formal similarity between impulsive and steady-state experiments has been demonstrated by Carrington (1961). Conceptually, a time-dependent demonstration of the process of vibrational relaxation can be valuable. Such an experiment is discussed for naphthalene-d₈ in its first excited singlet state.
Experimental

The coincidence of the 0-490 band of naphthalene-$d_8$ with the 315.9nm line of the air-filled flash lamp was discussed in Section V.4. The available emission intensity resulting from excitation at this wavelength was sufficient to permit the use of a second monochromator to select the emission. To induce vibrational relaxation, a higher pressure of naphthalene-$d_8$ was established by heating to 65°C at which the vapour pressure is 2.6Torr. The experimental procedure was the same as that used for phenanthrene (Section V.7) except that a Bausch & Lomb high intensity monochromator was used to select the emission wavelength.

Results

Figure VI.1 shows a simplified diagram of the energy levels in naphthalene-$d_8$. The zero vibrational level is initially excited. Since the probability of gaining a quantum is related to the probability of deactivation by microscopic reversibility, one can be sure that the $8(b_{1g})^2$ level, among others, will be populated by collisions. The sequence of collisions suffered by one molecule in relaxing from the $0^0$ state to the $8(b_{1g})^2$ state is random and many quantum states will be involved in such a multi-step process. Carrington (1962)
Fig. VI.1a. Schematic representation of energy levels in naphthalene-$d_8$.

Fig. VI.1b. Time dependence of fluorescence emission from the $8(b_{1g})^1$ state of naphthalene-$d_8$ reached as a result of vibrational relaxation after excitation of the $0^0$ state. The excitation pulse is shown as a full line. Time scale is 1.27ns/channel.
successfully treated vibrational relaxation by the direct application of the formalism of Markov chains.

The single vibronic level fluorescence spectrum from the $8(b_{lg})^1$ state shows that the $8(b_{lg})^1$ transition is reasonably strong and stands well clear of any complications. The analysing monochromator was centred on this band. Although the resulting emission transmitted at $8(b_{lg})^1$ by the monochromator was very weak (approximately 0.1 counts s$^{-1}$) an intensity-time curve was obtained and is illustrated in Figure VI.1b. The emission shows a build-up to a maximum followed by subsequent decay. The maximum occurs approximately 20ns after the peak of the excitation flash. The decay curve is not unlike that obtained for exciplex emission which, like vibrational relaxation, involves a bimolecular process.

Quantitative assessment of this result is not at present justified. However, this exercise has demonstrated that it will be possible for such experiments to be carried out with the existing apparatus.

2. THE ELECTRONIC SPECTRUM OF DIBENZOFURAN

Pinkham & Wait (1968) described two lowest singlet systems in the vapour absorption spectrum of dibenzofuran (diphenylene oxide), the first (and weaker of the two) with origin assigned at 31488.3cm$^{-1}$ (318nm) and the next at 33646.5cm$^{-1}$ (297nm). Byrne & Ross (1971) remarked that it was surprising that such a large molecule should show real evidence of two sharp systems and suggested
confirmatory studies. These have been carried out in collaboration with A.R. Lacey.

From the experimental evidence which follows, it must be concluded that the first system described by Pinkham & Wait is spurious and is due to an unidentified impurity. The first singlet system is therefore at 297nm and there is no evidence for another singlet state in the near vicinity.

Solution absorption spectrum

Figure VI.2a, taken from D.M.S. (1966) shows the main features of the absorption spectrum in light petroleum. The system studied in the present work corresponds to the long wavelength region from 260-300nm, the question being whether there is a weak system at longer wavelength which is obscured in solution or in solid solution. The origin, identified as such by the solution fluorescence spectrum (Nott 1971) is at 33100cm⁻¹ and is moderately strong; a stronger, double-headed peak lies at 0+500, 0+600cm⁻¹ with the most intense bands at 0+1700 and 0+2500cm⁻¹. The extinction coefficient of the origin band is approximately half that of the bands at 500-600cm⁻¹, in contrast to the intensity ratio indicated by Pinkham & Wait's vapour spectrum (see insert in Figure VI.3).

High resolution spectra

Lacey (1971) measured the vapour absorption spectrum using a 56m path length at room temperature. Only
Fig. VI.2  
(a) Solution absorption spectrum  
(b) Vapour emission spectrum of dibenzofuran recorded at 60°C with a bandpass of 160cm⁻¹.
Dibenzofuran vapour absorption.

Insert: Pinkham and Wait (1968).
Pinkham & Wait's second system was observed (Figure VI.3). Pinkham & Wait are imprecise in defining their experimental conditions, but this result is at least indicative of the absence of a longer wavelength absorption in Lacey's sample. More decisive measurements were made by Lacey on dibenzofuran in solid solutions, namely in durene and in cyclododecane. In neither case could the supposed long wavelength transition be seen, and in the latter host crystal, fluorescence was observed from the 297nm system. This last observation would settle the matter but for the possibility that the order of the electronic states is rearranged in a crystal environment. The following observations on the vapour fluorescence dispose of this possibility.

Vapour emission studies

Excitation at 298nm was provided by a deuterium-filled flash lamp and Bausch & Lomb double grating monochromator used with a 2nm bandpass. The emission was viewed at right angles through a Bausch & Lomb high intensity monochromator fitted with 3nm slits. Other experimental details were as described for phenanthrene (Section V.7).

The emission maximum was found to be at 308nm, which corresponds to an energy higher than Pinkham & Wait's first system. At room temperature the lifetime was 10.8ns, becoming shorter with shorter wavelength excitation. Even at temperatures up to 60°C, no emission could be
detected if band heads corresponding to Pinkham & Wait's absorption system at 318nm were excited and the emission scanned at longer wavelength. The experiment was repeated using a cut-off filter to absorb the exciting light in place of the analysing monochromator. At higher temperatures (85°C) a very weak longer-lived emission, almost certainly due to a low concentration impurity, could just be detected. The lifetime could not be accurately determined owing to the very low number of counts but it is likely to have been of the order of 50ns.

The vapour emission spectrum of dibenzofuran at 60°C was recorded using a 150W Xenon lamp and Bausch & Lomb high intensity monochromator for excitation at 297nm. A Zeiss MM12 quartz double prism monochromator and wavelength drive was used to scan the emission with a resolution of 160cm⁻¹. The spectrum is shown in Figure VI.2b. Again, no emission was detected for irradiation at 318nm.

Conclusion

The only evidence for a 318nm system is Pinkham & Wait's original observation. The sharpness of the 297nm system and the fact that this is the only emissive state in the vapour, solution and solid solution, provide strong evidence that the 297nm transition is to the first excited singlet state. The emission studies have aided in a reassignment of the origin and the principal frequencies, as determined by Lacey, have also been included in Figure VI.3.
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Erratum: The name 'Philips', when referring to the industrial firm, has been spelt incorrectly in this thesis. The correct spelling is as above.