Vibrational spectroscopy of selected halocarbons.

A thesis submitted for the degree of Doctor of Philosophy of the Australian National University.

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Declaration.

This thesis is my own original work, except where otherwise stated. It was completed in the Department of Chemistry at the ANU during the period February 1991 to May 1994. The programs NORCORD and OVER were supplied free of copyright, CALST was written by me, and the program identified as GAUSSIAN92 in this work refers to Gaussian 92™ of Gaussian Inc. and is referenced on page R3.

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Marilyn Olliff.

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Abstract.

The vibrational spectroscopy of selected halocarbons has been investigated in this work, with the intention of determining the absolute integrated absorption intensities in the atmospheric window region, and investigating the changes in intensities and force constants with changing numbers of fluorine atoms in the molecule. The halocarbons selected included commercially useful substances as well as two groups of fluorinated ethanes and chloroethanes. Two halopropanes with potential commercial uses were synthesised, since at the start of this project no samples of this type could be obtained from chemical manufacturers. A detailed analysis of the errors encountered in infrared spectroscopy was carried out and the infrared band intensities of 25 halocarbons were measured. These measurements are suitable for use in the calculation of global warming potentials for climate modelling.

Theoretical studies were carried out on 19 haloethanes to determine frequencies, force constants and intensities. Two approaches were used, a mechanistic method using a simple Urey-Bradley force field, and an electronic structure method using *ab initio* calculations. Comparisons between the frequencies from both types of calculations and the experimental results enabled confirmation of literature frequency assignments, where available, and the tentative assignment of some previously unassigned modes. Changes in force constants with changing numbers of fluorine atoms within the molecule were investigated and, where possible, comparisons were made between the calculated force constants from the Urey-Bradley force field and *ab initio* results.

Integrated absorbance intensities from the experimental results were compared to the calculated intensities from the *ab initio* computations for the regions 3500-450cm^{-1}, 1350-1000cm^{-1} and 3200-2800cm^{-1}. Intensity results were not available from the Urey-Bradley force field calculations. The region 1350-1000cm^{-1} includes the C-F and the C-C bond stretching vibrational modes and is of particular interest, since it coincides with the atmospheric window. It is because fluorocarbons absorb so strongly in this region that they are considered to be environmentally damaging. A scaling factor of 0.734 for the calculated intensities was derived, resulting in a good agreement between the experimental and calculated values in the 3500-450cm^{-1} and 1350-1000cm^{-1} regions. Attempts were made to find a relationship between the intensities in the C-F bond stretching region and the number of fluorine atoms in the molecule. A line of best fit was found for each group of halocarbons such that the intensity is proportional to the square of the number of fluorines. This information may assist in the prediction of vibrational spectra of halocarbons which have not yet been synthesised.

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List of abbreviations.

A	Absorbance, where $A = \log_e(I_o/I)$.
A_{10}	Absorbance, where $A_{10} = \log_{10}.(I_o/I)$.
ADFA	Australian Defence Force Academy.
AL	Atmospheric lifetime.
ANU	Australian National University.
BI	Band intensities.
CFC	Chlorofluorocarbon.
CFCa	Chlorofluorocarbon of type 'a' as defined in appendix A.
DMSO	Dimethyl sulfoxide.
F,F'	Non-bonded interaction constants for a Urey-Bradley force field.
FTIR	Fourier transform infrared.
GWP	Global warming potential.
H,H'	Bending force constants for a Urey-Bradley force field.
HCFC	Hydrochlorofluorocarbon.
HF	Hartree-Fock self-consistent field theory.
HFC	Hydrofluorocarbon.
HFCa	Hydrofluorocarbon of type 'a' as defined in appendix A.
I_o, I	Intensity of radiation incident on sample and emergent from sample respectively.
K,K'	Stretching force constants for a Urey-Bradley force field.
$K_{\tilde{\nu}}$	Absorption coefficient at wavenumber $\tilde{\nu}$.
MP2	Møller-Plesset second order perturbation theory.
$\tilde{\nu}$	Wavenumber in cm^{-1}.
ODP	Ozone depletion potential.
P-E	Perkin-Elmer.
PE	Potential energy.
Q	Normal coordinate.
RISC	Reduced instruction set central processor.
S	Band strength, band intensity.
SCF	Self-consistent field.
T	Kinetic energy.
UB	Urey-Bradley.
v	Vibrational quantum numbers.
V	Potential energy.
ψ	Wavefunction of a particle.
6-31G*	Polarised basis set as defined by Foresman and Frisch (1993).

Chapter 1.

Introduction

Halocarbons have proved to be beneficial in raising the standard of living in many parts of the world. Recent studies, however, have highlighted some serious disadvantages in the use of fluorine- and chlorine- containing compounds with regard to the effects they may have on the environment. The present work is an investigation of the molecular vibrations of a range of fluorine-containing halocarbons, motivated by the requirement for further research in this area. Experimentally, molecular vibrations may be studied using Fourier Transform Infrared (FTIR) Spectroscopy. In order to produce a set of reproducible results, a detailed examination of the errors found in the acquisition of quantitative spectroscopic measurements was carried out. Vibrational frequencies and force constants for a range of haloethanes have been calculated using a Urey-Bradley force field. Further theoretical studies of vibrational frequencies, intensities and force constants have been made using *ab initio* methods. From the experimental and theoretical results it has been possible to complete vibrational assignments for most of the compounds and to determine the change in absorbance due to changing numbers of fluorine atoms in a range of chloro- and hydro- fluoroethanes. This information can be used qualitatively when attempting to find new halocarbons with less environmentally damaging properties.

1.1 Halocarbons.

Halocarbons are non-flammable, odourless, and stable man-made compounds with many uses in the areas of refrigeration, air conditioning, cleaning and plastic foam manufacture. The three most commonly found groups of these substances are known as the chlorofluorocarbons (CFCs), the hydrofluorocarbons (HFCs), and the hydrochlorofluorocarbons (HCFCs). These molecules all consist of some combination of carbon and fluorine atoms, with chlorine atoms in CFCs, hydrogen atoms in HFCs, and both chlorine and hydrogen atoms in HCFCs. A numbering system has been developed by commercial manufacturers in order to simplify the nomenclature of the halocarbons. This numbering system is used throughout, and described in appendix A.

Since the early 1930s halocarbons have been manufactured for commercial use and, once used, are released into the atmosphere (ANZEC 1990). Due to their molecular stability, halocarbons accumulate in the lower atmosphere and slowly diffuse into the upper atmosphere, giving rise to two important environmental problems, global warming in the troposphere, and ozone depletion in the stratosphere. In the troposphere, intact halocarbon molecules are efficient absorbers of infrared radiation and so trap heat near the surface of the Earth (Dickinson and Cicerone 1986). In the stratosphere, ultra-violet radiation from the sun releases chlorine atoms from chlorine-containing halocarbons. The chlorine atoms react with ozone, breaking it down to oxygen and hence are partly responsible for the depletion of the ozone layer (Rowland 1989).

It is important, therefore, to investigate the physical and chemical properties of halocarbons in order to increase our understanding of the role played by these chemicals in global warming and ozone depletion. To this end, considerable research is being undertaken in the areas of chemical kinetics and reaction mechanisms relating to both ozone depletion potentials and atmospheric lifetimes of various halocarbons. The World Meteorological Organisation has published many of these works as part of the Global Ozone Research and Monitoring project (1989). Many papers are available in the literature on various aspects of the behaviour of atmospheric halocarbons including those by Hampson et al. (1989), Golombek and Prinn (1989), Brown et al. (1990), DeMore et al. (1990), Gierczak et al. (1990), Liu et al. (1990), Zhang et al. (1991). The model calculations carried out by Fisher et al. (1990 a & b) use many of the results obtained up to that time. The intensities of infrared absorption by CFCs, HFCs and HCFCs are used in computer modelling of potential climate changes, where the band intensities of all the trace gases in the atmosphere contribute to the overall effect. Intensity measurements have been made for some of these substances (Fisher et al. and references therein 1990 b, Varanasi & Chudamani 1988, Olliff & Fischer 1992) but some discrepancies in the results obtained by different research groups are apparent and are discussed in chapter three.

1.2 Infrared Radiation.

The electromagnetic spectrum between approximately 1 and 100μm (10,000-100cm^{-1}) is known as the region of infrared radiation (Thorne 1988). The Earth's surface is warmed by solar radiation, 99% of which extends through the UV, visible and near IR regio to the mid-IR region with wavelengths in the range of 0.2 to 4.0μm (50,000-2500cm^{-1}) , the absorbed radiation is re-emitted as thermal radiation in the infrared region of approximately 4.0 to 100.0 μm (2500-100cm^{-1}) (Coulson 1975). Infrared radiation is absorbed by many substances, giving rise to vibrational excitation of the molecules. In the atmosphere, infrared radiation is strongly absorbed by water vapour at wavelengths longer than 18μm and shorter than 8μm, and by carbon dioxide in the region of 12 to 18μm, leaving a gap between approximately 8 and 12μm (1250-833cm^{-1}) in which little or no absorption takes place. Approximately 25% of the thermal emission from the Earth is lost through this gap, known as the 'atmospheric window' (Dickinson and Cicerone 1986), keeping the troposphere at a temperature suitable to sustain life. Figure 1.1 shows the transmission of radiation through the atmospheric window.

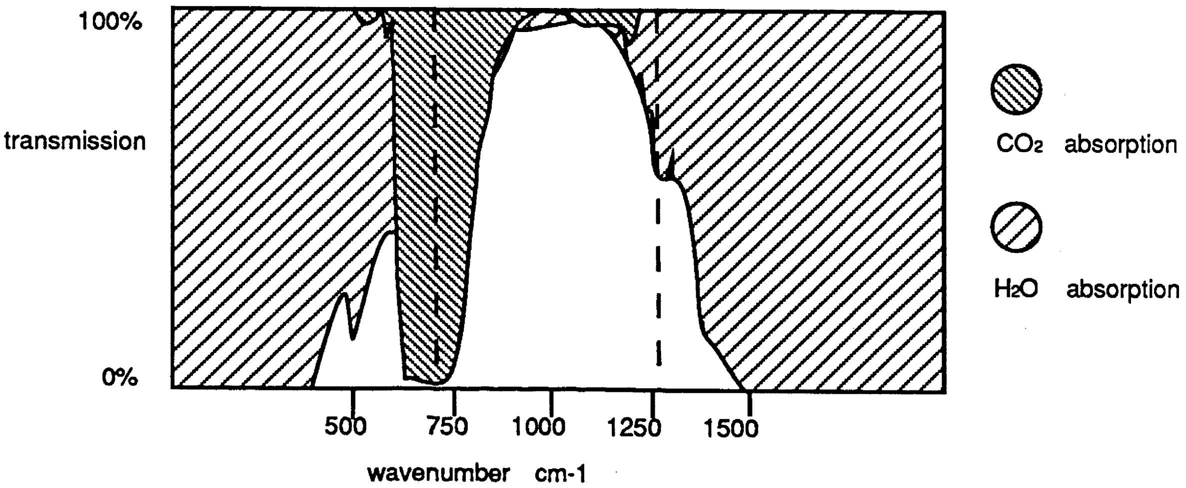


Figure 1.1. Absorption by water vapour and carbon dioxide showing the position of the atmospheric window (Wang et al. 1976).

It has been found (Fisher et al. and references therein 1990 b) that many halocarbons absorb strongly in the atmospheric window region. The accumulation of halocarbons in the troposphere may, therefore, reduce the loss of heat through radiation from the Earth's atmosphere, subsequently increasing the ambient temperature. Since halocarbons are stable compounds which are currently being released into the atmosphere, detailed studies of infrared absorption by these compounds are required and must be taken into consideration when predicting global warming. This work has been carried out in part to measure the infrared absorption potential of a range of halocarbons , with an emphasis on some new HFCs and HCFCs which have been proposed as suitable replacements for the more damaging CFCs currently being phased out.

Infrared spectroscopy allows the investigation of vibrational motions in molecules leading to an understanding of several physical properties. Vibrational frequencies depend on the molecular geometry, atomic masses and the forces between the atoms within the molecule. The intensity of the absorption is related to the change in dipole moment caused by the vibrational motion. Fundamental vibrations are those due to the transition between adjacent vibrational energy levels of a molecule in the ground state. Identifications of fundamentals, that is the assignment of an observed frequency to a particular fundamental mode leads to improved calculations of thermodynamic properties (Fogarasi & Pulay 1985). Forces between the atoms within a molecule depend on the masses and electronic structures of the atoms, the neighbouring atoms and the interatomic distances. A simple harmonic vibrational motion for a diatomic molecule has a potential energy close to the minimum of $V=1/2k(\Delta x)^2$ (Atkins 1988) where Δx is the displacement from the minimum and k is the force constant. Force constants may be calculated from vibrational frequencies. Conversely, if the force constants are known, then it is possible to calculate the spectrum, which in turn can be used to investigate the structure and conformation of the molecule (Califano 1976).

Part of this work involves assigning the observed frequencies to fundamental modes and to particular molecular motions. By identifying the motions which contribute to an observed frequency, molecules with similar bonds will be known to absorb in the same region. This is of particular interest in the case of halocarbons, where carbon-fluorine and carbon-carbon bond stretches and bends are known to absorb in the atmospheric window region. Vibrational assignments may be found in the literature for many haloethanes, as shown in chapter six. A large proportion of the work was completed in the 1950s and 1960s (Smith et al. 1952, Nielsen et al. 1953 a & b, Carney et al. 1961) when *ab initio* calculations were not available, leaving some tentative assignments and unassigned modes. By using molecular mechanics and *ab initio* methods in this work, calculations of frequencies and comparisons with the experimental spectra have made it possible to confirm some existing assignments and to suggest the assignments of some previously unidentified modes.

Once it is known which observed frequencies are due to the carbon-fluorine bond stretches, it becomes possible to study relationships between the infrared absorption and the number and position of fluorine atoms within the molecules. Theoretical calculations of force constants have been carried out in order to investigate the transferability of force constants between similar molecules and to study the trends in force constants with changes in the number and positions of fluorine atoms . When these properties are examined together it becomes possible to predict, at least qualitatively, the spectra of halocarbons as yet unsynthesised and the likely magnitude of infrared absorption in the atmospheric window region.

1.3. Selection of halocarbons for investigation.

The enormous numbers of halocarbons containing fluorine, chlorine and hydrogen made it necessary to select only a few groups for investigation. Two criteria were used in the selection of appropriate compounds. With the present concern about global warming, the initial requirement was that halocarbons of topical interest be used, resulting in a selection of both halocarbons currently manufactured by industry and those proposed as replacement substances. The desire to examine trends in vibrational absorption intensities and force constants lead to the second requirement, that of including closely related halocarbons, even though some of them may not have potential commercial uses. The vibrational spectroscopy of halomethanes has already been studied extensively by many research groups including Chen et al. (1976), Shimanouchi (1963), Giorgianni (1979) and references in Person and Zerbi (1982). Fluoroethanes are used extensively in refrigeration and cleaning, and can easily be grouped into CFCs and HFCs containing increasing numbers of fluorine atoms. This gives two sets of compounds suitable for studying trends in force constants and intensities with changes in the number of fluorine atoms. Recently halopropanes have been suggested as solvents by the chemical manufacturers Asahi Glass Co. (Yamabe 1989) and ICI (Dudman et al. 1990), so four of these have been included in this work.

1.3.1. Commercially useful halocarbons.

Several large chemical companies were surveyed to find which halocarbons are currently in use, and which compounds are being promoted as potential replacements. The companies approached were Du Pont de Nemours (USA), ICI (UK), ATOCHEM (France) and Asahi Glass Co. (Japan), these being among the largest producers of halocarbons in the world. Table 1.1 lists the compounds in use and their potential replacements. Some substances may eventually be replaced by compounds which are not halocarbons, but these will not be discussed in this work.

The general reluctance of companies to make available samples of products not yet on the market made it difficult to obtain prototype substances. Enquires at Du Pont de Nemours yielded little information due to the secrecy surrounding new developments, so considerable time was spent in contacting other manufacturers to obtain the most recent information.

The most commonly used and potent substances with respect to environmental damage are CFC12 used in refrigeration and air conditioning, and CFC113 used as a solvent. Ozone Depletion Potentials (ODP) relative to that for CFC11 are 1.0 for CFC12 and 0.89 for CFC113 (Fisher et al. 1990 a), and Global Warming Potentials

(GWP) also relative to CFC11, are 2.8 for CFC12 and 1.4 for CFC113 (Fisher et al. 1990 b).

Table 1.1. CFCs and potential replacements.

CFC in use	Molecular formula	Commercial use	Potential replacement	Replacement formula
CFC11	CCl_3F	Refrigerant, propellant, solvent	HCFC123 HCFC141b	$CHCl_2CF_3$ CH_3CCl_2F
CFC12	CCl_2F_2	Refrigerant, propellant, used in air conditioners	HFC134a HCFC22 HFC152a HCFC141b HCFC142b	CH_2FCF_3 $CHClF_2$ CH_3CF_2H CH_3CCl_2F CH_3CClF_2
CFC113	CCl_2FCClF_2	Solvent	HCFC141b HCFC123 Several possible halopropanes	CH_3CCl_2F $CHCl_2CF_3$ $CH_aF_bCl_c$-CF_2-$CH_xF_yCl_z$
CFC114	$CClF_2CClF_2$	Propellant, heat pumps	HCFC124 HCFC22 HCFC142b	$CHFClCF_3$ $CHClF_2$ CH_3CClF_2
CFC115	CF_3CClF_2	Refrigerant	HCFC22	$CHClF_2$

In mid 1991 ICI launched 'KLEA', the gas 1,1,1,2-tetrafluoroethane known as HFC134a, as a replacement for CFC12 in air conditioners and refrigerators. This halocarbon was considered to be the most appropriate replacement as with no chlorine atoms it has no known effect on ozone molecules in the stratosphere. However, with four carbon-fluorine bonds, the molecule absorbs radiation strongly in the region of the atmospheric window. After unsuccessfully requesting samples of HFC134a from several manufacturers, ATOCHEM in Sydney kindly donated a sample from their pilot plant. Subsequently a further sample was obtained from PCR Inc. in Florida USA.

The search for a 'drop-in' replacement for CFC113 has proved more difficult (Hey 1991). Among the properties which make CFC113 a good solvent is the fact that it has no known toxic effects and, although it must be used in a ventilated area to avoid suffocation (Millar 1989), minimal safety precautions make it easy and inexpensive to use. Some electronics industries have discontinued the use of halocarbons and are using combinations of soap and water, terpenes and flux-free soldering (Erskine 1990). Several halopropanes have been suggested as 'drop in' replacements for CFC113 by Asahi Glass Co. (Yamabe 1989) and ICI (Dudman et al. 1990). The halopropanes must have the following structure: at least one chlorine atom to enhance solvent characteristics; at least one hydrogen atom to introduce atmospheric instability, since

C-H groups react readily with atmospheric hydroxyl radicals by hydrogen abstraction; and a -CF_2- group in the centre so that HCl is not formed in the atmosphere, leaving a toxic propene (Dudman et al.1990). Initially, no halopropanes fulfilling these requirements were available for use, so two new halopropanes were synthesised as part of this project. Two additional halopropanes, HCFC225ca and HCFC225cb, were subsequently obtained from PCR Inc., enabling four to be used in the experimental section of this work.

1.3.2 Series selection and grouping.

In order to study relationships between the infrared absorption intensities of a range of haloethanes depending on the numbers and positions of the fluorine atoms in each molecule, the compounds selected have been arranged in groups of increasing numbers of fluorine atoms. Table 1.2 lists the compounds selected, showing the number of carbon-fluorine bonds, and where known, the atmospheric lifetime (AL), ODP and GWP of each molecule. For completion, some groups containing halocarbons with no known commercial use have been included. Due to their structure, it has been necessary to include some molecules in more than one group, and for completeness, molecules with no fluorine atoms have been included in the appropriate groups. Experimental work was completed for all compounds listed, except for CFC110, HFC170, and HFC152. CFC110 (hexachloroethane) and HFC170 (ethane) have been previously studied in detail (Tanabe & Saëki and references therein 1972), and a sample of HFC152 was not available.

Theoretical work was carried out on the two groups listed in Table 1.2 identified as CFCs with 2 carbon atoms and HFCs with 2 carbon atoms. The following chemicals were obtained from PCR Inc.: CFC111, CFC112, CFC112a, CFC114a, FC116, HFC161, HFC143, HFC143a, HFC134, HFC134a, HFC125, HCFC141b, HCFC124, FC218, HCFC225ca, HCFC225cb. CFC113, CFC113a, CFC114, CFC115, HFC152a, HCFC142b and HCFC123 were obtained from Aldrich Chemicals.

Table 1.2 Halocarbons selected for study.

CFC name	Molecular formula	Mol. wt.	No. of C-F bonds	ODP[a]	GWP[b]	AL[c] years
CFCs with 2 carbon atoms.						
CFC110	CCl_3CCl_3	236.74	0			
CFC111	CCl_3CCl_2F	220.29	1			
CFC112	$CFCl_2CCl_2F$	203.83	2			
CFC112a	CCl_3CClF_2	203.83	2			
CFC113	$CFCl_2CClF_2$	187.38	3	0.89	1.4	90
CFC113a	CCl_3CF_3	187.38	3			
CFC114	$CF_2ClCClF_2$	170.92	4	0.79	3.7	200
CFC114a	CF_3CCl_2F	170.92	4			
CFC115	CF_3CClF_2	154.47	5	0.45	7.6	400
FC116	CF_3CF_3	138.01	6	0.00		>500‡
HFCs with 2 carbon atoms.						
HFC170	CH_3CH_3	30.07	0	0.0		
HFC161	CH_3CH_2F	48.06	1	0.0		0.3
HFC152	CH_2FCH_2F	66.05	2	0.0		
HFC152a	CH_3CHF_2	66.05	2	0.0	0.026	1.7
HFC143	CH_2FCHF_2	84.04	3	0.0		3.8
HFC143a	CH_3CF_3	84.04	3	0.0	0.72	41
HFC134	CHF_2CHF_2	102.03	4	0.0		12.3
HFC134a	CF_3CH_2F	102.03	4	0.0	0.25	15.5
HFC125	CF_3CHF_2	120.02	5	0.0	0.51	28.1
(FC116)	CF_3CF_3		6			
HCFCs of topical interest with 2 carbon atoms.						
HCFC141b	CH_3CCl_2F	116.95	1	0.066	0.087	7.8
HCFC142b	CH_3CClF_2	100.50	2	0.053	0.34	19.1
HCFC123	CF_3CHCl_2	152.93	3	0.013	0.017	1.6
HCFC124	CF_3CHClF	136.48	4	0.016	0.092	6.6
HCFCs of topical interest with 3 carbon atoms.						
HCFC244ca	$CF_2HCF_2CH_2Cl$	150.50	4			
HCFC235cb	$CF_3CF_2CH_2Cl$	168.49	5			
HCFC225ca	$CF_3CF_2CHCl_2$	202.93	5	0.02†	0.04†	3.5†
HCFC225cb	CF_2ClCF_2CHClF	202.93	5	0.04†	0.15†	7†
FC218	$CF_3CF_2CF_3$	188.02	8	0.00†		

[a] Fisher et al. 1990 a.

[b] Fisher et al. 1990 b.

[c] World Meteorological Organisation (WMO) 1989 b.

† PCR Inc. 1992.

‡ Ramanathan et al. 1985

1.4. Syntheses of two halopropanes.

The initial unavailability of an appropriate 3-carbon compound led to the syntheses of two halopropanes. A literature search was carried out to find a suitable method for the synthesis of a halopropane fulfilling the criteria detailed in section 1.3.1. That is, a halopropane of the general formula

$$CH_aF_bCl_cCF_2CH_xF_yCl_z$$

where $a+b+c = x+y+z = 3$, and $0 \leq a, b, c, x, y, z \leq 3$.

The reaction of tetrafluoroethylene with appropriate halomethanes in the presence of aluminium chloride (Coffman et al. 1949, Paleta et al. 1971) is well known, for example,

$$CF_2{=}CF_2 + CHClF_2 \xrightarrow{AlCl_3} CF_3CF_2CHCl_2 + CF_2ClCF_2CHClF$$

A mixture of halogenated propanes is obtained.

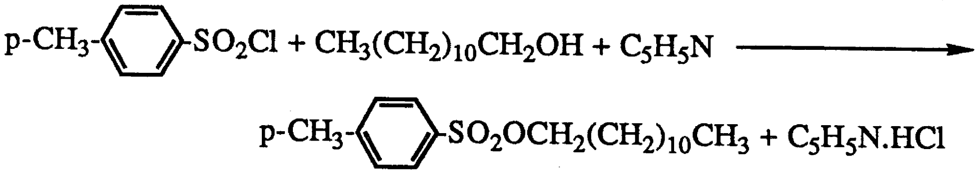
Chlorinated propanes can be fluorinated by the addition of antimony trifluoride or antimony pentafluoride depending on the starting material (Henne & Renoll 1937).

$$CH_3CCl_2CH_3 \xrightarrow{SbF_3} CH_3CF_2CH_3$$

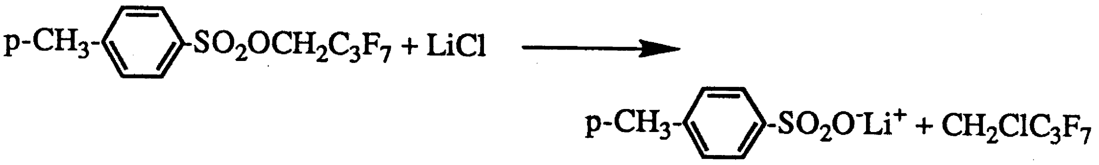
Provided that the end groups are hydrogen bearing carbons, the central $-CCl_2-$ group was found to be easily fluorinated. However attempts at subsequent addition of fluorine to an end group resulted in very low yields (Henne & Ladd 1938, Henne & Renoll 1939). Using 2,2-difluoropropane as synthesised by Henne & Renoll (1937) McBee and co-workers (1940) produced a number of chlorinated fluoropropanes by the photochemical reaction of chlorine. The resultant HCFCs were further fluorinated by reaction with equimolar amounts of SbF_3 and SbF_3Cl_2. Henne and Whaley (1942) used hydrogen fluoride in the presence of $SbCl_5$, to replace chlorine atoms in a dichloropropene. This was also attempted by McBee et al. (1948)

$$HF + CF_3CCl{=}CCl_2 \xrightarrow{SbCl_5} CF_3CHClCCl_2F + CF_3CHClCClF_2$$
$$+ CF_3CHClCF_3 + CF_3CCl_2CCl_2F + CF_3CCl_2CClF_2$$

Halogenated alkanes may be derived from fluorine containing alcohols (McBee et al. 1955). This method has also been proposed by ICI (Dudman et al. 1990), since by using the appropriate alcohol, high yields of the required hydrochlorofluoropropane may be obtained. From a manufacturers point of view, the starting materials make this method expensive, however, for this work only small amounts of product were necessary. The apparatus required to carry out this method of synthesis is very inexpensive compared to the cost of the equipment necessary when using $CF_2{=}CF_2$ or HF as reactants. In order to obtain an HCFC, the hydroxyl group of the alcohol must be replaced by a chlorine atom. The first step is to replace the hydroxyl with a tosyl group (McBee et al. 1955). A general method for producing esters of sulfonic acids was developed by Patterson and Frew (1906). An example of this type of reaction was carefully described by Marvel and Sekera (1940). In this case n-dodecanol was converted to n-dodecyl-p-toluene sulfonate,

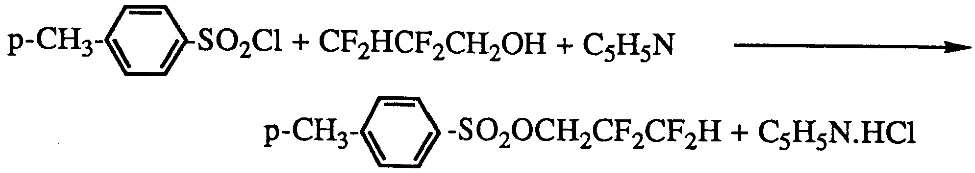


Several methods of preparing esters of p-toluene sulfonic acid were investigated by Tipson (1944). The use of dry pyridine to neutralise the HCl as fast as it formed was found to be the most satisfactory method, as long as the experiment was carried out at 0°C or below. Tipson (1944) gave detailed experimental procedures for producing several tosyl esters. The subsequent replacement of the tosyl group by a chlorine atom may be carried out by the reaction of the tosyl ester with lithium chloride (Tiers et al. 1953). For example,

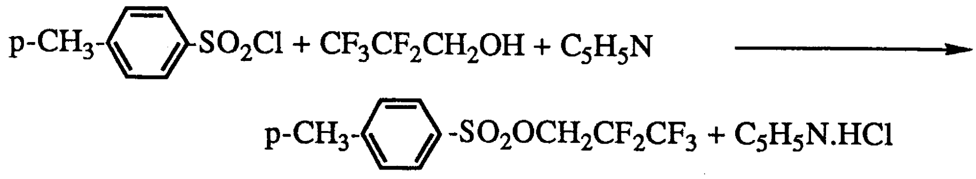


The methods of syntheses described using tetrafluoroethylene and hydrogen fluoride produce mixtures of halopropanes requiring separation. The simplest method is that used by McBee et al. (1955) as only one halopropane is produced from each alcohol used. 2,2,3,3-Tetrafluoropropanol and 2,2,3,3,3-pentafluoropropanol were readily available from PCR Inc., and from these alcohols, two suitable halopropanes, 1-chloro-2,2,3,3,3-pentafluoropropane (HCFC235cb) and 1-chloro-2,2,3,3-tetrafluoropropane (HCFC244ca), fulfilling all the structural criteria for a possible replacement solvent could be made, using the two steps described above.

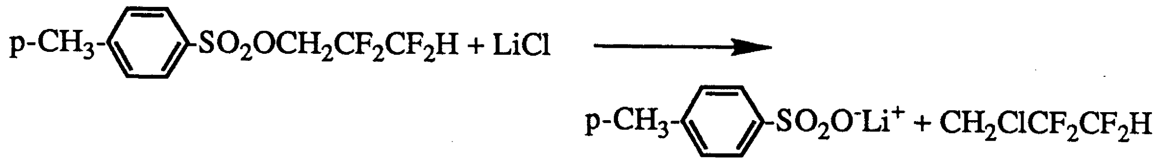
First, the production of the tosyl esters,



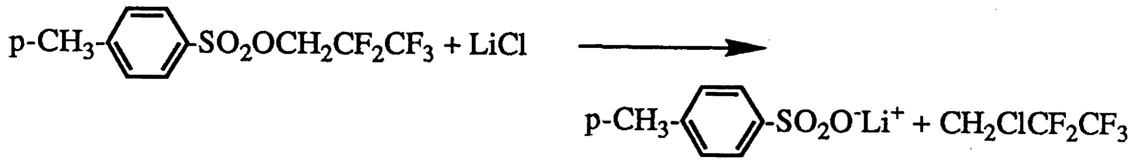
and



then the removal of the tosyl groups,



and



The experimental method used and the results of the syntheses are given in chapter two.

1.5 Fourier Transform Infrared Spectroscopy.

FTIR spectroscopy uses an interferometer to obtain an interference beam of the required radiation which is passed through the sample, and the resultant interferogram is converted into a frequency-based spectrum using a Fourier transformation. This is carried out quickly and easily by a computer, which is an integral part of the spectrophotometer. The initial spectrum gives the percentage of radiation transmitted through the sample, and a simple relationship between transmission and absorbance is used to convert the results into an absorbance spectrum.

1.5.1 The infrared spectrum.

The infrared spectrum gives the absorbance of radiation in the infrared region passing through a sample of the material under investigation. In this work, the mid-infrared region corresponding to 3500-450cm^{-1} (2.86-22.2μm) has been studied.

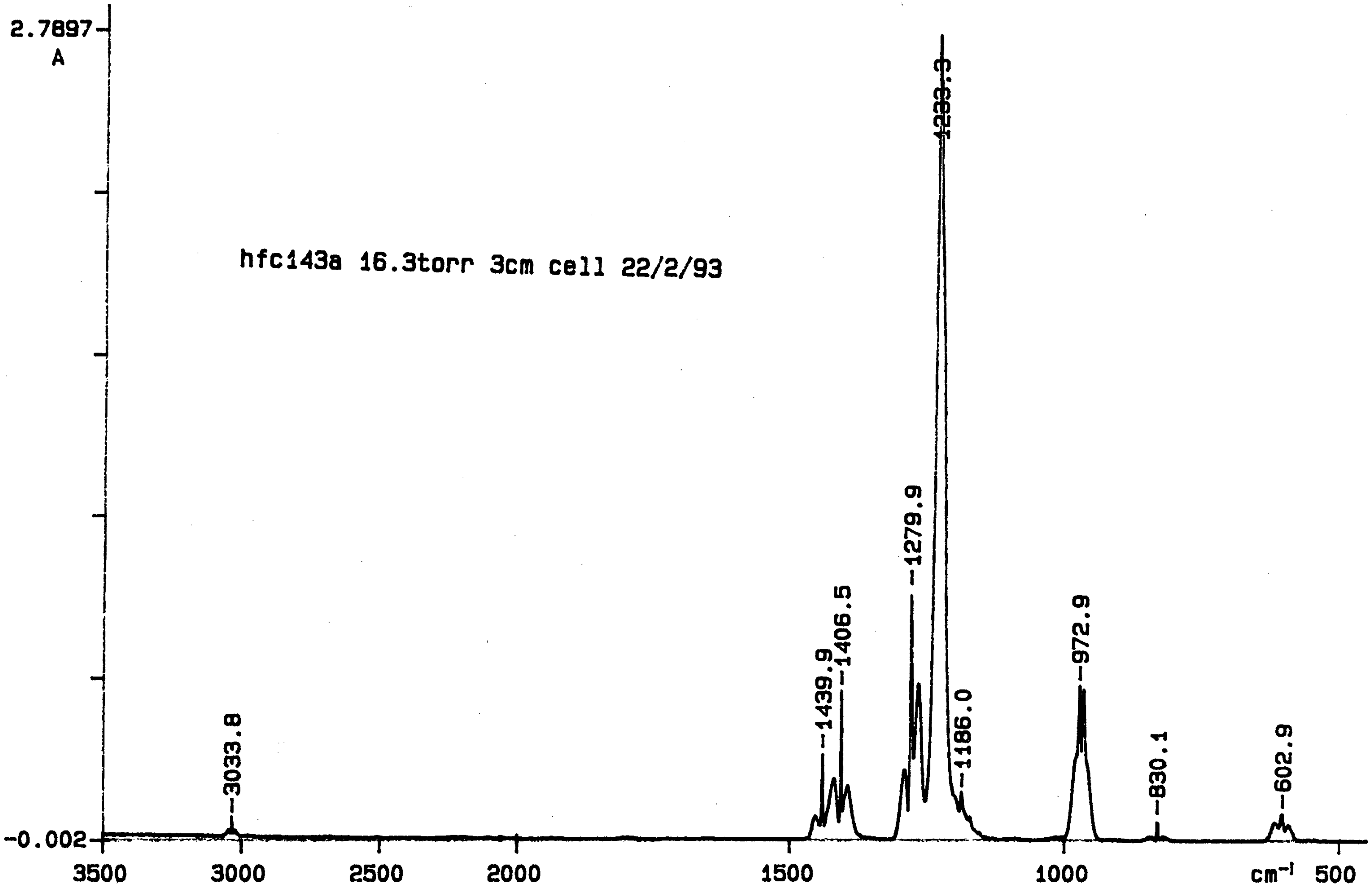


Figure 1.2. An absorbance spectrum of HFC143a (1,1,1-trifluoroethane) in the mid-infrared region.

The fraction of radiation not absorbed by the sample, known as the transmissivity, is related to the absorbance by the Beer-Lambert law (Atkins 1986),

$$I/I_o = e^{-Kcl} = e^{-A}$$

where:

I = intensity of radiation emergent from the sample,

I_o = intensity of radiation incident on the sample,

A = Absorbance = Kcl ,

K = absorption coefficient ,

c = concentration of sample ,

l = thickness of sample (path length) .

The relationship between absorbance and the fraction of radiation being transmitted is therefore logarithmic,

$$A = \log_e(I_o/I) = 2.303\log_{10}(I_o/I)$$

The FTIR Spectrophotometer automatically converts the transmissivity into absorbance, using log to the base 10. The spectra obtained show a plot of A_{10} vs $\tilde{v}$, where $\tilde{v}$ is the wavenumber in cm^{-1}. Figure 1.2 shows an example of an absorbance spectrum in the mid-IR region of 3500-450cm^{-1}.

1.5.2. Quantitative analysis.

Infrared spectroscopy is widely used in a qualitative way to identify compounds. Groups of atoms in a compound often absorb at a specific frequency, and so can be readily identified by noting the positions of the absorption bands in the spectrum. In this work, the magnitude of the absorbance is of interest as well as the position, as this also varies with different molecules. The magnitude of absorbance due to a particular vibration, known as the band intensity, may be obtained by summing the absorbance at each wavenumber within a band. Thus the band intensity gives a measure of the amount of radiation absorbed by a particular substance in a specified range and is one of the many parameters used in climate modelling to predict temperature increases in the troposphere.

1.5.2.1 Position and shape of absorbance bands.

When the frequency of the radiation incident on the sample is the same as the frequency of a molecular vibration, and a change in the dipole moment is caused by that vibration, absorption will occur. Since there are many possible vibrations within one molecule, there will be many different frequencies of radiation absorbed. This gives rise to a number of bands in the spectrum. In addition, within one vibrational energy level there are many rotational levels. Vibrational-rotational absorption transitions for linear molecules are governed by the selection rules $\Delta v=+1$, $\Delta J=0, \pm 1$, where Δv is the change in vibrational quantum number and ΔJ is the change in rotational quantum number. Figure 1.3 shows some examples of possible transitions.

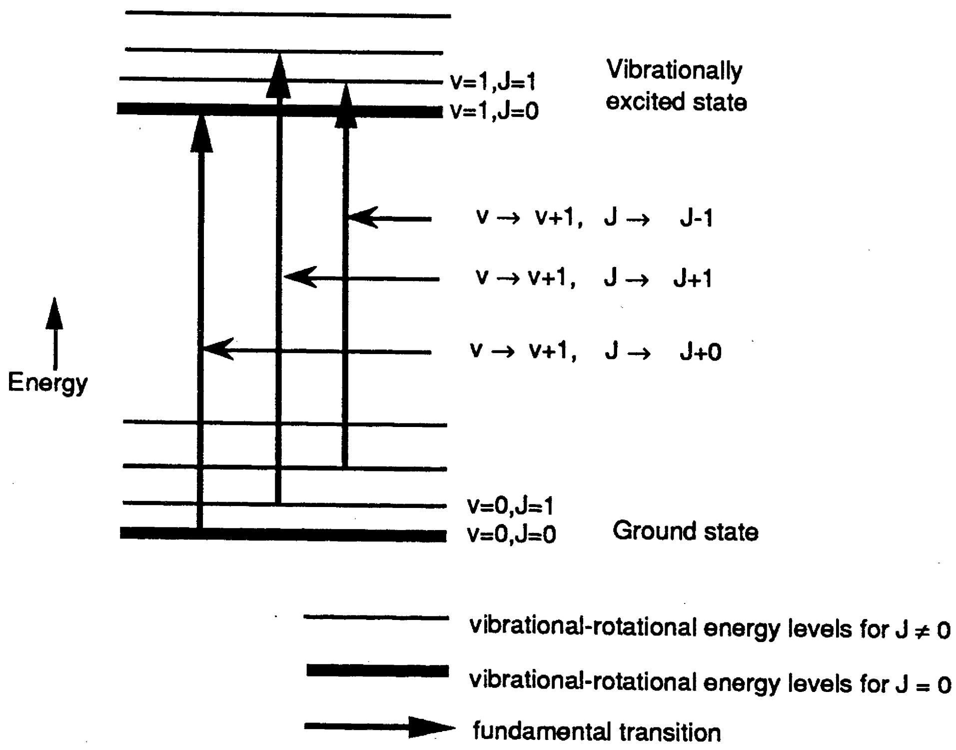


Figure 1.3 The fundamental transition $v = 1 \leftarrow v = 0$.

The rotational energy levels are inversely related to the moments of inertia of the molecule, thus the separation of levels is very small in heavy molecules and rotational lines in the spectrum for one vibrational transition may be very close together, giving rise to spectral bands. Depending on the resolution of the instrument, it may not be possible to resolve individual lines within a band.

A fundamental transition occurs when the molecule is excited from the ground state to the first vibrational level of a particular vibrational mode. The number of fundamental bands present in a spectrum can be calculated, and depends on the symmetry of the molecule and the number of different bending and stretching vibrational modes which occur. For the movement in three dimensional space of a molecule of N atoms, there are 3N degrees of freedom. 3 degrees of freedom describe the translational motion and 3 describe the rotation of the system about its axes, leaving 3N-6 degrees of freedom for the normal vibrations of a non-linear molecule (Brügel

1962). Fundamental bands will only appear in the spectrum for those vibrational modes which cause a change in the dipole moment of the molecule. The existence of a permanent dipole moment is not required for infrared active vibrations (Atkins 1986).

Bands other than fundamental bands may appear in the spectrum. These bands are forbidden by the selection rule of the harmonic oscillator, however, they are weakly observed because of the anharmonicity of the vibrations (Nakamoto 1986). They may be defined as:

(a) Overtones, when a molecule is excited to more than one vibrational quantum by one photon.

(b) Combinations, when more than one vibrational mode in the same molecule is excited by one photon.

(c) Hot bands, when a vibrationally excited molecule is excited further to a higher vibrational level. Hot bands with $\Delta v=1$ are allowed in the harmonic approximation.

The strength and shape of each band depends on the absorption coefficients of the band, the number of molecules of the gas present, the moments of inertia for both the upper and lower vibrational states, and the population of the rotational energy levels when the molecules are in the vibrational ground state. Figure 1.4 shows a simple rotational-vibrational band for a diatomic molecule. For the polyatomic halocarbons the individual lines are very close together and more complex bands are seen in the spectra. Fundamental bands are often of irregular shapes, depending on many factors, including:

(a) The rotational structure of the band.

The separation between the rotational levels is dependant on the rotational constants, which are inversely proportional to the moments of inertia of the molecule. Halocarbons containing little or no hydrogen have high moments of inertia, and so the rotational lines in the spectrum are very close together.

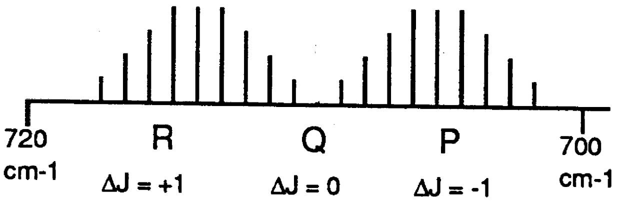


Figure 1.4 A simple rotational-vibrational band showing the P, and R branches.

For example CFC113a has C_{3v} symmetry, and is a symmetric top molecule, (two moments of inertia equal ($I_{\perp}$), one different ($I_{\parallel}$)), where the energy difference between the two states J", K" and J', K' can be expressed as,

$$\Delta E_{(J,K)} \approx B[J'(J'+1)-J(J+1)]+(A-B)[K'^2-K^2]$$

where

J', J are the upper and lower rotational quantum numbers respectively.

K', K are the upper and lower quantum numbers, denoting the component of angular momentum along the unique axis (Atkins 1986). $K \leq J$, when $\Delta K = 0$ the energy levels depend only on $I_\perp$.

A and B are the average rotational constants of the upper and lower states (since the changes in the rotational constants between both states are assumed to be small), where $A = h/(8\pi^2 cI_{\parallel})$ and $B = h/(8\pi^2 cI_\perp)$.

h = Planck's constant

c = velocity of light

$I_{\parallel}$ = the moment of inertia parallel to the principal axis of symmetry.

$I_\perp$ = the moment of inertia perpendicular to the principal axis of symmetry.

For CFC113a, $I_{\parallel} = 6.34 \times 10^{-45}$ kgm^2 and $I_\perp = 7.66 \times 10^{-45}$kgm^2 giving rotational constants A= 0.044 cm^{-1} and B=0.037 cm^{-1}. The rotational lines are so close together that fine structure can only be observed when using spectrophotometers of very high resolution. The highest resolution available for use in this work was 0.2cm^{-1}. Typically the mid-infrared spectra were recorded at 2.0cm^{-1}, and errors in the measurement of areas due to unresolved line spacings were reduced by using pressure broadening.

Spectral lines are not infinitely sharp, broadening of the lines can be due to natural (radiative) broadening, Doppler broadening and pressure broadening. Natural broadening arises from the uncertainty principle, where the energy spread is inversely proportional to the uncertainty in time associated with finding the molecule in that particular state (Thorne 1988). The line width can be approximately calculated from

$$\Delta E = h/2\pi\Delta t \quad \text{so that} \quad \Delta\bar{\nu} = 1/2\pi c\Delta t \qquad \text{(Atkins 1986)}$$

where Δt is the natural lifetime of the state. For a typical vibrational natural lifetime of $\Delta t \approx 10^{-4}$ secs (for an energy change of around 1000 cm^{-1}) the linewidth $\Delta\bar{\nu} \approx 5 \times 10^{-8}$ cm^{-1}. The line shape due to lifetime or natural broadening is Lorentzian.

For Doppler broadening, the line is of Gaussian shape, and the line width can be obtained from

$$\Delta\bar{\nu} = \frac{2\bar{\nu}_0}{c}\sqrt{\frac{2RT\ln 2}{M}} = 7.16 \times 10^{-7}\bar{\nu}_0\sqrt{\frac{T}{M}} \quad \text{(Thorne 1988)}$$

For example, for CFC113a, molecular weight M of 187.35, at 300K, the band centred at 909 cm^{-1} would have rotational linewidths of only 0.00082 cm^{-1} which cannot be experimentally observed with the resolutions of current commercial instruments.

The effects of pressure on absorption can be described in two ways:

i) Collision broadening.

The collision between two excited molecules results in a loss of the vibrational energy, hence shortening the lifetime of the state. This broadens the line as for uncertainty broadening, giving a Lorentzian distribution with linewidth $\propto 1/\Delta t$, where Δt is the lifetime of the state (Thorne 1988).

ii) Molecular interaction.

Depending on the proximity of neighbouring molecules, interactions between the molecules may cause perturbation in the molecular potential . This changes the transition frequency, enabling the perturbed molecule to absorb radiation of a slightly different wavelength,

$$\Delta\nu = [V_2(R)-V_1(R)]$$

where V_2 and V_1 are the perturbations to the excited state and ground state energy levels respectively and R is the distance between the molecules (Thorne 1988). These molecular interactions enable absorption over a wider range of frequencies than before, so that as an increase in pressure gives an increase in perturbations, the resultant spectral line is broadened.

Pressure broadening occurs both by the increase in the pressure of the vapour itself and by the addition of a non-absorbing gas such as nitrogen. An approximate broadening of the line may be calculated using the collision frequency, z. The collision frequency, in collisions per second, is given by kinetic theory (Atkins 1986),

$$z = \frac{\sqrt{2\sigma c_{rel} N}}{V}$$

where σ = collision cross-section,

c_{rel} = mean relative velocity = $\dfrac{8kT}{\sqrt{\pi\mu}}$

N = no. of molecules

V = volume

μ = reduced mass of colliding particles.

The average time between collisions, $t = \frac{1}{z}$, so for self broadening, the lifetime $\Delta t = \frac{t}{2} = \frac{1}{2z}$, since every collision removes 2 molecules from that state, and

$$\Delta t = \frac{h}{2\pi\Delta E}$$

where the energy change, $\Delta E = h\Delta\bar{\nu}c$, hence the change in linewidth becomes

$$\Delta\bar{\nu} = \frac{z}{\pi c}$$

Pressure broadening is typically much greater than natural or Doppler broadening. Experimentally, the pressure required to smooth out the rotational structure depends on the separation of the rotational lines. The moments of inertia of the molecules used in this work give very small rotational line separation, for example, for HFC143a which is one of the lightest molecules used, $A = 0.18\text{cm}^{-1}$ and $B = 0.17\text{cm}^{-1}$. The maximum resolution of the instruments available was $0.2\ \text{cm}^{-1}$, so that pressures of only a few torr were required to smooth out the bands. If the individual lines are not broadened, errors in measuring areas may be introduced since an instrument at 0.2cm^{-1} resolution does not recognise the small 'gaps' between the lines, but includes them in the total area.

(b) The direction of the transition dipole moment.

Infrared absorption occurs when there is a change in the dipole moment of the molecule. If this transition moment lies along the principal axis, the band is a parallel band, and $\Delta J = \pm 1$, $\Delta K = 0$,giving,

$$\Delta E(J,K) = B[J'(J'+1)-J(J+1)]$$

If the transition moment is perpendicular to this axis, $\Delta J = 0,\pm 1$, and $\Delta K = \pm 1$ and separate P,Q, and R branches are obtained for each K, causing overlapping of lines and an overall broadened band. For asymmetric top molecules, splitting of K occurs for $J \geq 1$ resulting in even more complex bands (King 1964).

(c) Isotopic substitution.

The energy required for transition varies with the mass of the molecules. This means that the same transition for different isotopomers has slightly different frequencies (Thorne 1988). If there is isotopic substitution of one or more atoms in the molecule, lines due to each isotope overlap each other, making the fine structure even more indistinct. For CFC113a, for different isotopes of chlorine, the changes to the moments of inertia, and hence A and B are very small, for example, for 3 atoms of ^{37}Cl, $A = 0.043\ \text{cm}^{-1}$, and $B = 0.036\ \text{cm}^{-1}$ compared to $A = 0.044\ \text{cm}^{-1}$, and $B = 0.037\ \text{cm}^{-1}$ when using the average molecular weight of chlorine of 35.45.

(d) Temperature.

A change in temperature changes the populations of the rotational levels in the ground state. All spectra were taken at room temperature, and changes due to a small change in temperature are discussed in section 3.1.2.

(e) Fermi resonance.

When two vibrational levels are very close together, mixing can occur between the two states, affecting the intensities of both bands and shifting them away from each other.

(f) Coriolis coupling.

Interactions between vibrational and rotational energy levels distort the band shape. While both Fermi resonance and Coriolis coupling make band centres more difficult to define accurately, band assignments can still be made, so this project will not cover these two phenomena.

1.5.2.2 Integrated absorption intensities.

The absorption coefficient, $K_{\bar{v}}$, gives a measure of the amount of radiation of wavenumber ,$\bar{v}$, which can be absorbed by the compound. It is independent of the quantity of material present, and so is a constant for a particular substance at a particular wavelength. The intensity of a band is the sum of the absorbance for all wavenumbers covered by the band, ie., the area under the spectral band. Absorbance for one spectral line $A_{\bar{v}} = K_{\bar{v}}cl$, so for a spectral band, which covers a range of wavenumbers, the area under the band in the spectrum is

$$\int_{band} A d\bar{v}$$

Since the absorbance obtained from the FTIR spectrophotometer is A_{10}, where A_{10} = A/2.303

the integrated absorbance coefficient can be obtained from

$$2.303\int_{band} A_{10} d\bar{v} = \int_{band} K_{\bar{v}} cl d\bar{v}$$

The Band Intensity (BI), often known as the band strength, S, is given by the sum of the absorbance coefficients for each wavenumber in the band.

$$S = \int_{band} K_{\bar{v}} d\bar{v}$$

$$= 1/cl \int_{band} K_{\bar{v}} cl d\bar{v}$$

$$= 2.303/cl \int_{band} A_{10} d\bar{v}$$

$\int_{band} A_{10} d\bar{v}$ is the area under the band and may be calculated directly by the on-line computer and associated software attached to the instrument. The relationship $S = \int_{band} K_{\bar{v}} d\bar{v}$ is only valid for a spectrophotometer with infinite resolving power, therefore since the instruments used have a finite resolving power, not all the possible values of $K_{\bar{v}}$ can be obtained. This problem can be alleviated by using pressures high enough to eliminate the rotational fine structure which cannot be resolved by the instrument. In the case of most halocarbons, the rotational structure is so dense that the pressures used in this work for intensity measurements easily smoothed out the bands. Figure 1.5 shows the effects of pressure broadening on a band.

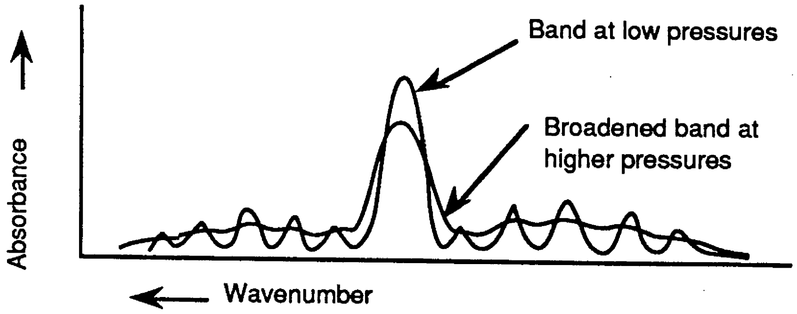


Figure 1.5 Changes in band shape due to pressure broadening.

1.5.3 Error analysis.

When reporting the results of quantitative analysis in infrared spectroscopy it is often the case that the results cannot be reproduced by research groups in different laboratories (Willis et al. 1987). For example, in the measurement of the band intensities for CFC113, the results of Varanasi & Chudamani (1988) and Rogers & Stephens (1988) differ by more than 20%. The use of a FTIR spectrophotometer with high signal-to-noise ratios and wavenumber accuracy has improved the reliability of quantitative analysis, however, the error range on measurements of absolute band intensities is still large (Willis et al. 1987). Possible sources of errors arise from both the equipment used and the interpretation of the spectra (Hirschfeld 1979). By closely examining each aspect of absorption intensity measurements, an attempt has been made to devise a method for measuring band strengths to give both accurate and reproducible results.

1.5.3.1 Deviation from the Beer-Lambert law.

For accurate values of absorption intensities, the absorbance must be linearly proportional to the concentration of the sample, that is, the Beer-Lambert law must hold (Griffiths & de Haseth 1986). Deviations occur depending on the nature of the sample and the way light passes through the sample (Willis et al. 1987).The use of compounds in the gaseous phase enables homogenous samples to be used, since the molecules are evenly dispersed throughout the cell. Scattering of light by the sample was negligible for these compounds at the low pressures used. Absorbance values obtained from the instrument must be in the range 0.1 to 3.0 absorbance units as recommended by the manufacturers. At absorbances of less than 0.1, very few photons are absorbed and noise levels may interfere with readings. At absorbances of more than 3.0, almost all photons are absorbed, that is, less than 1 in 1000 is transmitted and so inaccuracies may occur in the detection of the number of photons.

1.5.3.2 Errors arising from the sample and the sample cell.

Liquid samples broaden spectral bands and introduce problems in the measurement of path lengths and concentrations. Many of the halocarbons used were gaseous at room temperature. The solid and liquid halocarbons used had relatively high vapour pressures, and so it was easy to use them in the vapour state. However, errors may arise from the pressure measurements. Cappellani and Restelli (1992) observed very weak temperature dependence of the absorption intensities. This will contribute to the overall error, since all spectra were taken at room temperature. Impurities in the samples may distort the spectra and need to be considered when reporting results. Spectral artefacts arising from the sample cell can be reduced to a minimum by taking a background sample of the empty cell and subtracting this from the sample spectrum. The measurement of the cell length, giving the path length through the sample may also introduce small errors.

1.5.3.3 Instrumental errors.

The three main components of a spectrophotometer are the optical unit, the computer and the sample compartment. The optical unit consists of an internal source of a continuum of infrared radiation, an interferometer and a detector on the opposite side of the sample compartment. The radiation is split and recombined by the interferometer to give an interference pattern. This interferogram is recorded by the detector when it has passed through the sample, and the computer software controlling the instrumentation converts the time-based pattern into a frequency-based spectrum using a fast Fourier transform (Perkin-Elmer 1985). For this work, the optical unit is not under user control, so the instrument specifications giving the error limits have been used in the estimation of total errors.

The computer controls the collection of data from the detector, performs the Fourier transformation on the interferogram and stores the resultant spectra. Several other operations may be carried out such as apodisation, spectral subtraction of a background, conversion from transmission to absorbance, and integration of the area under a band. Computational errors due to averaging of data points, truncation of the interferogram and rounding of values are generally very small. Errors relating to the sample compartment come from inconsistent positioning of the sample and the presence of atmospheric gases around the cell. Section 3.1.3 presents some examples of these problems.

1.5.3.4 Errors in the interpretation of spectra.

In order to be able to compare band intensities, it is important that the range of the band be fixed (Olliff & Fischer 1992). Difficulties may be encountered when determining the limits of the band, since many bands overlap and may partially coincide with small combination and overtone bands not easy to identify. Once the range has been established, a baseline must be selected. Large discrepancies in literature values are often due, not to real 'errors', but to the fact that different band ranges and baselines have been selected but not specifically identified in the reporting of results. Care has been taken in this work in the choice of band range and baseline, and these values are given in the tables of absorbance intensity measurements. The techniques used in baseline selection were the same for all compounds so that some spectral features could be compared, however, when comparing results, variations in baselines for different spectra need to be taken into consideration.

When all the errors had been analysed as far as possible, a set procedure was formulated and followed for all experimental measurements of the infrared spectra.

1.5.4. Band intensity measurement.

When new substances are being developed for commercial use, the suitability, toxicity, ozone depletion potential, and manufacturing costs are investigated thoroughly. With the current concern on global warming, band intensities and lifetimes should also be criteria for selection, so that, when confronted with two or more potentially useful substances, those with the highest global warming potentials could be rejected. By comparing band strengths of a series of molecules, it may be possible to predict the approximate absorption intensities of proposed substances, without actually having to synthesise them. Those with long lifetimes and high band intensities in the atmospheric window region may then be discarded at an early stage, thus reducing development costs. Some band intensities have already been published(Fisher et al. and references therein 1990 b), however, since a set procedure has been derived for reducing errors in quantitative FTIR spectroscopy as part of this work, measurements have been taken for all available compounds in Table 1.2. Chapter four details the experimental methods used, and reports the results of this section of the work.

1.6 Calculations of vibrational frequencies, intensities and force constants.

In order to interpret the experimental spectra in more detail, fundamental vibrational frequencies, force constants, absolute intensities and potential energy distributions were calculated. The ethane series of CFCs and HFCs were selected for study, each with increasing number of fluorine atoms. The methods of calculations used depended on the availability of both computer time and suitable programs. The programs NORCORD and OVER, running on the ANU's VAX and subsequently SUN/UNIX systems, were used for normal coordinate analyses using a Urey-Bradley force field. The program GAUSSIAN92, which carries out *ab initio* calculations was available on a RISC processor at the Australian Defence Force Academy and on the ANU's Fujitsu Vector Processor.

1.6.1 Urey-Bradley normal coordinate analysis.

Normal coordinate analysis has been used to find a set of force constants for each of the HFCs and CFCs studied, and to facilitate the assignment of particular molecular vibrations to the absorption of energy at a particular frequency, by calculating the potential energy of the system. A normal coordinate describes the change in the arrangement of the atoms within a molecule with respect to one another for each fundamental or normal mode of vibration. When the geometry of the molecule is known, a set of Cartesian coordinates and internal coordinates can be determined, giving respectively, the relative positions of the atoms, and the possible stretches and bends between the bonds. From this information, with the masses of the atoms, the kinetic energy of the molecule can be calculated and subsequently, using a set of force constants, the fundamental vibrational frequencies can be determined.

The frequency of a normal vibration is obtained from the kinetic and potential energies of the system. The kinetic energy is determined by the masses of the atoms and their geometric arrangements in the molecule and the potential energy relates to the interaction between individual atoms and is described in terms of the force constants (Nakamoto 1986). For the displacement of any atom i, the Cartesian coordinates change as Δx_i, Δy_i, Δz_i, so that the kinetic energy of an n-atom molecule becomes

$$T = \frac{1}{2} \sum_{i=1}^{n} m_i \left[\left(\frac{d\Delta x_i}{dt}\right)^2 + \left(\frac{d\Delta y_i}{dt}\right)^2 + \left(\frac{d\Delta z_i}{dt}\right)^2 \right]$$

where m_i is the mass of the atom i. By using the mass weighted coordinates,
$q_1 = \sqrt{m_1}\,\Delta x_1$, $q_2 = \sqrt{m_1}\,\Delta y_1$, $q_3 = \sqrt{m_1}\,\Delta z_1$, $q_4 = \sqrt{m_2}\,\Delta x_2$ .....
the kinetic energy may be written as

$$2T = \sum_{i=1}^{3n} \dot{q}_i^2 \quad \text{where } \dot{q} = \frac{dq}{dt} \qquad \text{(Califano 1976)}$$

The potential energy of the system is a function of all the displacement coordinates. For small displacements the Taylor series expansion may be used:

$$V = V_0 + \sum_{i}^{3n} \left(\frac{\partial V}{\partial q_i}\right)_0 q_i + \frac{1}{2}\sum_{i\,j}^{3n} \left(\frac{\partial^2 V}{\partial q_i \partial q_j}\right)_0 q_i q_j + \frac{1}{6}\sum_{i\,j\,k}^{3n} \left(\frac{\partial^3 V}{\partial q_i \partial q_j \partial q_k}\right)_0 q_i q_j q_k + \ldots.$$

Let the potential energy of the equilibrium configuration V_0 be zero, hence the equilibrium position is at a minimum,

$$\left(\frac{\partial V}{\partial q_i}\right)_0 q_i = 0$$

The terms of the expansion greater than second order may be ignored (Nakamoto 1986) giving,

$$V = \frac{1}{2}\sum_{i\,j}^{3n} \left(\frac{\partial^2 V}{\partial q_i \partial q_j}\right)_0 q_i q_j$$

$\left(\frac{\partial^2 V}{\partial q_i \partial q_j}\right)_0$ may be written as the force constants f_{ij}, so named because they represent the proportionality factors between the displacements of the nuclei and the restoring forces acting upon them (Califano 1976). For a simple diatomic molecule, acting as a harmonic operator,

$$f = -kx = \mu \frac{d^2x}{dt^2}$$

where μ is the reduced mass of the molecule and the calculated wavenumber is obtained from

$$\tilde{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

With polyatomic molecules, problems arise in the calculations by the presence of the cross products q_iq_j. In order to eliminate the cross products, a new set of coordinates, the normal coordinates are used. The transformation from mass-weighted Cartesian coordinates can be shown as

$$Q_k = \sum_i l'_{ki} q_i$$

where the coefficients l'_{ki} relate each normal coordinate to each Cartesian coordinate such that the normal coordinate Q_k is a linear combination of all 3n Cartesian coordinates used to describe the molecule. The kinetic energy becomes

$$T = \frac{1}{2}\sum_i \dot{Q}_i^2$$

and the potential energy

$$V = \frac{1}{2}\sum_i \lambda_i Q_i^2$$

where λ_i is related to the force constants and is the polyatomic equivalent of $\frac{k}{\mu}$ for diatomic molecules. The equation of motion becomes

$$\ddot{Q}_i + \lambda_i Q_i = 0$$

with the solution

$$Q_i = Q_i^0 \sin(\sqrt{\lambda_i}\, t + \delta_i)$$

where Q_i^0 is the amplitude and δ_i is the phase constant of the motion, and the frequency of a normal vibration is

$$\nu_i = \frac{1}{2\pi}\sqrt{\lambda_i}$$

In order to obtain a reasonably accurate set of force constants, an approximate set of force constants is used to calculate the fundamental frequencies. If there are large discrepancies between the calculated and observed frequencies, the force constants are adjusted and the calculations repeated until a satisfactory correlation is obtained (Nakamoto 1986). When agreement between the calculated and observed frequencies is reached, the force constants are considered to be a representation of the potential energy of the system.

One of the difficulties encountered with this type of calculation is that the number of force constants of a molecule is generally larger than the number of frequencies, resulting in solutions which are not unique. For small molecules with high symmetry the calculations are more satisfactory as a number of the force constants are identical. (Califano 1976).

A generalised valence force (GVF) field consisting of bond stretching and bending force constants and the interaction force constants between each coordinate may be used, however the number of interaction constants is often too large to obtain reliable results. The simpler Urey-Bradley (UB) force field was introduced by Shimanouchi (1949) consisting of stretching, bending and repulsive force constants. The repulsive force constants represent the forces between non-bonded atoms. The method for calculation of UB constants is described by Overend and Scherer (1960). Fewer force constants are used for this method and since they relate specifically to stretches, bends and non-bonded interactions between two atoms should be easier to transfer to similar molecules. The general form of the potential field is given by

$$2V=\sum_{i}[2K_i' r_i\Delta r_i + K_i(\Delta r_i)^2] + \sum_{i<j}[2H_{ij}' r_i^2\Delta\alpha_{ij} + H_{ij}(r_i\Delta\alpha_{ij})^2] + \sum_{i<j}[2F_{ij}' q_{ij}\Delta q_{ij} + F_{ij}(\Delta q_{ij})^2]$$

where K, K′ are the stretching force constants, H, H′ are the bending force constants and F, F′ are the repulsive force constants between the non-bonded atoms. Δr, $\Delta\alpha$, and Δq are the changes in the bond lengths, bond angles and non-bonded atom separations respectively, and i and j represent the atoms involved in the vibration.

The advantage of using the UB force field is that the final force constants can be directly related to the internal coordinates, and when there is little internal torsion in the molecule, they are often transferable between similar molecules (Shimanouchi 1963). One disadvantage of this method is that redundancies may occur in the coordinates as the non-bonded distances must be included. Since the coordinates are not independent, the linear terms in the potential energy equation may not be zero (Califano 1976). The relationship between the molecular parameters is

$$q_{ij}^2 = r_i^2 + r_j^2 - 2r_ir_j\cos\alpha_{ij} \qquad \text{(Califano 1976)}$$

Using this relationship the redundant coordinates may be removed from the potential energy equation. The linear terms then become zero and F′ is introduced into the quadratic terms.

$$\begin{aligned}2V=\sum_i \Big[K_i + \sum_{j\neq i}(t_{ij}^2F'_{ij} + s_{ij}^2F_{ij})\Big](\Delta r_i)^2 \\ + \sum_{i<j}\Big[H_{ij} - s_{ij}s_{ji}F'_{ij} + t_{ij}t_{ji}F_{ij}\Big](r_{ij}\Delta\alpha_{ij})^2 \\ + 2\sum_{i<j}\Big[-t_{ij}t_{ji}F'_{ij} + s_{ij}s_{ji}F_{ij}\Big](\Delta r_i)(\Delta r_j) \\ +2\sum_{i<j}\Big[t_{ij}s_{ji}F'_{ij} + t_{ji}s_{ij}F_{ij}\Big]\sqrt{r_j/r_i}\,(\Delta r_i)(r_{ij}\Delta\alpha_{ij})\end{aligned}$$

where

$$s_{ij} = \frac{(r_i - r_j\cos\alpha_{ij})}{q_{ij}} \quad \text{and} \quad t_{ij} = \frac{(r_j\sin\alpha_{ij})}{q_{ij}} \qquad \text{(Overend \& Scherer 1960)}$$

The relationship between F and F′ has been established for the short distances between two non-bonded atoms such that F′ = -0.1F (Califano 1976). In all these calculations it is assumed that the repulsive forces between two atoms across 3 bonds is negligible (Califano 1976).

The programs NORCORD and OVER carry out a normal coordinate analysis using the UB force field method described by Overend and Scherer (1960). The sequence of calculations and perturbation cycle is given in the flowchart shown in figure 1.6.

Input to the program NORCORD consists of the Cartesian coordinates, the internal coordinates, the symmetry blocks of the molecule and the U matrix. The U matrix gives the magnitude of the contribution of each internal coordinate (columns) for each symmetry coordinate (rows). The internal coordinates include all the stretches and bends and the symmetry coordinates are determined using the appropriate character table, depending on the symmetry group of the molecule. All redundancies are removed during the calculations, a G matrix of kinetic energy data is computed, transformed into symmetry coordinates and saved on disk in a form ready for use by the program OVER. The internal and symmetry coordinates used for each symmetry group are given in chapter five, and the detailed input to NORCORD for each molecule is given in appendix B.

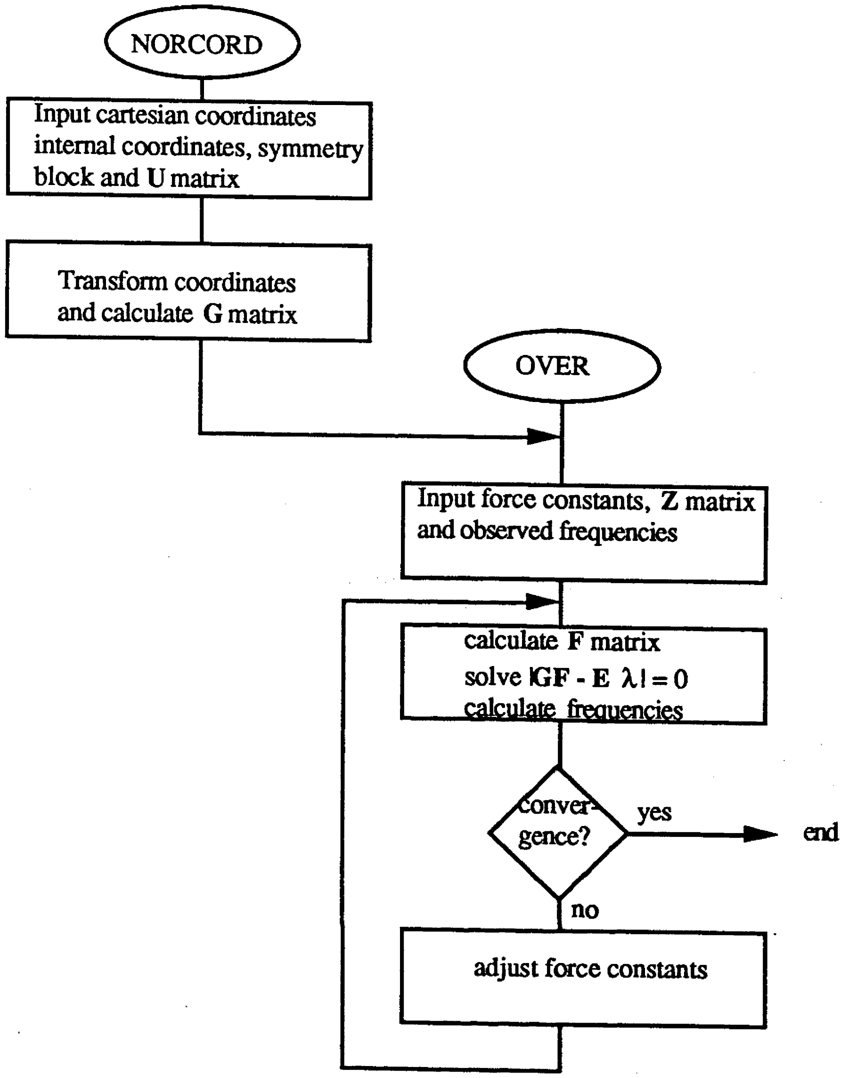


Figure 1.6. A block diagram of the force constant refinement.

The program OVER requires a set of approximate force constants to calculate the fundamental vibrational frequencies and the potential energy distribution. The exact values of the force constants within the molecules being studied were not available, so values found in the literature for C-H, C-F, C-Cl and C-C bonds (Bucker & Nielsen 1963, Naito et al. 1955) have been used to give an approximate set of force constants for the initial calculations. The input data also includes the observed frequencies from an infrared spectrum of the molecule, the kinetic energy and symmetry coordinate information from NORCORD, and the **Z** matrix. The **Z** matrix transforms the force constants into the F matrix in the required coordinates, such that the secular equation $|GF - E\lambda| = 0$ can be solved for all λ and hence the normal frequencies calculated (Overend & Scherer 1960). The coefficients of **Z** are calculated using the table of relationships between the force constants and F_{ij} and F_{ij}' in the publication by Overend and Scherer (1960). The method used for constructing the input to OVER is detailed in chapter five and the final force constants and calculated frequencies are given in chapter six. The detailed input for each molecule is given in appendix B. A copy of the programs adapted for use on the VAX computer was available here at the Australian National University. Errors were found in the programs when using bond lengths correct to only two decimal places or attempting to refine five or more force constants. Considerable time was spent amending the programs to facilitate their use, correcting the errors, and adapting them to run on the SUN/UNIX system. The transferability of force constants between different CFCs and different HFCs has been investigated in this work, and the results shown in chapter six. Attempts to fit the calculated frequencies to the observed frequencies for individual molecules have also been made, and the resulting trends in the force constants over each set of molecules is given in chapter six.

1.6.2 *Ab initio* calculations.

The *ab initio* method of computing model chemical structures and molecular properties uses the laws of quantum mechanics , the fundamental constants c, m, e, and h, (the speed of light, the masses and charges of electrons and nuclei, and Plank's constant respectively), and a set of mathematical approximations to calculate the solutions of the Schrödinger equations for the system (Foresman and Frisch 1993). The time-independent Schrödinger equation for the energy of a wavefunction Ψ can be written as,

$$H\Psi = E\Psi \qquad \text{(Atkins 1986.)}$$

the Hamiltonian operator,

$$H = \frac{-h^2}{8\pi^2 m}\nabla^2 + V$$

for a moving particle of mass m, where,

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

and V = the potential energy of the particle.

With appropriate boundary conditions, many properties of a particle can be found by solving the above equation for Ψ. There are many solutions depending on the stationary states of the system. For a stationary state, the time independent Schrödinger equation gives a wave function representing a wave oscillating with a single frequency.

The solution of the equation with the lowest energy is the ground state. For a molecule, Ψ is a function of the positions of all the particles (electrons and nuclei) in the system. A nucleus is treated as a single entity.

The potential energy of the system,

$$V = \sum_{j} \sum_{k<j} \frac{e_j e_k}{\Delta r_{jk}}$$

is the Coulomb interaction between each pair of charged particles j and k, with charge e_j and e_k and separation Δr_{jk}. For an electron the charge is -e, and for a nucleus the charge is Ze where Z is the atomic number for the atom (Foresman & Frisch 1993).

To solve Schrödinger's equation for a molecule, several approximations are made. The Born-Oppenheimer approximation allows the nuclear and electronic wavefunctions to be separated (Boggs 1992), since the mass of the nucleus is so much greater than the mass of the electron, and the nuclear motion is so much slower than electronic motion, making the nuclei appear stationary relative to the electrons. The Hamiltonian for the molecule can be written as

$$H = T(r) + T(R) + V(r,R)$$

where T is the kinetic energy , r represents the electronic coordinates and R the nuclear coordinates.

$$V(r,R) = -\sum_{i}^{elec} \sum_{I}^{nucl} \frac{Z_I e^2}{\Delta r_{iI}} + \sum_{i}^{elec} \sum_{j<i}^{elec} \frac{e^2}{\Delta r_{ij}} + \sum_{I}^{nucl} \sum_{J<I}^{nucl} \frac{Z_I Z_J e^2}{\Delta r_{IJ}}$$

The electronic and nuclear wavefunctions can then be separated. The energy obtained from solving the electronic wavefunction gives the potential energy surface of the system which can then be used as the potential for the nuclear Hamiltonian . Approximate solutions of the nuclear Schrödinger equation are necessary for predicting vibrational spectra (Foresman & Frisch 1993). All relativistic and spin coupling terms are omitted from the Hamiltonian since these contribute insignificantly when studying atoms lighter than the transition elements (Boggs 1992).

Different levels of *ab initio* calculations are possible depending on the mathematical approximations and methods used. The theoretical method chosen however, must strike a reasonable balance between the reliability of the results and the computing time required for the complete calculations. In this work Hartree-Fock (HF) self consistent field (SCF) and Møller-Plesset second order perturbation (MP2) levels of calculations have been used. GAUSSIAN92 uses the principle that a theoretical model should be uniformly applicable to molecular systems which are to be compared with each other, based on the practical availability of computer resources. It is not meaningful to compare results for similar molecules obtained at different levels of theory. Four halocarbons have been modelled using both HF and MP2 levels with the same basis sets, to show how the results for the same molecule differ with different levels of theory.

Theoretical models used by GAUSSIAN92 are characterised by a combination of theoretical procedure and basis set. The HF theory expands the wave function for a molecule as a linear combination of atomic spin orbitals. Electron correlation , that is the energy contributions arising from electrons interacting with one another, is excluded. Each electron sees all other electrons as an average distribution (Foresman & Frisch 1993). The variation principle used at HF level, states that if an arbitrary wavefunction is used to calculate energy then the value obtained is never less than the true energy. This gives a direction for the calculation for repeated iterations such that the result with the lowest energy is the best. Calculations are repeated for a pre-determined number of iterations. Minima are found on the energy surface where the first derivative is zero. Identification of the true minimum by the use of the second derivative enables optimisation of the geometry (Foresman & Frisch 1993). Once optimisation is completed, the theoretical bond distances and angles are used in the next step, that of calculating the force constants and the vibrational frequencies using an harmonic approximation. This method is insufficient to model reaction energetics, but is suitable for vibrational frequencies provided that a scaling factor is used. Frequencies obtained using HF SCF theory contain known systematic errors due to the neglect of the electron correlation. This results in an overestimation of about 10-12 %, so it is customary to scale the frequencies by 0.8-0.9. The scaling factor varies, depending on the level of theory used. The recommended scaling factors of 0.8953 for the HF results and 0.9427 for the MP2 results (Pople et al. 1993) were used in this work. Møller-Plesset perturbation theory for second-order energies, where some electron correlation is included, was used in the calculations for some of the molecules for comparison . A small perturbation is applied to the Hamiltonian to give a perturbed wave function of lower energy than that obtained by the HF method. Considerably more computer time is required for MP2 calculations and so only a few of the lightest molecules were modelled to see the difference in the results.

Another aspect of the approximations used relates to the basis functions. The basis set is the mathematical representation of the molecular orbitals restricting each electron to a particular region of space. A basis function represents a one-electron function, GAUSSIAN92 uses a linear combination of gaussian-type functions of the general form

$$g = cx^n y^m z^l e^{-\alpha r^2}$$

where α is a constant determining the size of the function; n,m, and l = 0,1,2.. depending on the orbital of the electron, and c is the normalisation constant (Foresman & Frisch 1993).

The larger the number of basis functions used, the more accurate the results, however, the cost in computer time for the larger basis sets cannot always be justified. The larger the basis set, the fewer constraints on the electrons, giving more accurate orbitals, however, the larger the set the more computing power required (Fogarasi & Pulay 1985). In this work, the basis set 6-31G* was used as this was the highest basis set available for the computer time allowed. This is the standard basis set for calculations involving up to medium sized systems; it allows orbitals to change size and shape for each atom beyond the ground state requirements, for example some small contribution from unfilled d orbitals is included for carbon atoms (Foresman & Frisch 1993).

Vibrational intensities are also computed, however they are thought to be only relatively correct, and may be used to indicate whether the absorbance of a fundamental mode is expected to be strong, medium or weak (Fogarasi & Pulay 1985). Raman depolarisations are also given by the program, but have only been used when other information does not conclusively confirm an assignment. Diagonal force constants in internal coordinates are calculated, however errors in bond lengths contribute to consistent overestimation, particularly of the stretching force constants and must be corrected as for the vibrational frequencies by the use of a linear scaling factor (Fogarasi & Pulay 1985). Initially, experimental geometry obtained from the literature was to be used for the theoretical frequencies, since the calculated SCF geometries are known to yield shorter bond lengths than expected (Fogarasi & Pulay 1985). However due to the lack of accurate experimental data for all the molecules, and since part of this work is to observe trends in force constants, it was decided to optimise the geometry, so obtaining systematic errors, rather than use the experimental geometries and work with random errors. A description of the input to GAUSSIAN92 is given in chapter five, and the results are presented in chapters six and seven. Detailed input to the program is given in appendix C.

1.6.3 Vibrational assignments, force constants and intensities.

For those molecules where the assignments of frequencies were in doubt, tentative assignments have been made using the results of both Urey-Bradley and *ab initio* calculations. These are discussed in chapter six. Vibrational assignments of fundamental modes are made by a combination of information. The literature was searched for assignments of all the relevant molecules. The symmetry species of each frequency calculated by *ab initio* methods is given by the program, and may be used to check assignments. Using this information and by studying the observed spectra it was possible to confirm most of the fundamental frequencies for the UB force field calculations. If no reasonable agreement between the observed and calculated frequencies could be found after several attempts at adjusting force constants, the observed frequencies were interchanged as far as possible to see if any improvement could be made.

Using the UB force field, one set of force constants has been derived for the CFCs and one for the HFCs. These force constants give only a reasonable fit across all the molecules in each group. Further refinements were carried out on individual molecules to obtain a better match between the observed and the calculated frequencies. The resultant force constants for each molecule were then compared to look for trends. Force constants in internal coordinates are available from the output from GAUSSIAN92. These force constants are not directly comparable with the UB results, except in the case of the stretching force constants, as the internal coordinates for the *ab initio* calculations are not identical to those for the UB calculations. Another difficulty encountered with comparing the force constants is that scaling factors are required for the *ab initio* results (Zhou et al. 1993).

New assignments made in this work are reported in section 6.1. The force constants are presented in section 6.2, and the intensities and optimised geometries are given in chapter seven. The infrared bands due to the carbon-fluorine and carbon-carbon bond stretches have been approximately identified and the changes in infrared absorption intensity with the change in number and position of fluorine atoms have been compared for the halocarbons studied.

1.7 Summary.

In order to gain an insight into the nature of the vibrational excitation of halocarbons, a combination of experimental and theoretical work has been carried out. The infrared band intensities of halocarbons of topical interest have been measured and an analysis of the errors encountered in infrared spectroscopy investigated. Theoretical vibrational analysis has enabled the tentative assignment of fundamental vibrational modes and the calculation of force constants for nineteen haloethanes. Investigations of both the trends in force constants across a group of like molecules and the relationships between the intensity of absorption and the number and position of fluorine-carbon bonds have been carried out. The use of this information may assist in the prediction of vibrational spectra of halocarbons which have not yet been synthesised.

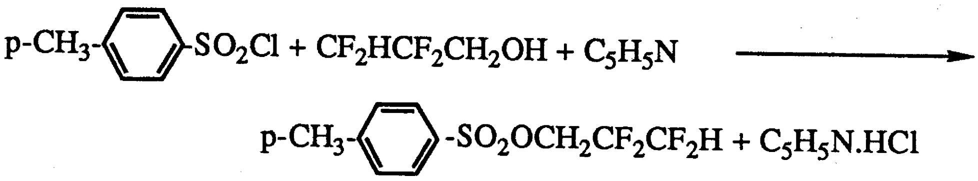
Chapter 2.

Halocarbon syntheses.

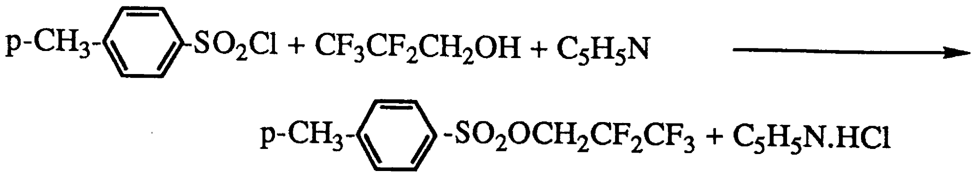
Two halopropanes were synthesised as part of this work since, at the start of the project, none of the substances fulfilling the requirements detailed in section 1.3.1 were available. An identical procedure was followed for the synthesis of both halopropanes, and consisted of two steps: the formation of a tosyl ester from an appropriate alcohol; and the substitution of the tosylate group by a chlorine atom. The method of Tipson (1944) described in section 1.4 was followed for the first reaction step, since the two alcohols 2,2,3,3-tetrafluoropropanol and 2,2,3,3,3-pentafluoropropanol were available from Aldrich chemicals and may be readily converted into suitable halopropanes. The second step of the reaction was carried out according to the method by McBee et al. (1955) detailed in section 1.4.

2.1 Experimental methods.

STEP 1. The formation of the tosyl ester was carried out using (A) 2,2,3,3-tetrafluoropropanol, and (B) 2,2,3,3,3- pentafluoropropanol. A 250ml three-necked flask was fitted with a thermometer and appropriate volumes of fluorinated propanol and pyridine were mixed using a magnetic stirrer, in the molar ratio 1:4 . The base of the flask was immersed in a water/ice bath and tosyl chloride added at a rate such that the temperature of the mixture did not rise above 10° C. The mixture was stirred for approximately 3 hours.The quantities of reactants used for step 1 were as follows:
(A) 25ml (0.278mole) of 2,2,3,3-tetrafluoropropanol with 53g (0.278mole) of tosyl chloride in 100ml of pyridine.



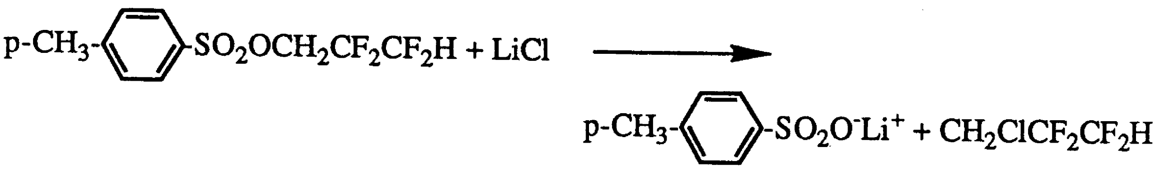
(B) 9ml (0.090mole) of 2,2,3,3,3-pentafluoropropanol with 17.5g (0.092mole) of tosyl chloride in 36ml of pyridine.



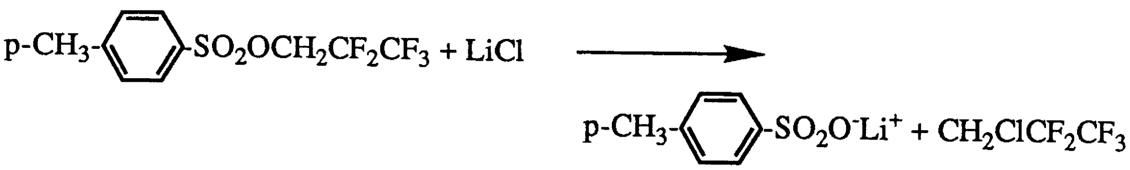
Pyridine hydrochloride crystals were observed in the mixture in the reaction vessel in both cases. After 3 hours, sufficient (approximately 15 x no. of ml of alcohol) 1M hydrochloric acid was added slowly to dissolve the pyridine hydrochloride and any other impurities. A similar quantity of ether was added to dissolve the new tosylate, which could then be separated from the aqueous layer using a separating funnel. After separation, the ether + tosylate solution was dried by the addition of anhydrous magnesium sulphate. The magnesium sulphate was then filtered off and the ether was allowed to evaporate, leaving the pure tosylate. 2,2,3,3-Tetrafluoropropyltosylate is a clear oily liquid, and 2,2,3,3,3-pentafluoropropyltosylate is a white crystalline solid. The purity of each tosylate was checked using thin-layer chromatography. Small amounts of 2,2,3,3-tetrafluoropropanol, 2,2,3,3,3-pentafluoropropanol, tosyl chloride in acetone, and the products of experiments A and B were spotted onto a glass chromatographic plate. The plates were left to stand in a 50:50 mixture of cyclohexane:ethyl acetate until the solvent had risen to near the top of the plate. An infrared spectrum was taken of each reactant and purified product.

STEP 2. The substitution of the tosyl group by a chlorine atom was carried out using (C) 2,2,3,3-tetrafluoropropyltosylate and (D) 2,2,3,3,3-pentafluoropropyltosylate. Using a 500ml 3-necked flask fitted with a thermometer, an inlet from N_2 gas and an outlet to two liquid N_2 traps, a known amount of the appropriate tosylate made in step 1 was added to lithium chloride in dimethyl sulfoxide (DMSO) and the mixture heated to 160° C for 2.5 to 3 hours. Enough DMSO was used to dissolve both reactants and to cover the inlet tube from the N_2 gas. As the chlorofluoropropane products are very volatile the easiest way to collect them was to flush them out of the reaction mixture with N_2 gas, and trap them in a glass tube cooled by liquid nitrogen. Lithium tosylate remained in the reaction vessel with the DMSO. The quantities of reactants used for step 2 were as follows:

(C) 50g (0.175mole) of 2,2,3,3-tetrafluoropropyltosylate with 8.0g (0.189mole) of lithium chloride in 300ml DMSO.



(D) 23g (0.076mole) of 2,2,3,3,3-pentafluoropropyltosylate with 4.0g (0.094mole) of lithium chloride in 200ml DMSO.



The trap containing the frozen product was quickly transferred to the vacuum line and kept under liquid N_2 during evacuation. A trap-to-trap distillation was carried out to collect the pure liquid halopropane in a clean, evacuated vessel. 1-chloro-2,2,3,3-tetrafluoropropane and 1-chloro-2,2,3,3,3-pentafluoropropane are clear oily liquids. A mass spectrum was taken for each of the final products.

2.2 Results and product characterisation.

The results of each experiment in step 1 were found to be as follows:
(A) 0.278mole of 2,2,3,3-tetrafluoropropanol were treated with an equivalent amount of tosyl chloride in 100ml of pyridine. 64.6g (0.226mole) of 2,2,3,3-tetrafluoropropyltosylate were obtained, a yield of 81.3%.
(B) 0.090mole of 2,2,3,3,3-pentafluoropropanol were treated with an equivalent amount of tosyl chloride in 36ml of pyridine. 23.1g (0.076mole) of 2,2,3,3,3-pentafluoropropyltosylate were obtained, a yield of 84.4%.

The thin-layer chromatogram showed the movement of the tosyl chloride, and each of the products of experiments A and B. The tosylates did not travel so far up the plate as the tosyl chloride sample. No trace of tosyl chloride was seen arising from the spots made with the purified products of experiments A and B. The alcohols could not be detected by this method of thin-layer chromatography. Figure 2.1 shows the infrared spectra of 2,2,3,3-tetrafluoropropanol (liquid sample), tosyl chloride (solid sample in nujol) and the purified product (liquid sample) from experiment A. Figure 2.2 shows the spectra of 2,2,3,3,3-pentafluoropropanol (liquid sample), tosyl chloride (solid sample in nujol) and the purified product (solid sample in nujol) from experiment B.

The results of each experiment in step 2 were found to be as follows:
(C) 0.175mole of 2,2,3,3-tetrafluoropropyltosylate were treated with an excess of lithium chloride to give 15.95g (0.106mole) of 1-chloro-2,2,3,3-tetrafluoropropane, a yield of 60.6%.

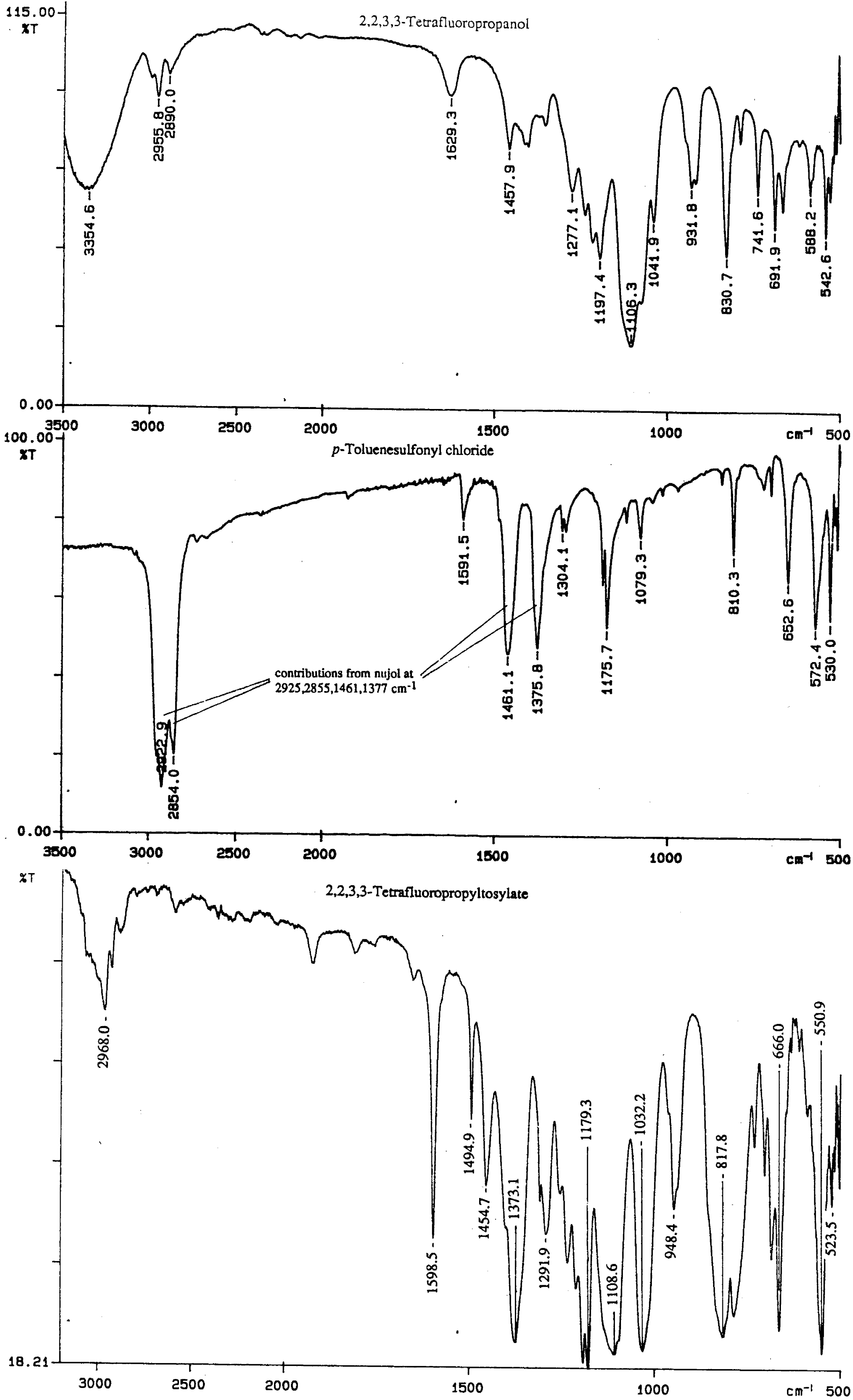


Figure 2.1. Experiment A: infrared spectra of reactants 2,2,3,3-tetrafluoropropanol and toluenesulfonyl chloride, and product 2,2,3,3-tetrafluoropropyltosylate.

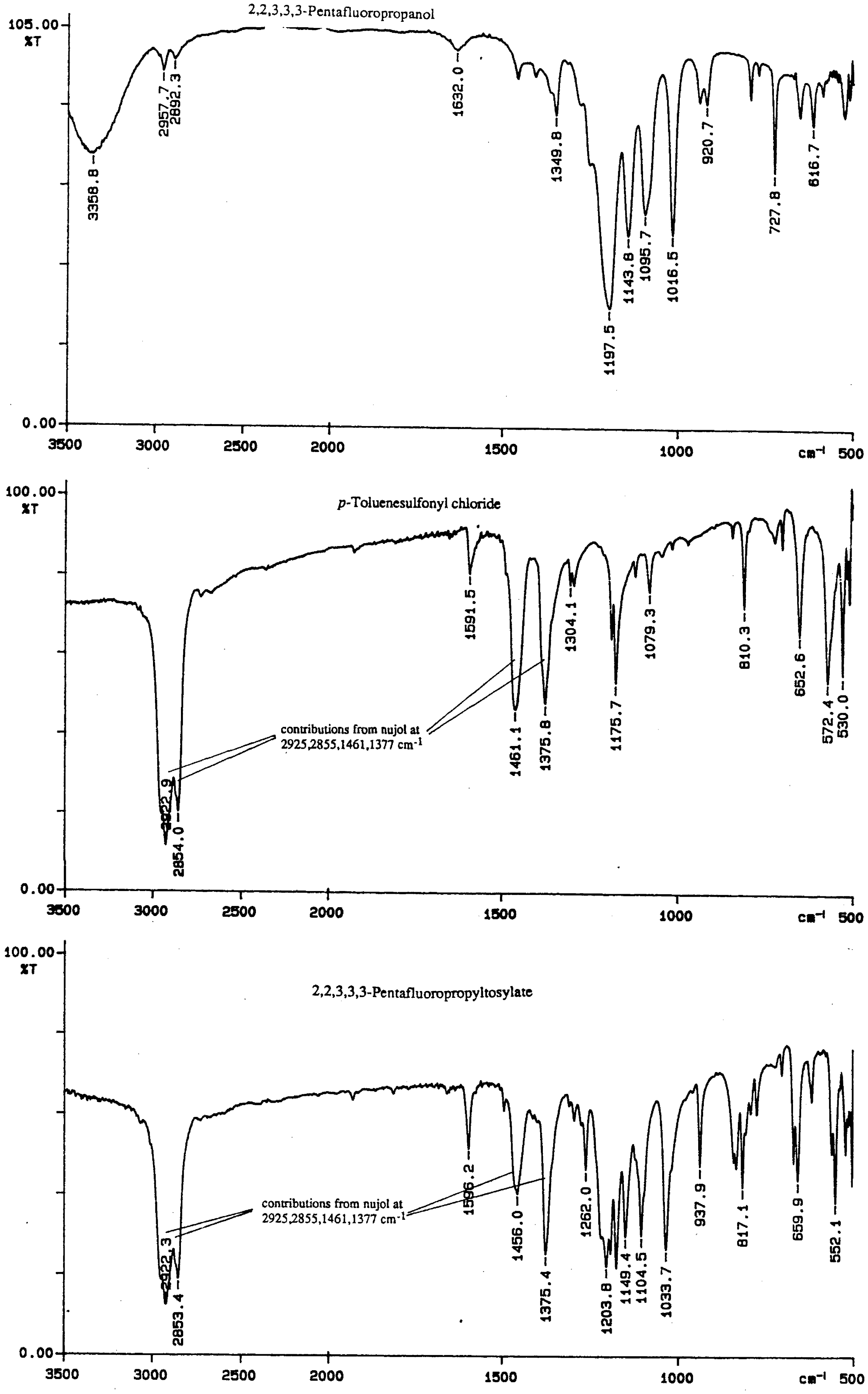


Figure 2.2. Experiment B: infrared spectra of reactants 2,2,3,3,3-pentafluoropropanol and toluenesulfonyl chloride, and product 2,2,3,3,3-pentafluoropropyltosylate.

(D) 0.076mole of 2,2,3,3,3-pentafluoropropyltosylate were treated with an excess of lithium chloride giving 9.1g (0.054mole) of 1-chloro-2,2,3,3,3-pentafluoropropane, a yield of 71.1%.

Figure 2.3 shows the infrared spectra of 1-chloro-2,2,3,3-tetrafluoropropane, HCFC244ca, and 1-chloro-2,2,3,3,3-pentafluoropropane, HCFC235cb. The mass spectra of HCFC244ca and HCFC235cb are presented in figure 2.4. The infrared spectrum of HCFC235cb was compared to that by Paleta et al. (1971) for confirmation of identification. Microanalysis results for HCFC244ca gave 24.8% carbon (23.94% calc.) 2.1% hydrogen (2.01% calc.) and 23.5% chlorine (23.56% calc.). No microanalysis for fluorine was available.

2.3. Discussion.

The thin-layer chromatography results for step 1 of the syntheses showed that no tosyl chloride remained with the products. The infrared spectra of reactants and products shown in figures 2.1 and 2.2 have been used for further identification. From the experiments, it was possible that some ether remained with the product. Checks were also made for the presence of the starting alcohol, tosyl chloride and pyridine, although it was expected that since pyridine is soluble in water, it was successfully separated from the product in ether.

The spectra of both starting alcohols show two distinctive features due to the presence of -OH, a broad band centred near 3360cm^{-1} and weaker broad band around 1420cm^{-1} (Lin-Vien et al. 1991). Both of these bands are absent on the spectra of the corresponding products. Other characteristic C-OH bands are obscured by the presence of bands due to C-F stretches and bends. The fluorines of the alcohol are distinguished mainly by strong absorption in the 1200-1100cm^{-1} region due to C-F stretches, and by many peaks below 850cm^{-1} due to C-F bending modes. Similar bands can be seen in the spectrum of the product.

The presence of a para-substituted benzene ring can be seen in both the spectra of tosyl chloride and the tosylate products, mainly identified by bands in the regions 3000cm^{-1} and 1620-1585cm^{-1}. These areas are partly obscured by the presence of nujol in the case of the solid samples, but can be distinguished more easily in the spectrum of 2,2,3,3-tetrafluorotosylate. Typical changes in the spectra when comparing the $-SO_2Cl$ and the $-SO_2O-$ groups may be seen as shifts from 1385-1375cm^{-1} to 1375-1365cm^{-1} and from 1175-1170cm^{-1} to 1195-1180cm^{-1} (Lin-Vien et al. 1991).

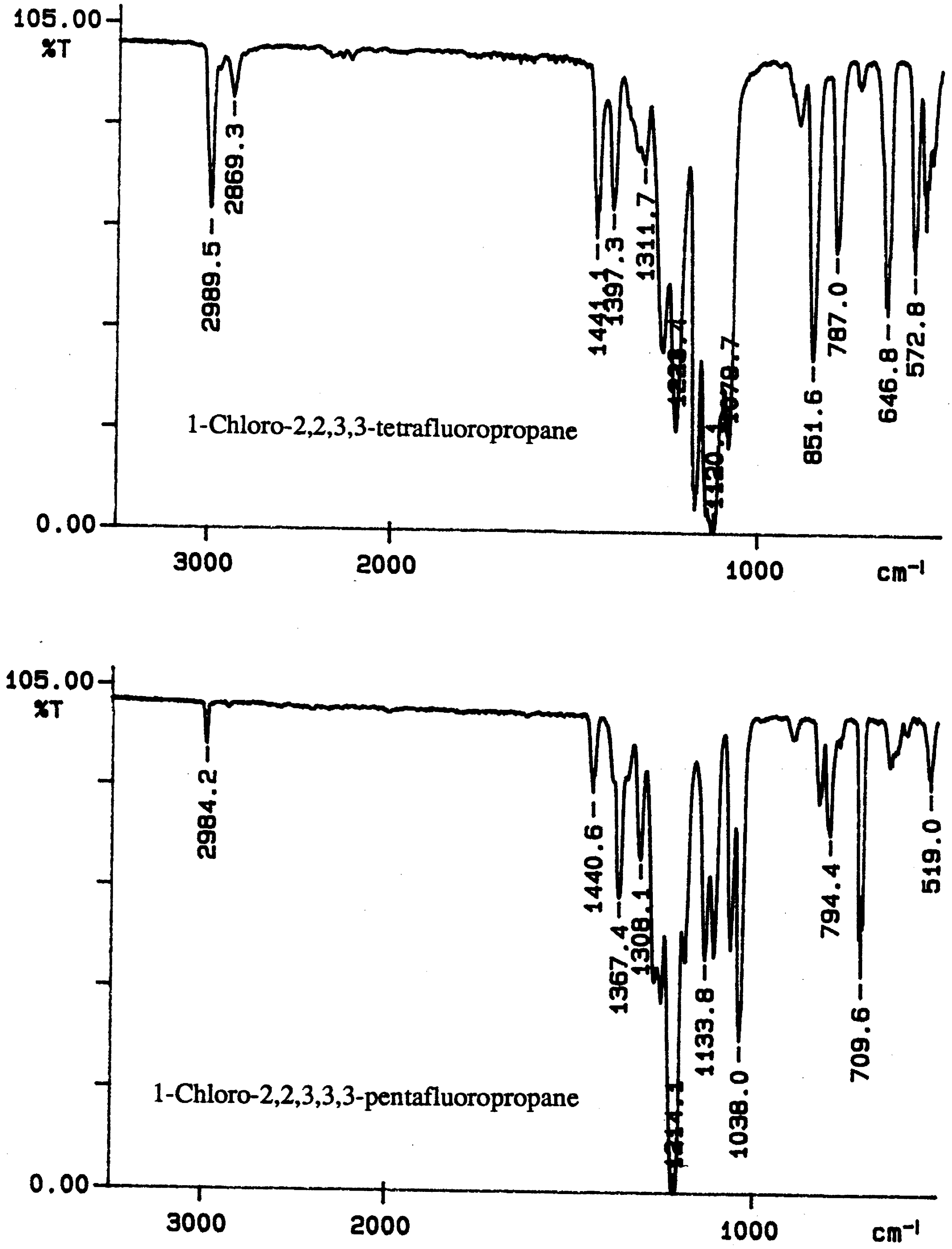


Figure 2.3. Infrared spectra of the product of experiment C, 1-chloro-2,2,3,3-tetrafluoropropane, and experiment D, 1-chloro-2,2,3,3,3-pentafluoropropane.

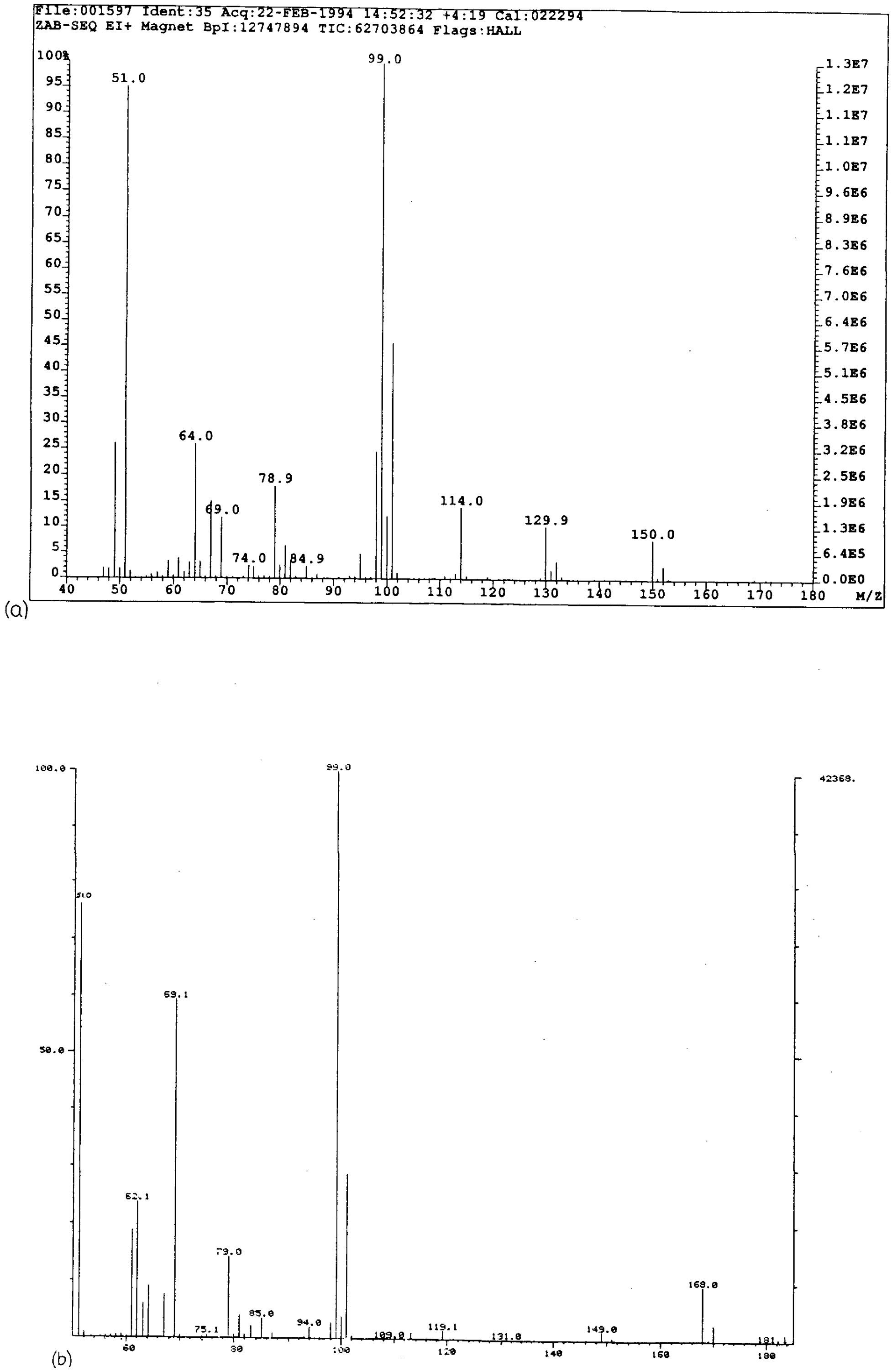


Figure 2.4. Mass spectra of (a) 1-chloro-2,2,3,3-tetrafluoropropane (HCFC244ca) and (b) 1-chloro-2,2,3,3,3-pentafluoropropane (HCFC235cb).

These changes are small, and while some evidence of these shifts may be seen, they are again obscured by the presence of strong nujol bands at 1461cm^{-1} and 1377cm^{-1}, and in the case of the tosylates, the strong absorption of C-F bands. The thin-layer chromatogram confirmed that the tosyl chloride had reacted in step 1.

Pyridine has strong bands in the 750-700cm^{-1} region, which have not been observed in the tosylate spectra. The presence of diethyl ether may be detected by predominant bands at 2989, 2871, 1394, and 1138cm^{-1} (Lin-Vien et al. 1991). Again these bands are difficult to identify, but since there are no strong peaks at 2989 or 2871cm^{-1} in the spectrum of 2,2,3,3-tetrafluoropropyltosylate, and no strong peaks at 1394 or 1138cm^{-1} in the spectrum of 2,2,3,3,3-pentafluoropropyltosylate, it was concluded that a sample of both tosylates, of purity suitable to be used in step 2, had been produced.

In step 2, the conversion of the tosylates to halopropanes has been confirmed by infrared and mass spectroscopy. The infrared spectra of both products are free from contamination by tosylates, as can be seen from the fact that the broad band around 3000cm^{-1} due to the presence of the benzene ring has been replaced by the characteristically sharp peaks of isolated C-H stretches. The bands near 1595cm^{-1} also due to the tosylate group are absent. DMSO absorbs strongly in the region of 1102cm^{-1}, however, this band would be obscured by absorption due to the C-F stretches in the product spectra. DMSO also absorbs in the regions of 3001, 1443, 1420 and 673cm^{-1} (Aldrich Chemical Co. 1989), these bands are not present on the spectra of the products, indicating that the halopropanes were successfully separated from the solvent. No infrared spectra of HCFC244ca were found in the literature.

Table 2.1. Comparison of the infrared spectral peaks of HCFC235cb.

Paleta et al. (1971) cm^{-1}		this work cm^{-1}	
2988	weak	2984.2	weak
1253	medium	1251.4	medium
1216	very strong	1214.1	very strong
1186	medium	1186.2	medium
1132	medium	1133.8	medium
1109	medium	1108.6	medium
1061	medium	1062.9	medium
1038	medium	1038.0	medium strong
798	medium weak	794.4	medium weak
709	medium	709.6	medium

Identification of HCFC235cb was confirmed by comparison of the infrared spectrum shown in figure 2.3 with the results given by Paleta et al. (1971). Table 2.1

shows the positions of the most significant absorption peaks of HCFC235cb. The small discrepancies between the results are most likely due to the different choice of peak maxima, for example, the peak at 2984.2cm^{-1} is part of a broader band. No illustration of the spectrum was presented by Paleta et al. (1971) for direct comparison, however, the correlation between the peaks leads to the assumption that HCFC235cb has been synthesised.

Further confirmation of the products was obtained from the fragments shown in the low resolution mass spectra of the samples in figure 2.4. Table 2.2 lists the molecular weights of fragments of both halopropanes.

Table 2.2. Molecular weights of fragments of HCFC244ca and HCFC235cb.

HCFC244ca fragment	molecular weight		HCFC235cb fragment	molecular weight	
$CF_2HCF_2CH_2Cl$	150 ,152	ratio 3:1	$CF_3CF_2CH_2Cl$	168, 170	ratio 3:1
$-CF_2CH_2Cl$	99 , 101	ratio 3:1	$-CF_2CH_2Cl$	99 , 101	ratio 3:1
$-CF_2CF_2H$	101		$-CF_2CF_3$	119	
$-CH_2Cl$	49 , 51	ratio 3:1	$-CH_2Cl$	49 , 51	ratio 3:1
$-CF_2H$	51		$-CF_3$	69	
$-CF_2-$	50		$-CF_2-$	50	

The presence of a chlorine atom in some of the fragments of both molecules resulted in peaks in the spectrum 2 units apart due to the two isotopic forms ^{35}Cl and ^{37}Cl which naturally occur in the ratio 3:1. The mass spectrum of HCFC244ca given in figure 2.4 (a) shows the fragments listed in table 2.2 in the expected ratios. The molecular weights 150 and 152 for the whole molecule appear in the spectrum in the ratio 3:1. The fragments $-CF_2CH_2{}^{37}Cl$ and $-CF_2CF_2H$ both have a molecular weight of 101, which is consistent with the fact that the observed ratio of 99 and 101 is not 3:1, as would be expected if $-CF_2CF_2H$ did not exist. Similarly, $-CH_2{}^{37}Cl$ and $-CF_2H$ have the same molecular weight of 51, resulting in a different ratio of molecular weights of 49 to 51. Fragments shown at 129.9 and 131.9 may be due to the loss of both one H and F atom; at 114, due to the loss of both one H and Cl atom; at 98 and 100, due to loss of both $-CF_2H$ and an H atom; at 100 due to loss of both $-CH_2Cl$ and an H atom; and at 64 due to loss of both $-CF_2H$ and a Cl atom. The mass spectrum of HCFC235cb in figure 2.4 (b) shows the fragments listed for that compound in table 2.2. The fragments containing a chlorine atom appear in the spectrum in the expected ratios of 3:1. Fragments shown at 149 and 151 may be attributed to the loss of one F atom, and the fragment at 131 may be $-CCF_2CF_3$.

The microanalysis of HCFC244ca gave a satisfactory result for chlorine content at 23.5%, but gave an error in the order of 4% for the carbon and hydrogen contents. Unfortunately, the compound was found to be too volatile for the analysis of fluorine.

From a close examination of all the results it was concluded that samples of 1-chloro-2,2,3,3-tetrafluoropropane, HCFC244ca, and 1-chloro-2,2,3,3,3-pentafluoropropane, HCFC235cb, had been produced. The quantities and purities of the products were considered to be acceptable for use in the spectral band intensity measurements which were made as part of this work.

Chapter 3.

Fourier Transform Infrared (FTIR) Spectroscopy.

The possible sources of errors in band intensity measurement have been outlined in section 1.5.3. This chapter presents the results of several experiments carried out to find, where possible, the contribution to the overall error of various aspects of the work. A list of procedures to be followed when measuring band intensities, in order to obtain the most accurate results, is given at the end of the chapter .

3.1 Sources of experimental errors.

3.1.1 The sample cell.

Two airtight glass cells were used for all the measurements. The cells were fitted with O-rings and potassium bromide windows of 40mm. diameter. The path lengths for the cells were 3.415±0.005cm and 10.429±0.005cm. When not in use the cells were kept in a desiccator to protect the windows from moisture. Figure 3.1 illustrates the cell.

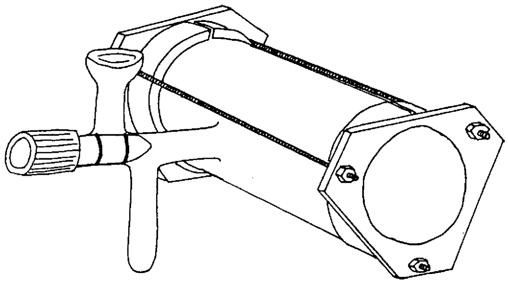


Figure 3.1 The sample cell.

It is important to keep the windows free from dirt or grease, however, they should not be polished between recordings of spectra for one compound as this may change the base transmission line of the radiation. The cells have been tested extensively for leakage, and will hold a vacuum at less than 10^{-4}torr for more than a week.

3.1.2 The vapour.

All samples were used in the vapour state. The pressure was measured using a Baratron differential pressure head of range 0-100torr (1torr = 0.1333kPa), with digital readout accurate to 0.3% of the full scale reading. The pressures used were mostly in the range 15-50torr, giving percentage errors ranging from 2.0 to 0.6%. In a few cases the presence of very strong bands meant that lower pressures were required to keep the absorbance within a suitable range, increasing the error in pressure measurement to a maximum of ± 4.0%.

As described in section 1.5.2.1 it is important to broaden the bands so that the fine structure is smoothed out. To this end, a few spectra were taken for each compound so that suitable pressure ranges could be chosen for accurate measurements and the cell of the most appropriate length used for selected bands. The lowest pressure must be such that the fine structure is not observed at the highest resolution, and the absorbance maximum at the centre of the band exceeds 0.1 absorbance units. The highest pressure must be such that the maximum absorbance value does not exceed 3.0 absorbance units. These absorbance limits are recommended by the instrument manufacturers for a linear relationship between concentration and absorbance, in accordance with the Beer-Lambert law. When using the 3cm cell, higher pressures may be used to achieve the same absorbance as that obtained in the 10cm cell. This had the effect of reducing pressure errors. In the case of very weak bands the 10cm cell was more appropriate as the longer path length enabled higher absorbances to be achieved, without having to use very high pressures.

Changes in temperature may affect the absorption due to changes in populations of energy levels. Hannah (1988) reported that the intensity of an absorption band changes by approximately 0.1% per °C. However, Cappellani and Restelli (1992) observed only weak temperature dependence of the absorption intensities of some HFCs and HCFCs over a temperature range of 60°C. All spectra in this work were taken at room temperature, which did not vary by more than a few degrees. It was assumed from this, that the change in intensity due to temperature fluctuations was negligible.

All compounds were purchased at the highest purity available from the manufacturers. When using CFC113a, the presence of CFC13 was detected on the infrared spectrum. Two trap-to-trap vacuum distillations were carried out, and no more problems were encountered, since CFC113a freezes at 14°C, whereas CFC13 is a gas at this temperature with a boiling point of -81.4°C (PCR Inc. 1992). During many of the manufacturing processes of halocarbons, other halocarbons are sometimes formed as by-products. Bands due to contaminants may therefore coincide with the sample bands, and so not be seen in the spectra. This phenomenon may be noticed by large discrepancies in area measurements due to varying ratios of sample/contaminant pressures when each sample is collected. This error cannot be quantified, so all spectra were carefully scrutinised for impurities, and discarded if either unexpected peaks were observed, or large discrepancies in areas were found. No attempt was made to correct the data using the percentage purity given by the suppliers, but this purity is reported with the band intensity results in chapter four.

3.1.3. The spectrophotometer.

Most of the spectra were recorded on a Perkin-Elmer (P-E) 1600 in the Department of Chemistry. However, since it was possible that discrepancies arose in the data, some spectra were taken on a P-E 1800 in the Research School of Chemistry at the ANU and a Bio-Rad F60 belonging to the Australian National Library. Table 3.1 gives the manufacturers error ranges for the three instruments used.

Table 3.1 Error ranges for the FTIR spectrophotometers used.

Instrument	max. resolution	wavenumber accuracy
Perkin-Elmer 1600	2.0cm^{-1}	±0.02cm^{-1}
Perkin-Elmer 1800	0.2cm^{-1}	±0.01cm^{-1}
Bio-Rad F60	0.1cm^{-1}	±0.01cm^{-1}

There is no currently accepted method to measure ordinate accuracy in an FTIR spectrophotometer (Perkin-Elmer 1985), but the transmission line has a repeatability better than 0.1%, and the absorbance is linear from 0 to 3.0 for the P-E instruments. The signal to noise ratio in A is 3500:1 at a resolution of 2cm^{-1} and 700:1 at a resolution of 0.2 cm^{-1} for the P-E instruments.

The sample compartments on the P-E instruments can easily be purged using nitrogen gas. When air is in the compartment, absorption by carbon dioxide and water vapour may be seen in the spectra, with intensities varying from day to day. By eliminating air from the compartment while recording all spectra, the possibility of changes in the trace gases in the laboratory could be ignored. It was not possible to purge the compartment of the Bio-Rad instrument. However, by ratioing all sample spectra with a background spectrum of the evacuated cell, spectral artefacts due to atmospheric conditions could be almost eliminated. The time between the recordings of the background and sample spectra was kept to a minimum.

The position of the sample cell within the compartment is important. Special holders were made to accommodate the cells. The following results show the difference in area measurements when the cell is set at an angle of 10° to the infrared source. As shown in table 3.2, the difference in these results is very small for such a large misalignment of the cell, however, care was always taken in the positioning of the cell.

Table 3.2. Comparison of areas of CFC113a with a 10° misalignment of the sample cell

Position	Areas under the bands for each range in absorbance units x cm^{-1}					
	1300-700 cm^{-1}	1290-1238 cm^{-1}	1238-1200 cm^{-1}	945-880 cm^{-1}	880-825 cm^{-1}	750-690 cm^{-1}
Normal	126.60	31.42	45.61	5.85	37.55	5.41
10° offset	125.52	31.42	45.84	5.87	36.44	5.39

A slightly longer path length may increase absorbance, however, reflection of the IR beam at the surface of the cell window (since it is no longer at 90°) may result in a reduction of intensity.

3.2. Errors in computation and interpretation.

When recording a spectrum, the cell windows and trace gases in the sample compartment may also absorb some of the infrared radiation, and consequently distort the spectrum. This problem was overcome by recording a spectrum of the evacuated cell and storing it as a 'background' transmission spectrum. Each time the sample spectrum was taken, it was then ratioed with the 'background' spectrum before being converted from transmission to absorbance. This eliminated any absorption due to the cell or compartment, leaving a spectrum due to the vapour alone. Very slight errors could be introduced by incorrect alignment of the cell in subsequent runs, but this was reduced to a minimum by the use of special holders. A new background was taken before starting a new compound as minute amounts of dirt or grease may have accumulated on the windows when the cell was in use. If, for any reason, the windows were cleaned, a new background was taken and used for subsequent vapour spectra.

When an interferogram undergoes Fourier transform, it must be truncated. This results in a series of side-lobes at the sides of the spectral bands, which interfere with the real spectral features. An apodisation function reduces side-lobes at the cost of broadening the bands. Apodisation functions are included in the instrument software. Some apodisation is required to reduce errors in the selection of baseline points, so in order to optimise the results, weak Norton-Beer apodisation, as supplied by the manufacturers of the spectrophotometers, was used in this work. Figure 3.2 illustrates the effects of apodisation. The difference in integrated areas is very small for the different apodisation routines, but the ripples on the wings of the bands do affect baseline point selection.

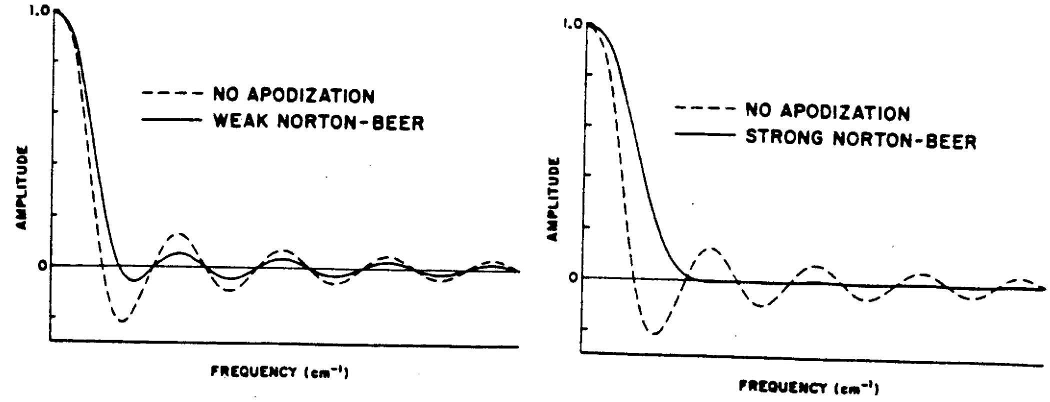


Figure 3.2. Weak and Strong Norton-Beer apodisation compared to a band with no apodisation (Perkin-Elmer 1985).

For this error analysis and the instrument comparisons, the gas $CHClF_2$, HCFC22, was used as it has low moments of inertia, and hence relatively widely spaced rotational structure, which may contribute to area discrepancies. Thus if the errors are small with HCFC22, they can be expected to be smaller with the haloethanes. Table 3.3 shows the differences in the absorbance when different apodisation routines are used.

Table 3.3. Comparison of the effects of apodisation functions using HCFC22 data.

Apodisation	area under band in absorbance units x cm^{-1}.		
	1300-700cm^{-1}	1200-1050cm^{-1}	850-750cm^{-1}
None	52.03	33.20	10.66
Weak Norton-Beer	51.50	32.98	10.47
Strong Norton-Beer	51.38	32.79	10.42

The difference in the results between no apodisation and apodisation is larger than that between the two apodisation routines. However, since the differences between weak and strong Norton-Beer functions are in the order of 0.2% to 0.6%, it is necessary to name the apodisation function used when publishing the results. It cannot be judged which of the two functions is more 'correct' since the change in linewidth by one function may be equivalent to a change in band range or movement in baseline by a different function, therefore, discrepancies due to alternative functions are not included in the overall error.

Overall, band intensities were measured for the approximate atmospheric window regions of 1250-833cm^{-1} and 1300-700cm^{-1}. Band intensities were also measured for individual bands. For each compound analysed, a spectrum using the relevant mid-range pressure was studied, looking closely at the wings of each band. Points were selected on each side of the band, so that they included the wings of the band, but not the start of an adjacent band. If bands overlapped, then they were not separated , and one range was used to include both bands. Difficulties arose when trying to estimate the intensities due to individual fundamental bands, however, some estimations were made by examination of the spectra.

In order to measure the area under a band, a baseline must be selected to enclose the relevant area. There are several possible approaches to the selection of a baseline (Willis et al. 1987). For this work the baseline was chosen by selection of a point in the spectrum where no apparent absorption occurred. A horizontal line was then constructed through this point, enclosing an area between the specified band ranges as shown in figure 3.3. Where possible, the baseline point was selected close to the bands to be measured, however, where the absorbance at the limits of a band were significantly higher than the zero absorption line, the baseline point was selected at any position within the range of the spectrum where the absorbance was close to zero. By close inspection of high resolution spectra, it was seen that the magnitude of absorbance at the selected baseline point for repeated recording of the same spectra varied by a maximum of ±0.5%.

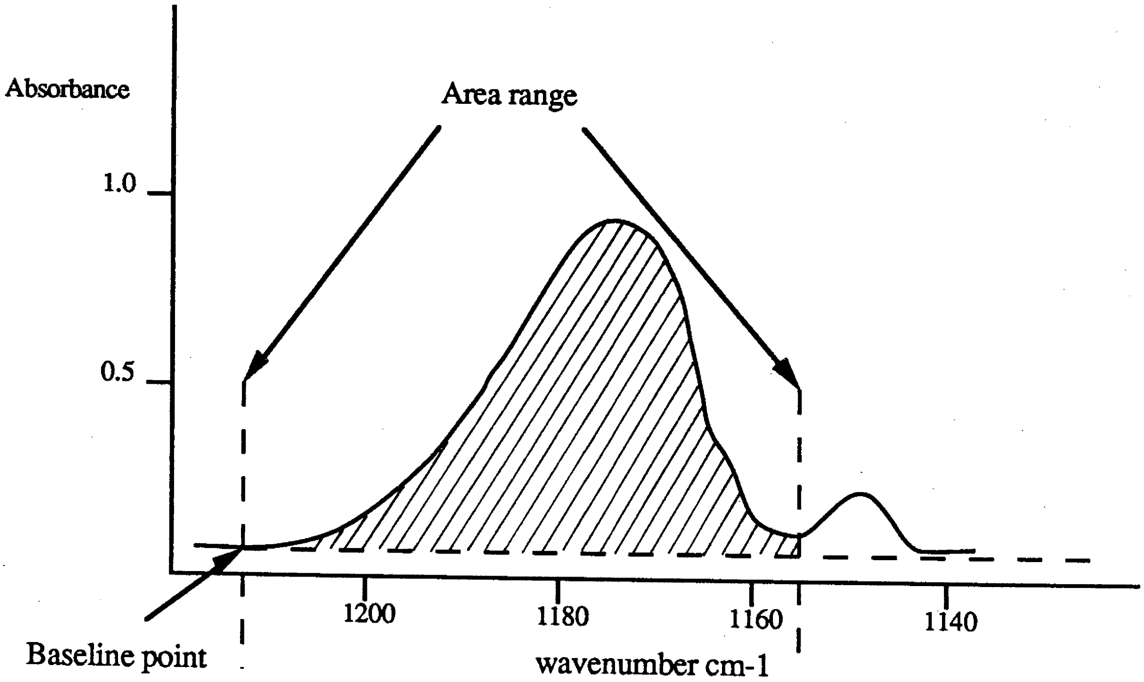


Figure. 3.3. Measurement of area under a band.

Due to instrumental 'drift' reported by Perkin-Elmer (1985) near the 3500cm^{-1} end of the spectrum where the absorbance line sometimes tended to go below zero for no known reason, the baseline point was usually restricted to the region between 2000 and 500cm^{-1}. For very weak bands in the region 3500 to 2800cm^{-1}, where bands due to C-H stretches occur, it sometimes became necessary to draw a baseline between the points of the range limits, to avoid errors due to the instrumental 'drift'. No satisfactory explanation for the random instrumental 'drift' was obtained from Perkin-Elmer or from this work, however it was usually very small.

3.3. Comparison of results between different instruments.

A series of spectra for HCFC22 at several different pressures was recorded using a P-E 1600, a P-E 1800 and a Bio-Rad F60 instrument. Table 3.4 shows the results with the percentage deviation from the overall average band intensity for the compound. It can be seen that the deviations are small, and are not dependent on the resolution or the manufacturer. The maximum deviation, taking into consideration all band intensities for all instruments and resolutions, is that between the band intensity of the 1200-1050cm^{-1} band taken on the P-E 1800 at 0.2cm^{-1} resolution, and the same band on the Bio-rad F60 at 0.1cm^{-1} where the gap is 3.8%.

Table 3.4. Average band intensities in cm^{-2}atm^{-1} from all three FTIR spectrophotometers used.

Band range cm^{-1}	P-E 1600 res. 2.0cm^{-1}	P-E 1800 res. 0.2cm^{-1}	Bio-Rad res. 2.0 cm^{-1}	Bio-Rad res. 0.2cm^{-1}	Overall average
1300-700	2695 +0.2%	2697 +0.3%	2690 0.0%	2677 -0.5%	2690
1200-1050	1737 -0.3%	1717 -1.5%	1731 -0.6%	1783 +2.3%	1742
850-750	560 -1.6%	573 +0.7%	568 -0.2%	575 +1.0%	569

When the band is very wide, as in the case of the 1300-700cm^{-1} band, the differences are considerably smaller. Two out of the three sets of results for the spectra taken for 2.0cm^{-1} resolution fall between those of the spectra at higher resolution, suggesting that the discrepancies are not due to problems with rotational fine structure contributing to area errors. It is not possible to determine which instrument is 'right' and which is 'wrong', so as with the apodisation function, it becomes necessary to name the instrument used when reporting results.

3.4. Experimental procedure for measuring band intensities.

When all possible sources of errors are considered, the most significant errors arise from the pressure measurements. When attempting to reproduce reported band intensities, some differences in results may occur which cannot be quantified and it becomes important to specify several experimental constraints when presenting results. From the experiments carried out as detailed in this chapter, the instrument type, the apodisation routine, the band limits, the baseline point and the purity of the compound should be reported with the results. For this work, the error range is considered to be in the order of ±4% for a P-E 1600 with 2.0cm^{-1} resolution, weak Norton-Beer apodisation and the range limits, baseline points and purity specified for each compound in chapter four.

Having examined each error as far as possible, the following list is a set of procedures which was followed for the measurement of band intensities .

1. Cell and cell windows were cleaned prior to recording the background spectra for a new compound. The cell windows were not removed until all data for that compound had been collected.
2. All spectra, where possible were recorded using pressures of between 10 and 100torr.
3. A suitable pressure range for linear absorbance and band smoothing was determined for each compound.
4. All spectra were taken at room temperature.
5. Spectra with unexpected peaks or large discrepancies in areas suggesting contamination were discarded.
6. The sample compartment was purged with dry nitrogen gas.
7. The sample cell was always placed in the same position in the compartment.
8. A background spectrum was taken using the evacuated cell before starting measurements for a new compound.
9. The P-E 1600 at 2.0cm^{-1} resolution with weak Norton-Beer apodisation was used throughout.
10. Band ranges and a single baseline point for the construction of a horizontal baseline were selected for each compound and used for all spectral measurements.

Chapter 4.

Integrated absorption intensities of selected halocarbons.

The integrated absorption intensities, or band intensities (BI), have been measured for twenty-five of the compounds selected. The method used, results and discussion are reported in this chapter. Values of BI for the atmospheric window are given, as well as values for smaller and less well defined regions of the mid-infrared spectrum.

4.1. Experimental methods.

Taking care to adhere to the procedures listed in section 3.4, the following method was used for each substance. The cell described in section 3.1.1. was evacuated using a vacuum line fitted with both a rotary and a diffusion pump. The vacuum attained was at a pressure of less than 10^{-4}torr, which is adequate for these experiments. A background spectrum was recorded with the evacuated cell in the purged compartment of the spectrophotometer. This spectrum was stored on disk for later use. The cell was then removed from the instrument and filled with the selected vapour at a pressure fulfilling the requirements of pressure given in section 3.1.2. Using the background spectrum just saved, the new spectrum was recorded and ratioed to the background spectrum to give a spectrum of the vapour alone. Using ranges and a baseline point appropriate for the compound, areas under the spectral bands were calculated. The cell was then evacuated and refilled with the same vapour at a different pressure and a new spectrum recorded. This process was repeated at least 10 times for each compound so that data for a range of pressures were obtained. The length of cell and the ranges of pressures used for each compound are given in table 4.1. The purity of the substance given by the manufacturer is also listed in table 4.1.

4.2 Band intensity results.

Table 4.2 shows the average band intensities for selected regions of the spectra. Literature values for some of the compounds are shown for comparison.

Table 4.1. Cell size, pressure ranges and purity for all halocarbons used.

Halocarbon	Cells used (cm)	Pressure (torr)	Mol. wt.	Purity	B.pt. (°C)
CFC111	10.429	4-9	220.3	97%	137-138
CFC112	10.429	7-12	203.8	97%	92.8
CFC112a	10.429	4-9	203.8	97%	91.5
CFC113	10.318	4-25	187.4	99.9% †	47-48 †
CFC113a	10.318,3.245	3-32	187.4	99% †	46 †
CFC114	10.429, 3.415	7-13	170.9	99% †	3.8 †
CFC114a	10.429,3.415	8-15	170.9	97%	3
CFC115	10.429,3.415	4-15	154.5	98% †	-39 †
FC116	10.429,3.415	3-15	138.0	99%	-78.1
HFC161	10.429,3.415	20-96	48.1	97%	-37.1
HFC152a	3.415	15-31	66.1	98% †	-25 †
HFC143	10.429,3.415	13-21	84.0	99%	5
HFC143a	3.415	10-20	84.0	99%	-47
HFC134	10.429,3.415	7-18	102.0	99%	-19.7
HFC134a	3.415	20-29	102.0	99%	-26.5
HFC125	3.415	12-21	120.0	98%	-48.5
HCFC141b	3.415	25-55	117.0	97%	32
HCFC142b	3.415	14-36	100.5	98% †	-10 †
HCFC123	3.415	18-36	152.9	99% †	28.7 †
HCFC124	3.415	18-36	136.5	98%	-12
HCFC244ca	10.429, 3.415	5-30	150.5		liquid
HCFC235cb	10.429, 3.415	8-30	168.5		liquid
HCFC225ca	10.429, 3.415	7-15	202.9	88%	51.1
HCFC225cb	10.429, 3.415	7-15	202.9	95%	56.1
FC218	3.415	7-15	188.0	98%	-39

Purity and boiling point data from PCR catalogue 1992, except for those marked † which came from Aldrich Chemical catalogue 1992.

Table 4.2. Absolute integrated absorption intensities (cm^{-2} atm^{-1}) of the regions 1250-833cm^{-1} and 1300-700cm^{-1}. Total refers to the range 3500 - 450 cm^{-1}.

		total	1250-833	1300-700	(a)	(b)	(c)
CFC111	CCl_3CCl_2F	2015	926	1946			
CFC112	CCl_2FCCl_2F	2708	1975	2579			
CFC112a	CCl_3CClF_2	2622	2053	2639			
CFC113	CCl_2FCClF_2	3402	2616	3289	3401	3126	3507*
CFC113a	CCl_3CF_3	3177	2514	3143			
CFC114	$CClF_2CClF_2$	3979	3577	3836	4141		3937*
CFC114a	CCl_2FCF_3	3803	3107	3707			
CFC115	$CClF_2CF_3$	4588	3867	4190	4678		
FC116	CF_3CF_3	5049	2640	4965			5327
HFC161	CH_3CH_2F	1064	507	510			
HFC152a	CH_3CHF_2	1746	1392	1398	1648		1719
HFC143	CH_2FCHF_2	2043	1557	1591			
HFC143a	CH_3CF_3	3210	2252	2750		3401	
HFC134	CHF_2CHF_2	2802	2343	2400			
HFC134a	CH_2FCF_3	3481	2010	2703	3272	3169	3261
HFC125	CHF_2CF_3	4224	3159	3522		3908	
HCFC141b	CH_3CCl_2F	1941	1199	1761	1912	1732	
HCFC142b	CH_3CClF_2	2717	2261	2281	2577	2474	2643
HCFC123	$CHCl_2CF_3$	3145	2026	2745	2859	2552	3160
HCFC124	$CHClFCF_3$	3641	2469	3171		4043	
HCFC244ca	$CHF_2CF_2CH_2Cl$	2788	2011	2218			
HCFC235cb	$CF_3CF_2CH_2Cl$	3893	2846	3446			
HCFC225ca	$CF_3CF_2CHCl_2$	4379	3122	3824			
HCFC225cb	CF_2ClCF_2CFHCl	4196	3027	3710			
FC218	$CF_3CF_2CF_3$	5887	2330	5460			

(a) H.Magid. Personal comm. reported in Fisher et al. (1990 b) range 1535-440cm^{-1}.
(b) D.G.Gehring. Personal comm. reported in Fisher et al. (1990 b) range undefined.
(c) Cappellani & Restelli (1992) range 1500-600 cm^{-1} ; otherwise * Varanasi & Chudamani (1988) range 1300-700 cm^{-1}.

For each halocarbon, individual band intensities were calculated from the area under selected spectral bands. Using data obtained for at least 10 spectra, the average band intensity was calculated for each band within a compound.

For each band, the range of wavenumbers in cm^{-1}, the position of maximum absorbance in cm^{-1}, the position of the point in cm^{-1} through which the baseline was drawn, and the average band intensity are presented in tables 4.3 to 4.27, one table for each of the twenty-five halocarbons investigated. The average band intensity for each spectral band was calculated using the series of intensity results measured for each band for each compound. The maximum percentage variation from the average band intensity is given in the tables, along with the standard deviation to show the spread of the individual results. A typical spectrum for each compound is given in figures 4.1 to 4.25 corresponding to the tables 4.3 to 4.27.

4.3 Discussion.

Band intensity values for the total range (3500-450cm^{-1}) given in table 4.2 have larger errors associated with them than the results for the two smaller regions shown, since baseline errors become relatively more significant over wide ranges where no absorbance occurs (Olliff & Fischer 1994). It can be seen from table 4.2 that in some cases there are considerable differences between the band intensities of the region 1250-833cm^{-1} and the region 1300-700cm^{-1}. This is of interest when calculating global warming potentials, as different research groups use different window regions. For example, the results reported by Fisher et al (1990 b) covered the region 1535-440cm^{-1}, Cappellani & Restelli (1992) covered the region 1500-600cm^{-1}, and Varanasi & Chudamani (1988) covered the region 1300-700cm^{-1}, although Dickinson and Cicerone (1986) defined the atmospheric window as being 1250-833cm^{-1}. These results are given in table 4.2 for comparison with the results from this work, however direct comparisons are not possible, since all the criteria relating to band intensity measurements, as detailed in chapter three, were not given in the literature.

Tables 4.3-4.27 list the band intensities for individual bands for each compound. It was sometimes difficult to identify individual bands due to overlapping areas. Results are presented for each range selected, and also for a group of bands (indicated by '*' in the tables) adjacent to each other where the separation of individual bands was considered to be somewhat arbitrary. The position of maximum absorbance recorded on the spectrum for each band is not always the band centre, due to the problem of overlapping bands or the absence of a Q branch. However, the wavenumbers of these positions are given in the tables as a means of identifying the bands. The band intensity is the average value for 10 or more recorded spectra for each compound. Of these 10 values, the maximum percentage deviation from the average is given in both the positive and negative directions. In most cases it can be seen that the deviations are well within the predicted error range of ±4%, however, occasionally large errors occurred in individual results. In order to show that these large errors were infrequent, the standard deviation has also been reported, in the same units as the band intensities, to show the spread around the average of the majority of the results.

In some cases, for individual band intensities, it was observed that absorbance by one band was less than the average while absorbance by an adjacent band was more. This situation was reversed in another spectrum for the same compound, suggesting that the absorbance appears to vary by some small amount independent of the concentration of the substance. For example, in the case of CFC114a, the adjacent bands 1355-1266cm^{-1} and 1266-1206cm^{-1} were respectively 450.5 and 1375.3cm^{-2}atm^{-1} at one pressure, and 464.8 and 1362.4cm^{-2}atm^{-1} respectively for another pressure. When grouping these bands for the region 1355-1206cm^{-1}, the resultant band intensities were 1825.8 and 1827.2cm^{-2}atm^{-1} respectively, much closer to each other than the individual values. There seems to be no obvious explanation for this phenomenon, however, the problem could arise in part from inaccuracies introduced into the areas under individual bands by separating them at a point where the absorbance is not close to zero, as is the case for the CFC114a bands previously discussed.

The 'true' area under the band is not calculated since the exact band shape is not known. Figure 4.26 (a) gives an example of areas calculated for two overlapping bands. Figure 4.26 (b) illustrates areas which may be considered to be closer to the 'true' areas, however, these areas are difficult to measure. As can be seen from figure 4.26, a small amount of area is lost by the truncation at the range limit, and a small amount is gained, since the absorbance at the range limit between the two bands is greater than for either of the individual bands. Using the same compound at a different pressure, changes in these losses and gains may contribute to area discrepancies. When the bands are measured as a group, errors associated with the individual bands are reduced since the total area is the same as that obtained from adding area 1 to area 2. For bands of more complex shapes, it becomes even more difficult to decide on the magnitude of the wings of overlapping bands, making the determination of absolute band intensities of individual bands impracticable. However, satisfactory results for band intensities may be reported, provided that the method used for area calculation is specified.

Table 4.3. Band intensities for CFC111, pentachlorofluoroethane.

Band range (* group) cm^{-1}	Position of max. abs. cm^{-1}	Waveno. of baseline point cm^{-1}	Band Intensity $cm^{-2}atm^{-1}$	Max. % variation from average band intensity	Standard deviation $cm^{-2}atm^{-1}$
1155-1088	1114	700	287	±2.5	3.59
1057-980	1018	700	105	-1.4, +1.7	0.88
940-870	911	700	187	-1.7, +1.9	1.76
870-834	856	700	336	-2.8, +3.8	6.28
834-762	810	700	706	-2.4, +2.7	8.81
762-700	731	700	316	-1.6, +2.1	3.44
* 940-700	810	700	1545	-2.3, +2.7	18.90

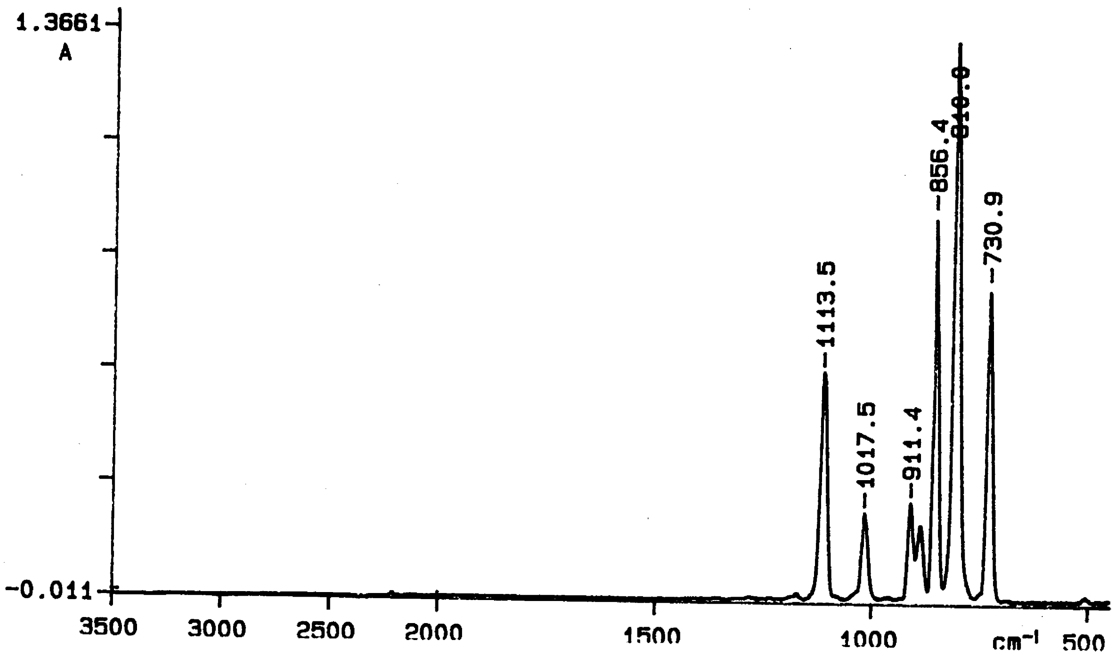


Figure 4.1. Infrared spectrum of CFC111, using 6.3torr and a 10cm cell.

Table 4.4. Band intensities for CFC112, 1,1,2,2-tetrachlorodifluoroethane.

Band range (* group) cm^{-1}	Position of max. abs. cm^{-1}	Waveno. of baseline point cm^{-1}	Band Intensity cm^{-2}atm^{-1}	Max. % variation from average band intensity	Standard deviation cm^{-2}atm^{-1}
1225-1063	1121	680	678	-1.4, +1.0	5.72
1063-995	1032	680	207	-2.9, +1.7	2.38
* 1225-995	1121	680	885	-1.8, +1.2	7.60
973-810	844	680	1160	-2.0, +1.4	11.92
810-725	788	680	579	-2.0, +1.5	6.20
* 973-725	788	680	1739	-2.0, +1.4	18.11
645-612	627	680	4.7	-12.3, +12.5	0.38
498-463	484	680	10.5	-13.2, +9.9	0.60

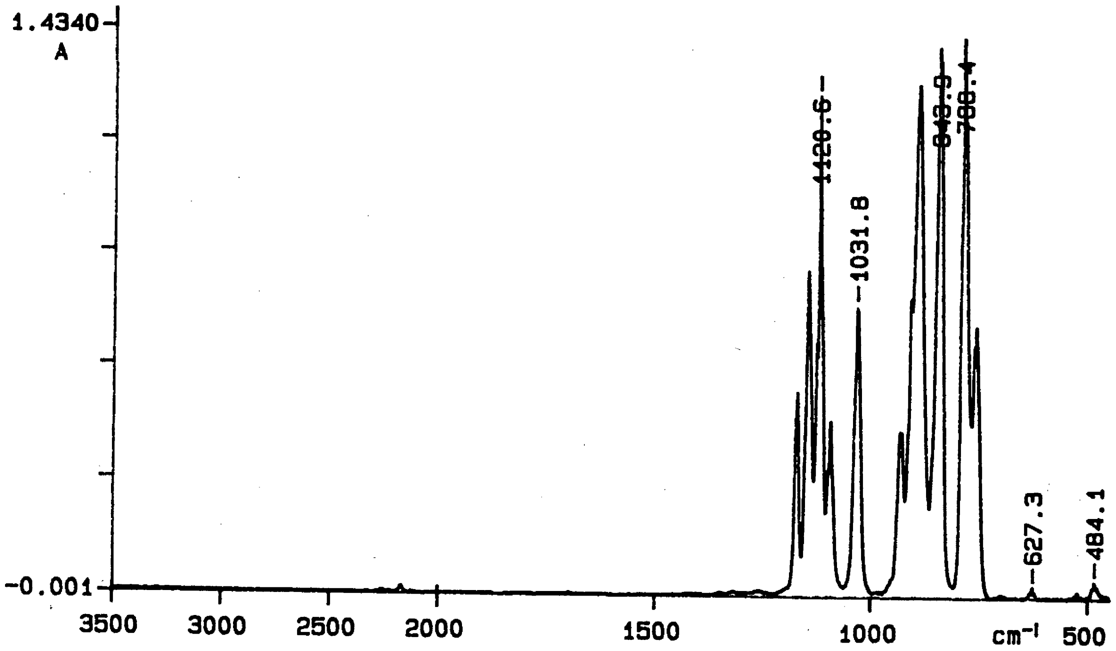


Figure 4.2. Infrared spectrum of CFC112, using 11.0torr and a 10cm cell.

Table 4.5. Band intensities of CFC112a, 1,1,1,2-tetrachlorodifluoroethane.

Band range (* group) cm^{-1}	Position of max. abs. cm^{-1}	Waveno. of baseline point cm^{-1}	Band Intensity cm^{-2}atm^{-1}	Max. % variation from average band intensity	Standard deviation cm^{-2}atm^{-1}
1215-1150	1171	700	821	-2.4, +1.0	6.87
1056-985	1036	700	446	-3.0, +0.7	4.12
922-812	856	700	718	-2.8, +0.9	6.82
812-723	783	700	575	-3.1, +0.8	5.66
* 922-723	856	700	1293	-2.9, +0.9	12.45
650-610	627	700	37.5	-4.1, +2.4	0.77

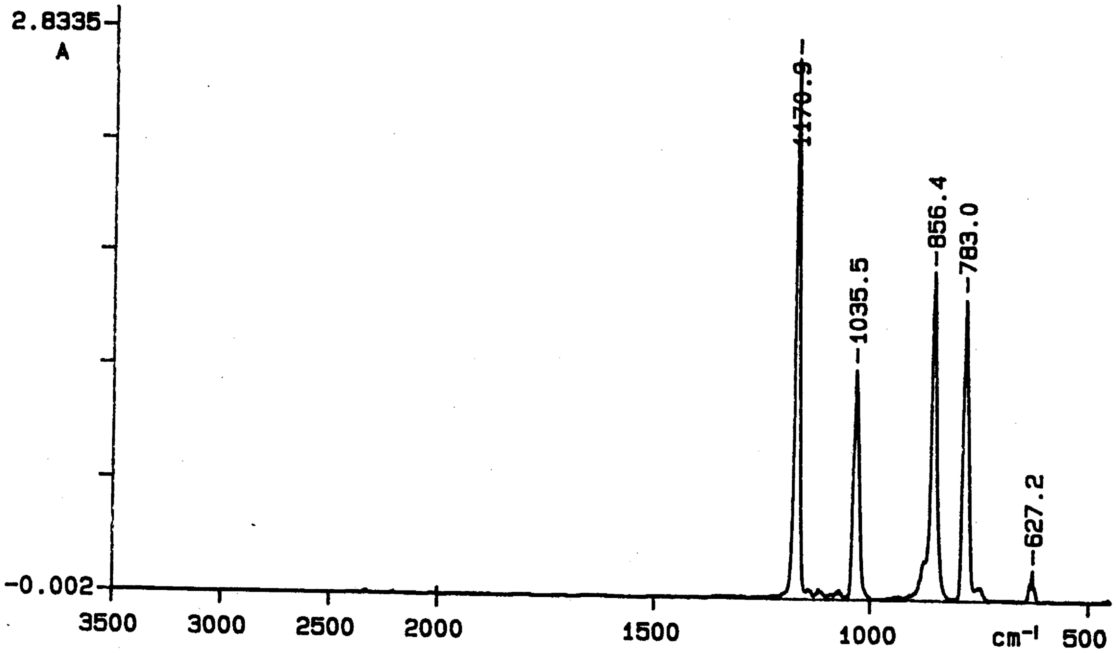


Figure 4.3. An infrared spectrum of CFC112a using 6.8torr and a 10cm cell.

Table 4.6. Band intensities of CFC113, 1,1,2-trichlorotrifluoroethane.

Band range (* group) cm^{-1}	Position of max. abs. cm^{-1}	Band Intensity $cm^{-2}atm^{-1}$	Linear regression for areas from individual spectra (1.0 for exact fit)
1237-1138	1180	841	0.999
1138-1078	1118	486	0.999
1078-997	1042	461	0.998
* 1237-997	1118		
954-847	910	765	0.999
846-765	816	665	0.999
* 954-765	816		

Results taken from Olliff and Fischer.

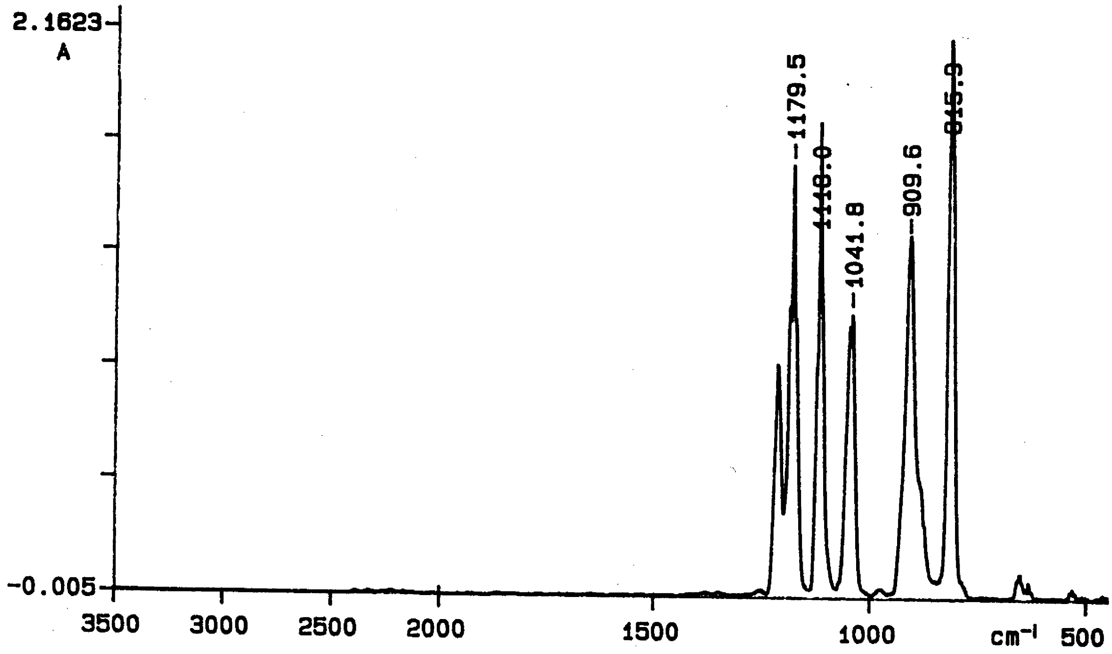


Figure 4.4. Infrared spectrum of CFC113 using 9.7torr and a 10cm cell.

Table 4.7. Band intensities of CFC113a, 1,1,1-trichlorotrifluoroethane.

Band range (* group) cm^{-1}	Position of max. abs. cm^{-1}	Band Intensity $cm^{-2}atm^{-1}$	Linear regression for areas from individual spectra (1.0 for exact fit.)
1290-1238	1256	727	0.996
1238-1200	1225	1278	0.998
* 1290-1200	1225	2005	
945-880	909	134	0.999
880-825	858	873	0.997
* 945-825	858	1007	
750-690	713	126	0.997
590-525	561	39	0.999

Results taken from Olliff and Fischer 1992.

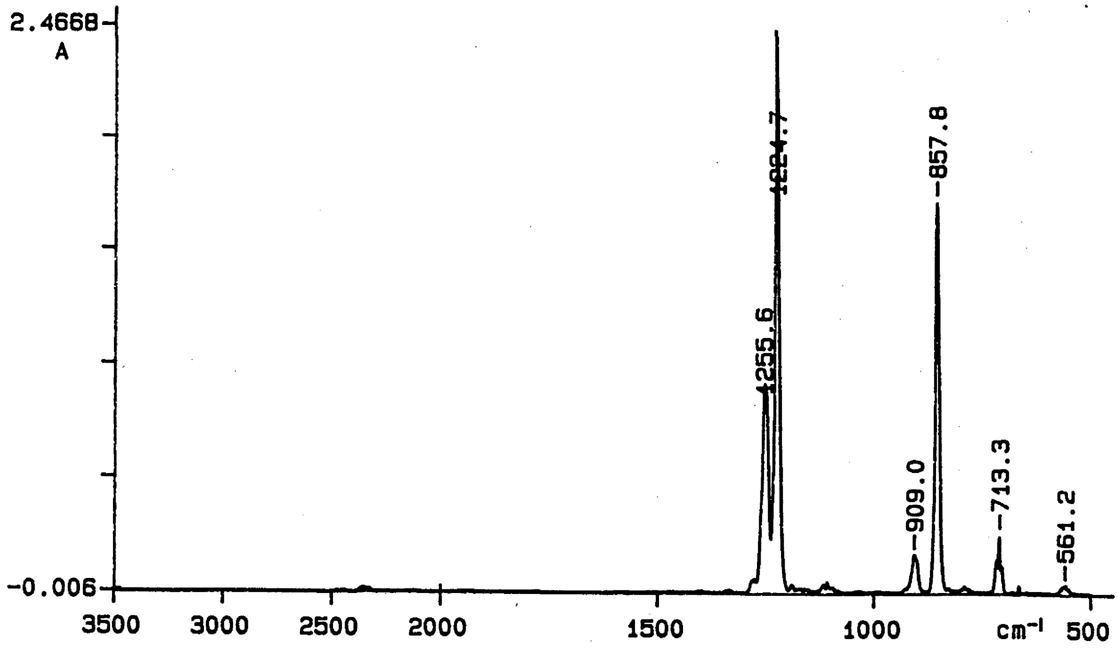


Figure 4.5. Infrared spectrum of CFC113a using 16.8torr and a 3cm cell.

Table 4.8. Band intensities of CFC114, 1,2-dichlorotetrafluoroethane.

Band range (* group) cm^{-1}	Position of max. abs. cm^{-1}	Waveno. of baseline point cm^{-1}	Band Intensity cm^{-2}atm^{-1}	Max. % variation from average band intensity	Standard deviation cm^{-2}atm^{-1}
1312-1253	1271	700	191	-4.6, +2.5	3.83
1253-1216	1231	700	138	-1.8, +1.2	1.08
1216-1079	1185	700	1847	-3.1, +2.2	26.54
1079-1019	1052	700	546	-3.7, +2.0	8.47
* 1312-1019	1185	700	2722	-3.1, +2.1	39.02
972-902	922	700	437	-2.3, +1.7	5.49
902-862	887	700	151	-3.1, +2.3	2.34
862-820	847	700	479	-4.3, +2.0	8.40
* 972-820	847	700	1067	-3.3, +1.9	16.06
758-713	735	700	16.0	-15.6, +10.4	1.16
698-653	678	700	16.7	-4.2, +6.0	0.53
636-586	616	700	44.6	-5.9, +3.6	1.11

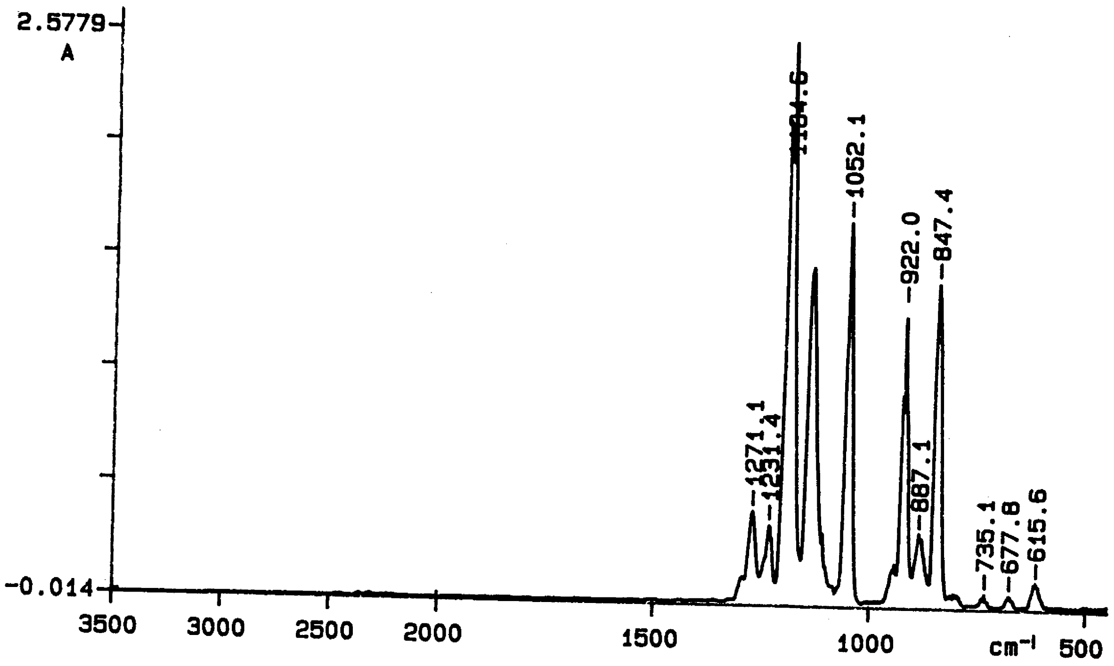


Figure 4.6. Infrared spectrum of CFC114 using.9.5torr and a 10 cm cell.

Table 4.9. Band intensities of CFC114a, 1,1-dichlorotetrafluoroethane.

Band range (* group) cm^{-1}	Position of max. abs. cm^{-1}	Waveno. of baseline point cm^{-1}	Band Intensity cm^{-2}atm^{-1}	Max. % variation from average band intensity	Standard deviation cm^{-2}atm^{-1}
1355-1266	1294	700	456	-3.2, +2.5	9.03
1266-1206	1232	700	1354	-5.6, +4.7	48.15
1206-1160	1195	700	124	-8.7, +3.0	4.18
1160-1070	1110	700	483	-5.0, +1.4	9.09
1070-1024	1052	700	57.4	-13.6, +13.0	4.64
* 1355-1024	1232	700	2474	-4.1, +3.1	60.95
955-861	920	700	1100	-3.7, +2.5	22.26
861-822	847	700	51.5	-11.8, +9.0	3.04
* 955-822	920	700	1152	-3.1, +2.2	21.42
756-713	735	700	128	-3.6, +1.2	1.71
603-575	589	700	12.2	-5.0, +4.1	0.28
575-543	560	700	16.7	-5.7, +3.5	0.46
* 603-543	560	700	28.9	-5.4, +3.8	0.72

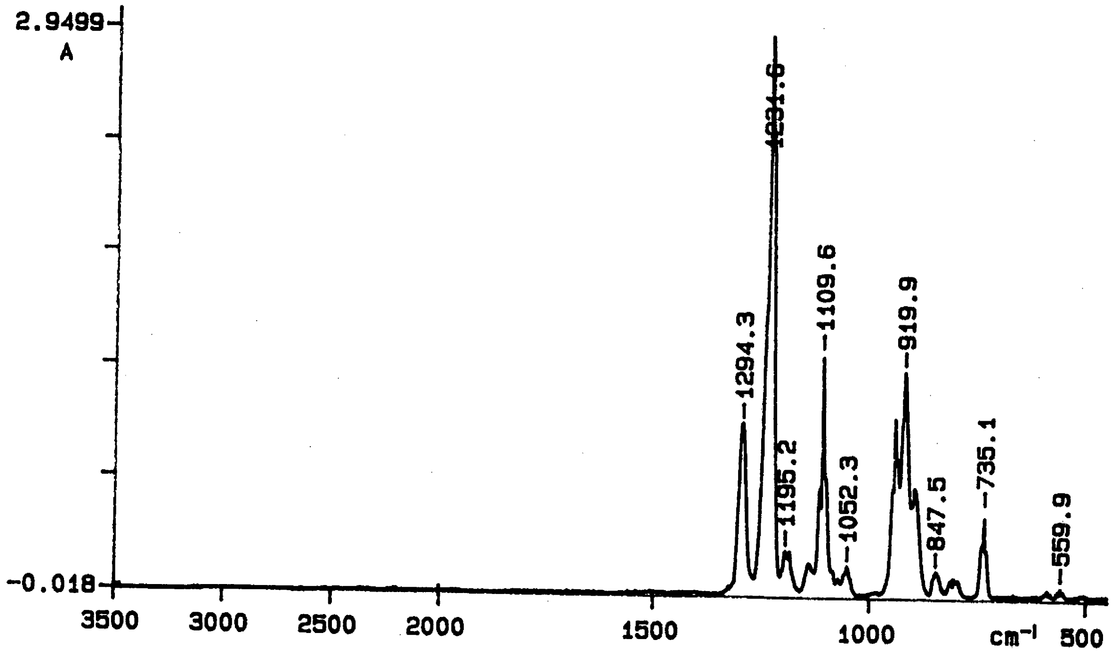


Figure 4.7. Infrared spectrum of CFC114a using 7.9torr and a 10cm cell.

Table 4.10. Band intensities of CFC115, chloropentafluoroethane.

Band range (* groups) cm^{-1}	Position of max. abs. cm^{-1}	Waveno. of baseline point cm^{-1}	Band Intensity $cm^{-2}atm^{-1}$	Max. % variation from average band intensity	Standard deviation $cm^{-2}atm^{-1}$
1378-1314	1349	700	220	-5.4, +6.0	7.76
1273-1211	1239	700	1851	-4.7, +1.7	32.11
1211-1156	1184	700	497	-3.3, +4.1	11.66
1156-1066	1131	700	744	-2.0, +2.5	9.57
* 1273-1066	1239	700	3093	-1.6, +1.3	32.70
1025-931	982	700	891	-4.2, +4.1	23.46
781-738	762	700	96.7	-4.2, +4.7	2.45
666-628	647	700	43.3	-7.1, +6.0	1.72
580-538	560	700	16.8	-5.8, +5.9	0.63

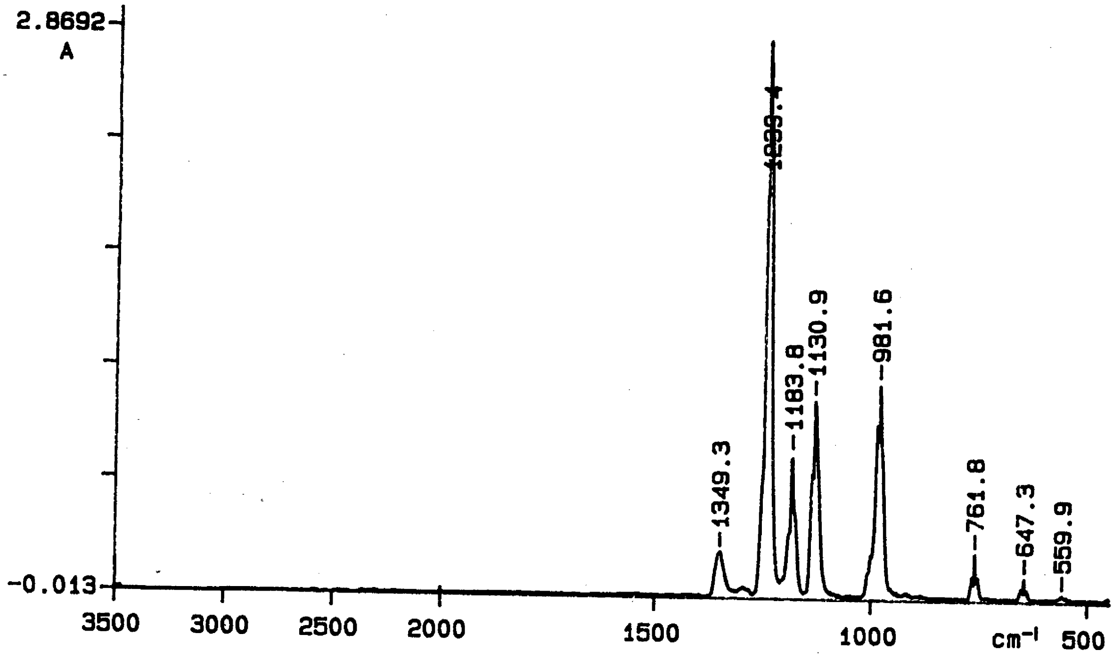


Figure 4.8. Infrared spectrum of CFC115 using 4.3torr and a 10cm cell.

Table 4.11. Band intensities of FC116, hexafluoroethane.

Band range (* group) cm^{-1}	Position of max. abs. cm^{-1}	Waveno. of baseline point cm^{-1}	Band Intensity cm^{-2}atm^{-1}	Max. % variation from average band intensity	Standard deviation cm^{-2}atm^{-1}
1359-1295	1328	1070	91.4	-9.2, +9.2	5.64
1277-1222	1250	1070	3757	-4.8, +2.5	92.32
1220-1186	1206	1070	33.4	-15.9, +11.4	3.28
* 1277-1186	1250	1070	3790	-4.6, +2.5	91.19
1157-1134	1139	1070	41.5	-7.4, +7.5	1.99
1134-1084	1115	1070	1011	-3.6, +1.5	14.75
* 1157-1084	1115	1070	1053	-3.7, +1.5	15.91
737-692	714	1070	130	-5.4, +2.7	3.21
542-495	519	1070	29.3	-11.0, +11.1	2.41

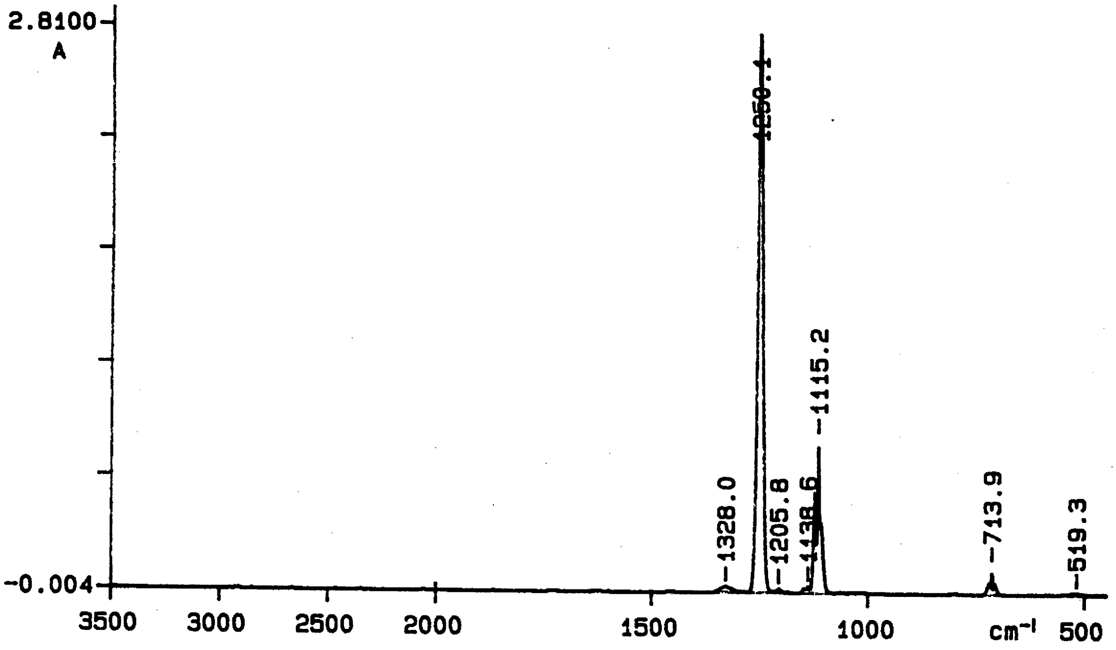


Figure 4.9. Infrared spectrum of FC116 using 5.2torr and a 3cm cell.

Table 4.12. Band intensities of HFC161, fluoroethane.

Band range (* group) cm^{-1}	Position of max. abs. cm^{-1}	Waveno. of baseline point cm^{-1}	Band Intensity $cm^{-2}atm^{-1}$	Max. % variation from average band intensity	Standard deviation $cm^{-2}atm^{-1}$
3080-2820	2999	3500	437	-1.4, +3.5	7.59
1552-1433	1448	3500	25.5	-17.6, +9.3	2.20
1433-1343	1396	3500	89.7	-2.6, +2.2	1.26
* 1552-1343	1396	3500	115.2	-5.9, +3.8	3.40
1224-1110	1120	3500	73.3	-2.9, +2.0	1.10
1110-985	1061	3500	361	-1.1, +0.6	2.29
* 1224-985	1061	3500	434	-1.3, +0.9	3.20
930-825	880	3500	69.4	-3.0, +2.4	1.13

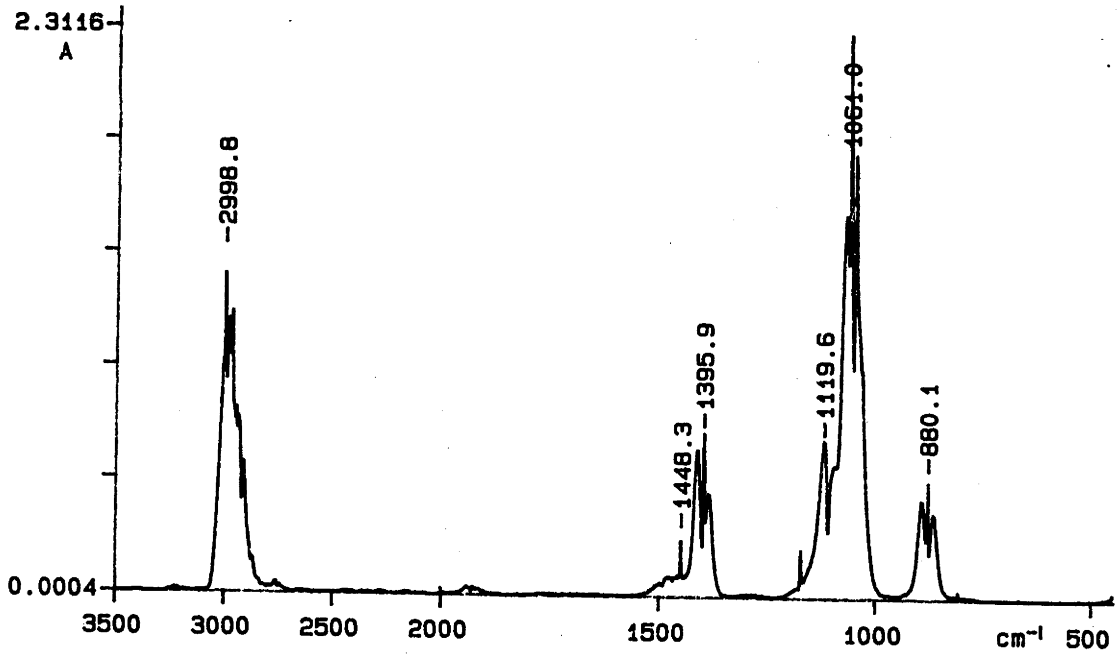


Figure 4.10. Infrared spectrum of HFC161 using 45.6torr and a 10cm cell.

Table 4.13. Band intensities of HFC152a, 1,1-difluoroethane.

Band range (* group) cm^{-1}	Position of max. abs. cm^{-1}	Waveno. of baseline point cm^{-1}	Band Intensity cm^{-2}atm^{-1}	Max. % variation from average band intensity	Standard deviation cm^{-2}atm^{-1}
3100-2910	2975	3100	195	-1.5, +2.0	1.95
1500-1300	1412	700	344	-2.0, +2.3	4.22
1210-1020	1139	700	1093	-1.6, +0.7	7.82
1005-900	943	700	261	-1.9, +1.5	2.37
900-830	868	700	33.8	-3.3, +6.6	0.99
* 1005-830	943	700	295	-2.0, +2.0	3.16
610-530	569	700	24.3	-6.6, +9.7	1.20
510-450	468	700	48.8	-2.7, +6.0	1.33

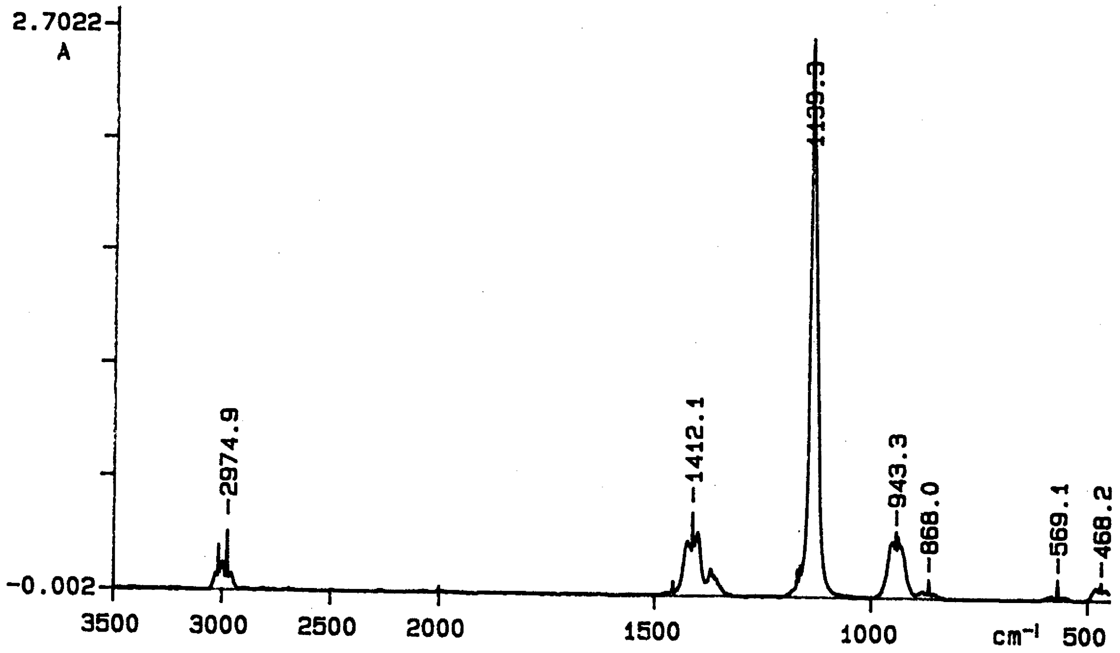


Figure 4.11. Infrared spectrum of HFC152a using 25.3torr and a 3cm cell.

Table 4.14. Band intensities of HFC143, 1,1,2-trifluoroethane.

Band range (* group) cm^{-1}	Position of max. abs. cm^{-1}	Waveno. of baseline point cm^{-1}	Band Intensity $cm^{-2}atm^{-1}$	Max. % variation from average band intensity	Standard deviation $cm^{-2}atm^{-1}$
3055-2866	3005	3055-2866	186	-0.5, +1.3	1.26
1503-1408	1433	800	70.1	-0.8, +1.0	0.38
1408-1345	1379	800	68.8	-1.0, +0.8	0.35
1345-1290	1319	800	41.8	-1.3, +1.5	0.35
1290-1214	1249	800	56.1	-1.3, +1.7	0.50
1214-1033	1107	800	1369	-1.5, +1.0	12.90
* 1503-1033	1107	800	1606	-1.3, +1.0	14.15
945-832	911	800	135	-1.1, +1.2	0.96
777-727	753	800	9.22	-1.9, +3.7	0.14
613-545	577	800	15.9	-2.1, +2.5	0.21
545-450	476	800	73.3	-1.5, +2.1	0.89
* 613-450	476	800	89.2	-1.5, +2.0	1.09

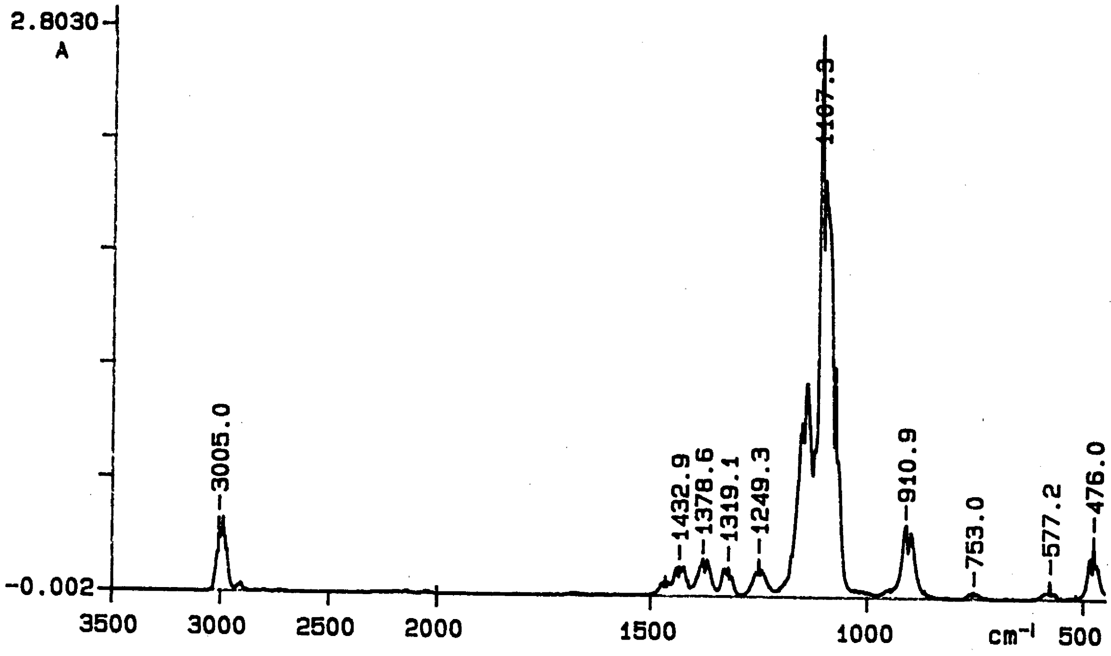


Figure 4.12. Infrared spectrum of HFC143 using 15.6torr and a 10cm cell.

Table 4.15. Band intensities of HFC143a, 1,1,1-trifluoroethane.

Band range (* group) cm^{-1}	Position of max. abs. cm^{-1}	Waveno. of baseline point cm^{-1}	Band Intensity cm^{-2}atm^{-1}	Max. % variation from average band intensity	Standard deviation cm^{-2}atm^{-1}
3068-2999	3034	3068-2999	27.7	-2.6, +4.0	0.53
1474-1319	1407	700	354	-4.7, +2.8	8.22
1319-1252	1280	700	488	-1.4, +0.8	3.52
1252-1113	1233	700	1837	-1.1, +1.0	12.27
* 1474-1113	1233	700	2679	-1.4, +1.2	21.95
1050-928	973	700	408	-1.6, +1.1	3.43
862-796	830	700	18.8	-9.1, +12.7	1.12
643-570	603	700	77.7	-3.6, +2.0	1.27

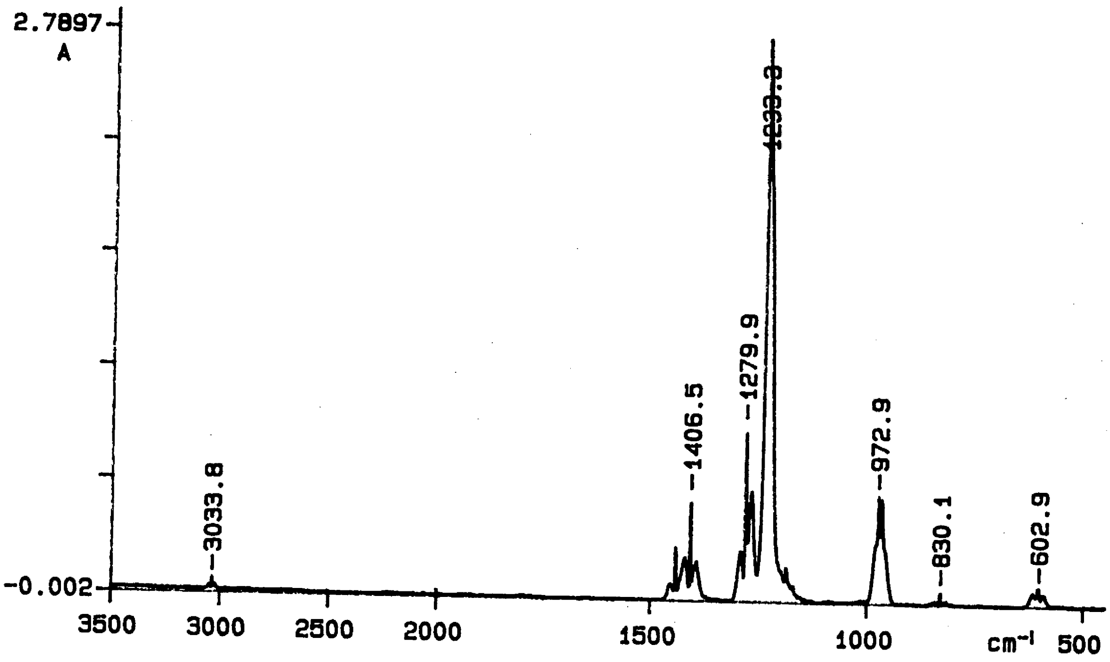


Figure 4.13. Infrared spectrum of HFC143a using 16.3torr and a 3cm cell.

Table 4.16. Band intensities of HFC134, 1,1,2,2-tetrafluoroethane.

Band range (* group) cm^{-1}	Position of max. abs. cm^{-1}	Waveno. of baseline point cm^{-1}	Band Intensity cm^{-2}atm^{-1}	Max. % variation from average band intensity	Standard deviation cm^{-2}atm^{-1}
3059-2938	2995	3059-2938	128	-1.8, +1.2	1.64
1420-1369	1391	650	15.7	-10.1, +6.0	1.13
1369-1262	1309	650	175	-2.7, +1.8	3.43
* 1420-1262	1309	650	191	-3.3, +2.2	4.56
1257-1180	1205	650	124	-2.4, +1.7	2.20
1180-1089	1133	650	2145	-0.8, +0.5	12.11
* 1257-1089	1133	650	2269	-0.9, +0.6	14.30
938-873	905	650	21.6	-3.6, +4.4	0.75
802-738	779	650	35.7	-3.0, +3.9	1.06
570-505	541	650	41.6	-2.4, +2.6	0.86

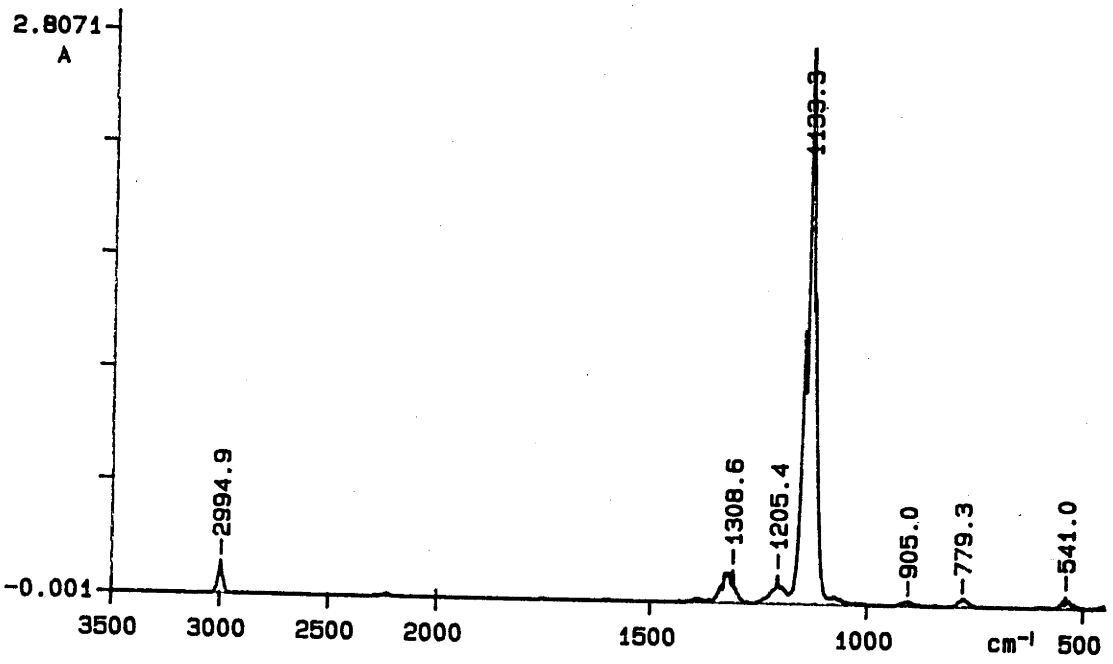


Figure 4.14. Infrared spectrum of HFC134 using 15.8torr and a 3cm cell.

Table 4.17. Band intensities of HFC134a, 1,1,1,2-tetrafluoroethane.

Band range (* group) cm^{-1}	Position of max. abs. cm^{-1}	Waveno. of baseline point cm^{-1}	Band Intensity cm^{-2}atm^{-1}	Max. % variation from average band intensity	Standard deviation cm^{-2}atm^{-1}
3100-2750	2984	3100	80.4	-6.1, +6.7	4.20
1490-1447	1464	720	34.1	-2.1, +1.7	0.40
1447-1397	1428	720	79.8	-1.6, +0.6	0.52
* 1490-1397	1428	720	114	-1.8, +0.9	0.87
1344-1243	1301	720	1030	-1.6, +0.9	7.50
1243-1133	1191	720	1366	-1.9, +1.0	12.63
1133-1027	1105	720	370	-2.2, +1.3	3.80
1027-920	973	720	220	-2.3, +1.3	2.28
* 1344-920	1191	720	2986	-1.8, +0.9	25.61
873-800	843	720	62.3	-3.7, +3.0	1.11
700-594	666	720	132	-3.0, +1.5	1.87
594-500	549	720	38.6	-4.1, +4.5	1.17

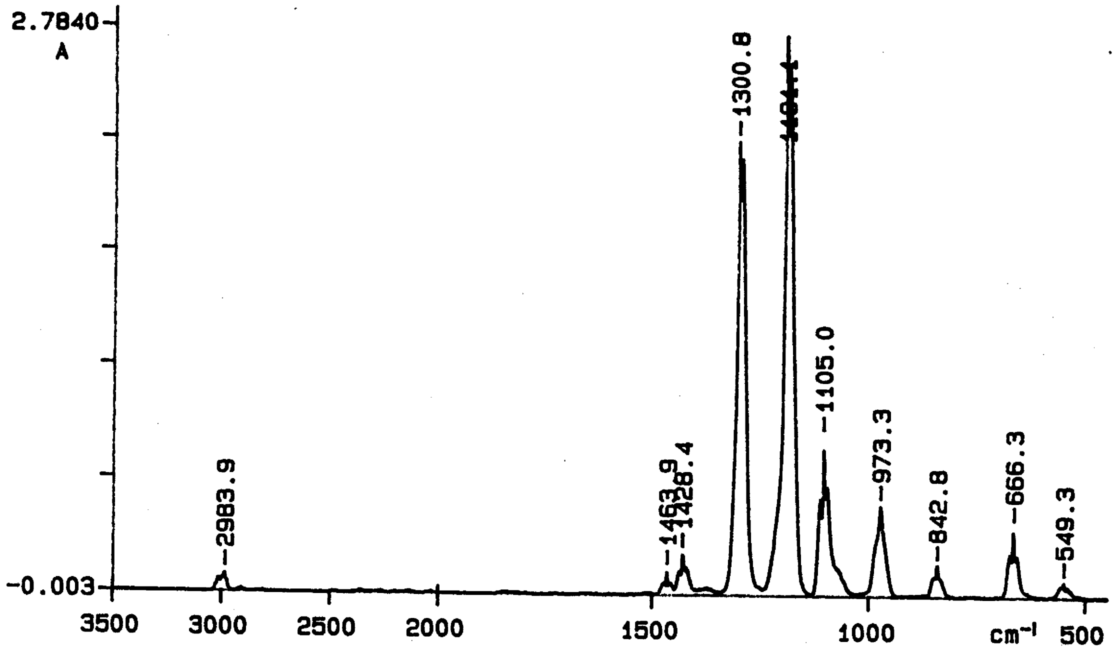


Figure 4.15. Infrared spectrum of HFC134a using 27.6torr and a 3cm cell.

Table 4.18. Band intensities of HFC125, pentafluoroethane.

Band range (* group) cm^{-1}	Position of max. abs. cm^{-1}	Waveno. of baseline point cm^{-1}	Band Intensity cm^{-2}atm^{-1}	Max. % variation from average band intensity	Standard deviation cm^{-2}atm^{-1}
3040-2960	3001	3040-2960	51.2	-2.5, +2.0	0.67
1476-1412	1444	650	14.7	-6.0, +5.4	0.55
1412-1337	1357	650	37.2	-4.2, +2.4	0.76
1337-1255	1308	650	588	-1.6, +1.4	5.69
1255-1171	1209	650	1981	-2.5, +0.8	18.76
1171-1051	1146	650	969	-2.1, +0.9	8.99
* 1476-1051	1209	650	3590	-2.2, +0.9	33.33
915-824	867	650	167	-1.8, +1.6	1.76
756-693	727	650	128	-2.2, +1.6	1.44
605-557	578	650	55.3	-1.7, +2.8	0.82
549-496	523	650	25.4	-4.0, +5.1	0.77

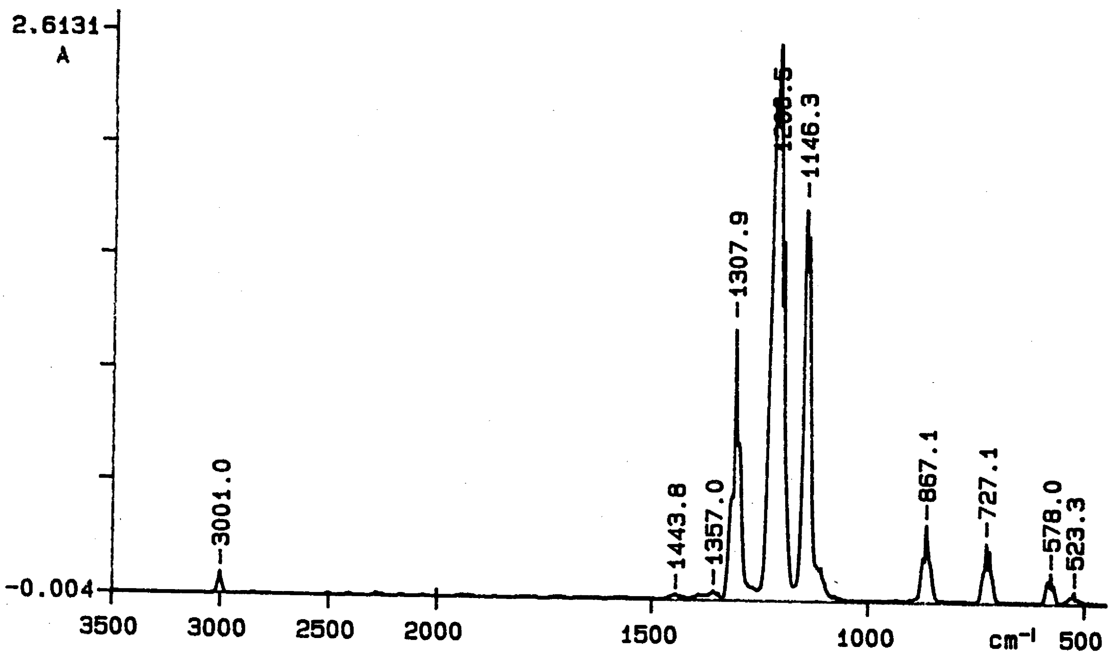


Figure 4.16. Infrared spectrum of HFC125 using 20.8torr and a 3cm cell.

Table 4.19. Band intensities of HCFC141b, 1,1-dichloro-1-fluoroethane.

Band range (* group) cm^{-1}	Position of max. abs. cm^{-1}	Waveno. of baseline point cm^{-1}	Band Intensity cm^{-2}atm^{-1}	Max. % variation from average band intensity	Standard deviation cm^{-2}atm^{-1}
3054-2985	3013	3054-2985	25.1	-2.1, +1.0	0.20
2985-2914	2954	2985-2914	8.19	-8.0, +3.4	0.27
* 3054-2914	3013	3054-2914	33.3	-1.8, +1.2	0.29
1475-1417	1445	650	18.5	-1.6, +2.0	0.20
1417-1359	1387	650	65.7	-0.7, +0.7	0.29
* 1475-1359	1387	650	84.2	-0.9, +1.0	0.45
1207-1137	1161	650	336	-0.5, +0.3	0.71
1137-1050	1102	650	575	-0.3, +0.2	1.07
* 1207-1050	1102	650	911	-0.3, +0.2	1.75
960-880	927	650	259	-0.5, +0.2	0.47
800-700	754	650	555	-0.7, +0.6	2.01
621-560	593	650	79.1	-0.8, +0.3	0.29

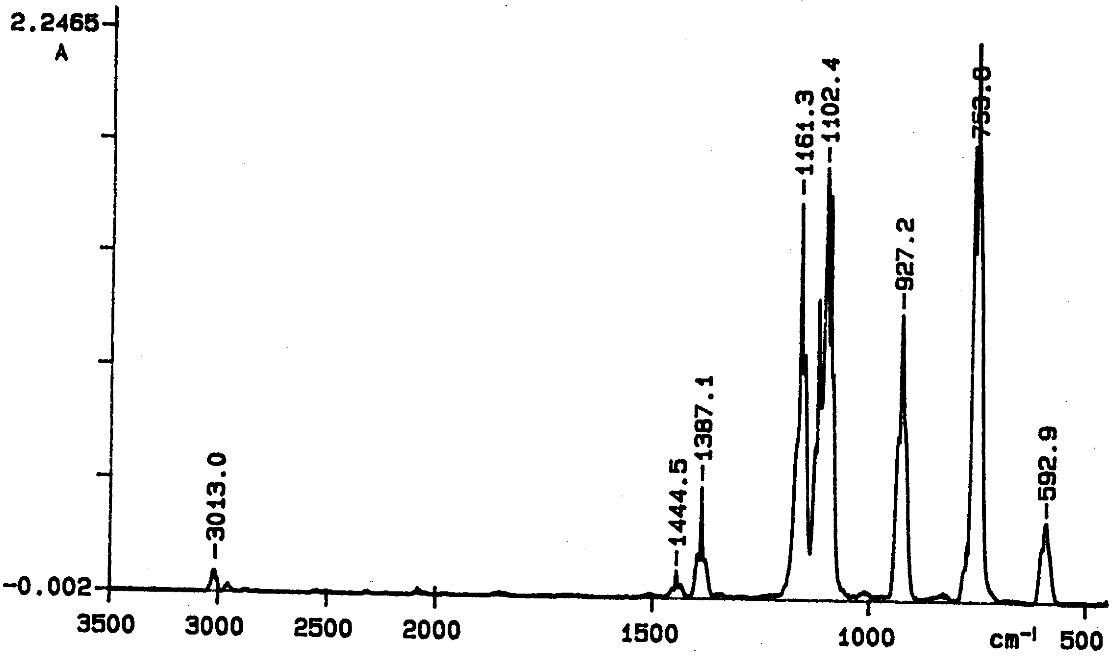


Figure 4.17. Infrared spectrum of HCFC141b using 47.9torr and a 3cm cell.

Table 4.20. Band intensities of HCFC142b, 1-chloro-1,1-difluoroethane.

Band range (* group) cm^{-1}	Position of max. abs. cm^{-1}	Waveno. of baseline point cm^{-1}	Band Intensity $cm^{-2}atm^{-1}$	Max. % variation from average band intensity	Standard deviation $cm^{-2}atm^{-1}$
3077-2991	3021	3077-2991	25.5	-2.6, +1.7	0.29
2991-2936	2961	2991-2936	6.22	-6.6, +2.9	0.17
* 3077-2936	3021	3077-2936	31.7	-2.0, +1.8	0.33
1474-1423	1447	600	19.5	-6.5, +7.1	0.72
1423-1356	1395	600	136	-0.6, +2.7	1.31
* 1474-1356	1395	600	156	-1.6, +3.0	1.93
1268-1159	1192	600	995	-1.3, +1.4	7.09
1159-1060	1134	600	671	-1.4, +1.3	5.17
* 1268-1060	1192	600	1666	-1.3, +1.4	12.23
1001-932	967	600	200	-1.2, +1.6	1.66
932-865	904	600	389	-1.8, +1.5	4.03
* 1001-865	904	600	589	-1.6, +1.5	5.44
718-641	682	600	174	-1.4, +2.2	1.92
574-510	543	600	53.5	-3.7, +3.4	1.08

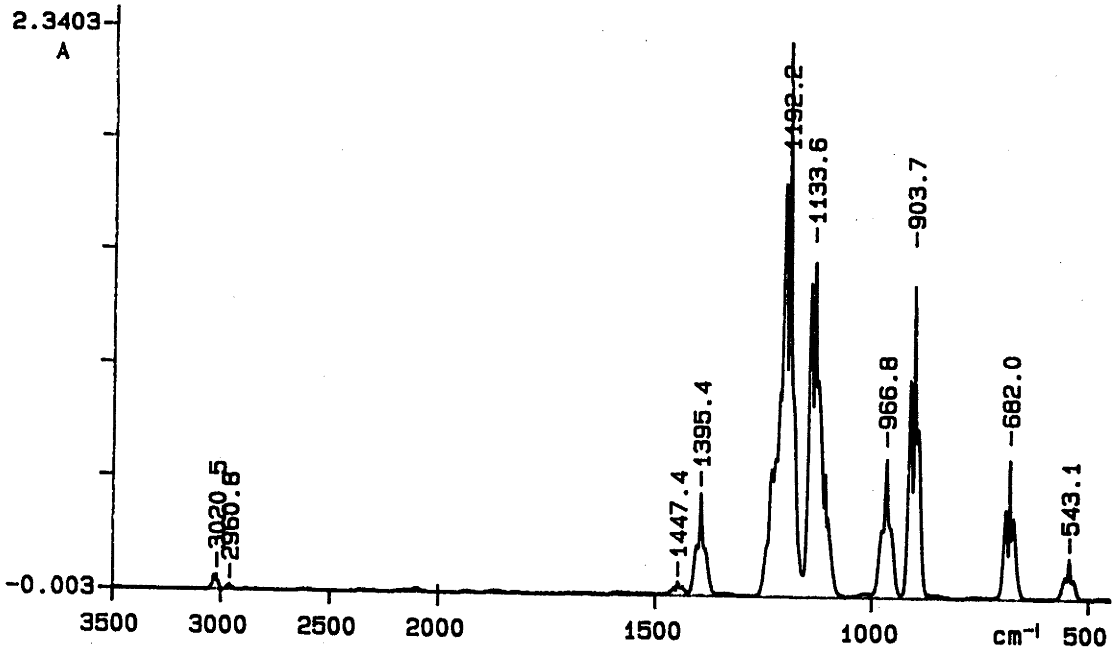


Figure 4.18.Infrared spectrum of HCFC142b using 32.8torr and a 3cm cell.

Table 4.21. Band intensities of HCFC123, 1,1-dichloro-2,2,2-trifluoroethane.

Band range (* group) cm^{-1}	Position of max. abs. cm^{-1}	Waveno. of baseline point cm^{-1}	Band Intensity cm^{-2}atm^{-1}	Max. % variation from average band intensity	Standard deviation cm^{-2}atm^{-1}
3031-2972	3011	3031-2972	13.2	-0.9, +2.6	0.13
1342-1303	1324	700	279	-0.5, +1.1	1.29
1303-1256	1279	700	557	-0.7, +0.9	2.84
1256-1172	1195	700	844	-0.7, +0.6	4.26
1172-1119	1146	700	656	-0.6, +0.6	3.01
1119-1082	1107	700	51.5	-0.8, +1.4	0.31
1082-1040	1064	700	30.3	-2.2, +1.9	0.37
* 1342-1040	1279	700	2418	-0.6, +0.6	11.69
1019-966	999	700	37.8	-1.8, +1.9	0.39
893-800	842	700	493	-0.6, +0.4	1.84
800-731	770	700	71.6	-1.1, +0.9	0.50
* 893-731	842	700	565	-0.6, +0.6	2.17
691-647	672	700	96.2	-1.0, +1.7	0.74
647-614	633	700	9.58	-3.6, +3.1	0.22
* 691-614	672	700	106	-1.1, +1.5	0.84
578-542	559	700	12.4	-3.0, +3.0	0.28
542-505	527	700	16.0	-3.4, +4.1	0.33
* 578-505	527	700	28.4	-2.7, +2.9	0:56

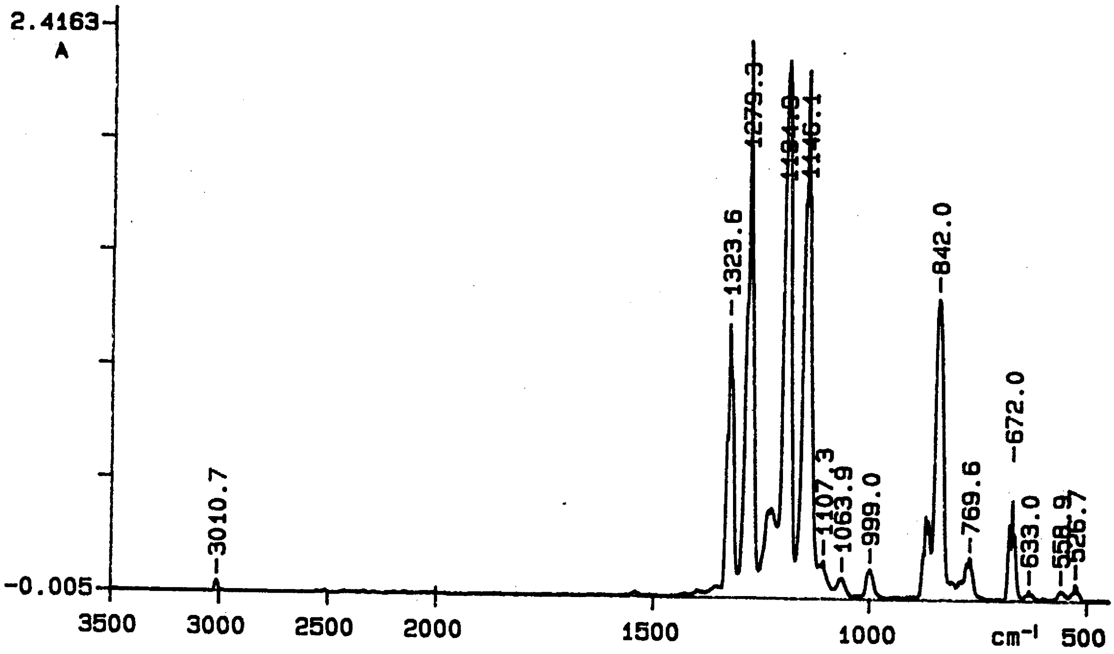


Figure 4.19. Infrared spectrum of HCFC123 using 35.8torr and a 3cm cell.

Table 4.22. Band intensities of HCFC124, 1-chloro-1,2,2,2-tetrafluoroethane.

Band range (* group) cm^{-1}	Position of max. abs. cm^{-1}	Waveno. of baseline point cm^{-1}	Band Intensity cm^{-2}atm^{-1}	Max. % variation from average band intensity	Standard deviation cm^{-2}atm^{-1}
3026-2970	3002	3026-2970	19.0	-1.9, +2.3	0.23
1433-1324	1377	1500	179	-1.1, +1.3	1.30
1324-1254	1286	1500	605	-1.3, +1.2	4.38
1254-1187	1215	1500	977	-1.3, +1.3	7.35
1187-1125	1166	1500	774	-1.4, +1.0	5.31
1125-1071	1107	1500	395	-1.1, +1.3	2.88
* 1433-1071	1166	1500	2930	-1.3, +1.0	20.32
925-849	885	1500	289	-1.4, +1.3	2.16
849-786	818	1500	147	-1.8, +2.1	1.62
* 925-786	885	1500	436	-1.5, +1.5	3.69
720-671	697	1500	130	-1.3, +2.0	1.28
590-552	573	1500	13.8	-4.3, +5.3	0.37
552-506	531	1500	24.8	-3.8, +3.7	0.56
* 590-506	531	1500	38.6	-4.0, +3.4	0.88

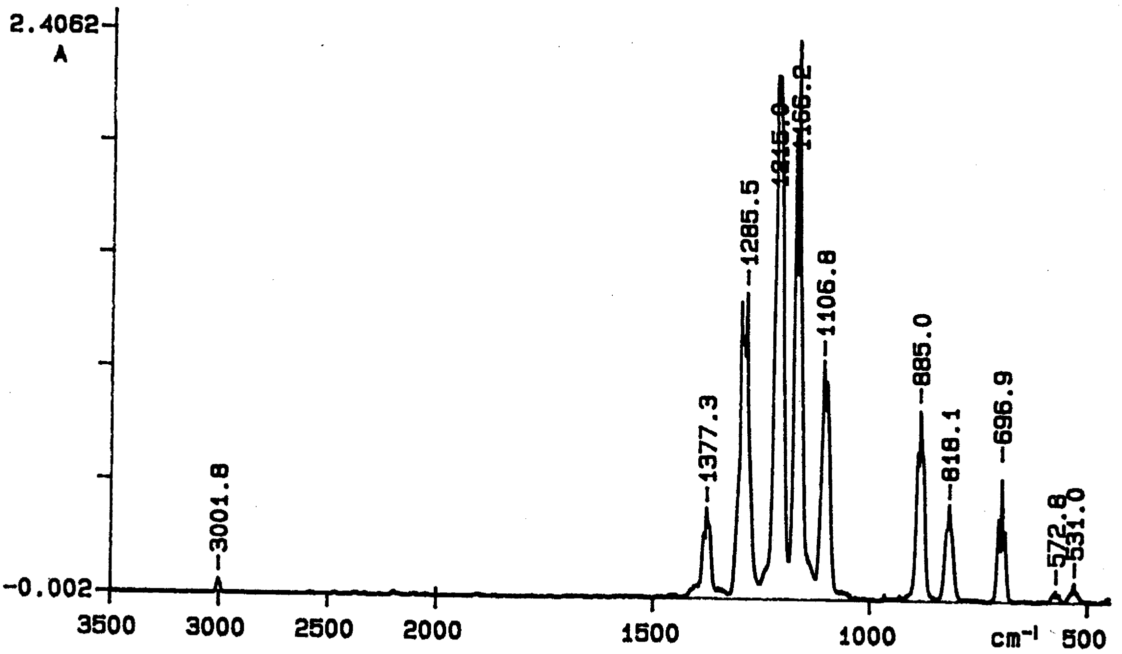


Figure 4.20. Infrared spectrum of HCFC124 using 28.6torr and a 3cm cell.

Table 4.23. Band intensities of HCFC244ca, 1-chloro-2,2,3,3-tetrafluoropropane.

Band range (* group) cm^{-1}	Position of max. abs. cm^{-1}	Waveno. of baseline point cm^{-1}	Band Intensity $cm^{-2}atm^{-1}$	Max. % variation from average band intensity	Standard deviation $cm^{-2}atm^{-1}$
3100-2720	2990	3100-2720	128	-1.1, +2.4	1.81
1500-1370	1441	2000	108	-0.6, +2.1	1.28
1370-1295	1312	2000	72.5	-1.7, +2.0	0.91
1295-1000	1120	2000	1986	-1.9, +1.8	24.50
* 1500-1000	1120	2000	2167	-1.9, +1.8	26.51
930-815	852	2000	150	-1.9, +2.4	2.21
805-750	787	2000	64.3	-1.6, +2.5	0.96
690-620	647	2000	90.2	-1.6, +1.9	1.07
595-495	573	2000	119	-2.0, +2.5	1.95

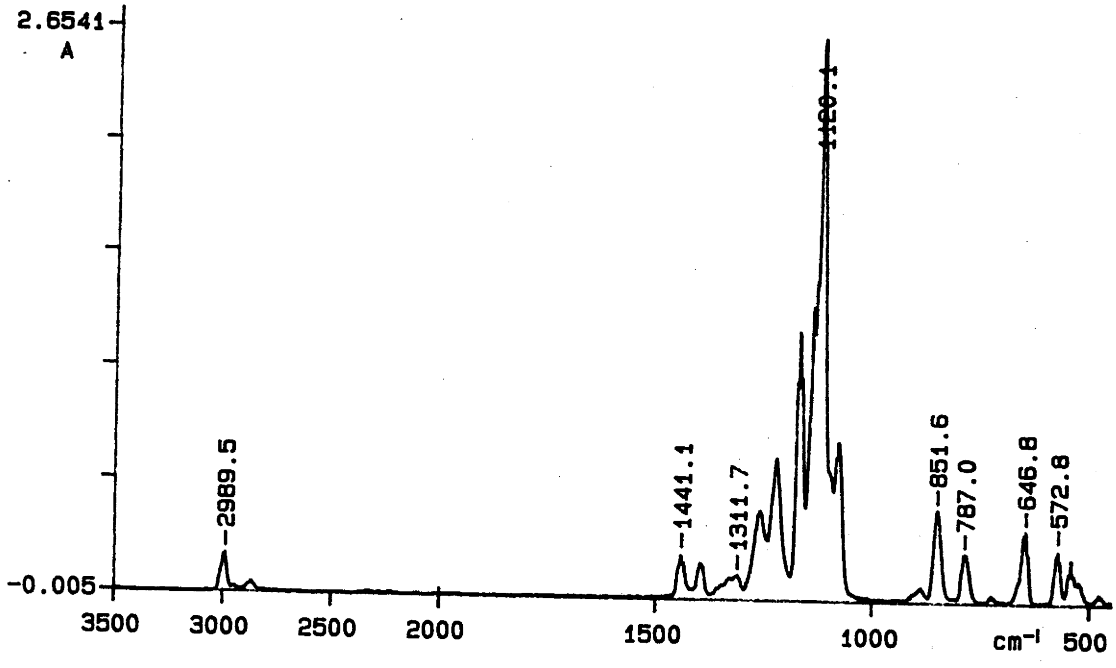


Figure 4.21. Infrared spectrum of HCFC244ca using 12.7torr and a 10cm cell.

Table 4.24. Band intensities of HCFC235cb, 1-chloro-2,2,3,3,3-pentafluoropropane.

Band range (* group) cm^{-1}	Position of max. abs. cm^{-1}	Waveno. of baseline point cm^{-1}	Band Intensity $cm^{-2}atm^{-1}$	Max. % variation from average band intensity	Standard deviation $cm^{-2}atm^{-1}$
3020-2935	2984	3020-2935	21.3	-3.2, +4.8	0.46
1465-1415	1441	1500	39.0	-3.7, +2.5	0.66
1415-1328	1367	1500	194	-1.7, +2.6	3.00
1328-1160	1214	1500	2467	-3.2, +2.0	35.19
1160-1082	1134	1500	396	-2.7, +2.4	6.13
1082-1000	1038	1500	423	-3.1, +2.0	7.09
* 1465-1000	1214	1500	3520	-3.1, +1.8	52.38
845-750	794	1500	136	-4.4, +2.3	2.99
750-690	710	1500	133	-3.8, +2.0	2.28
* 845-690	710	1500	269	-4.1, +2.2	5.20
655-570	632	1500	51.9	-6.3, +3.8	1.74
550-490	519	1500	37.9	-7.7, +5.3	1.58

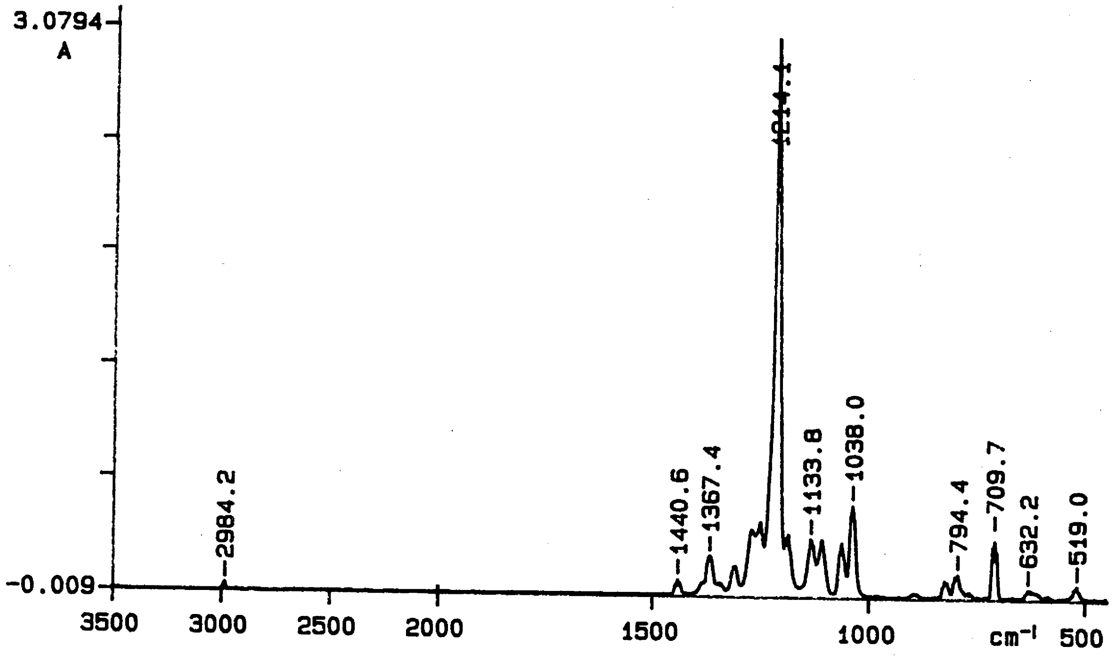


Figure 4.22. Infrared spectrum of HCFC235cb using 5.3torr and a 10cm cell.

Table 4.25. Band intensities of HCFC225ca, 1,1-dichloro-2,2,3,3,3-pentafluoropropane.

Band range (* group) cm^{-1}	Position of max. abs. cm^{-1}	Waveno. of baseline point cm^{-1}	Band Intensity cm^{-2}atm^{-1}	Max. % variation from average band intensity	Standard deviation cm^{-2}atm^{-1}
3050-2965	3016	3050-2965	12.7	-4.7, +2.3	0.23
1420-1320	1349	1000	236	-3.9, +2.4	3.79
1320-1100	1209	1000	2824	-2.6, +2.1	36.10
* 1420-1100	1209	1000	3060	-2.7, +2.1	39.55
1065-1010	1041	1000	317	-3.1, +1.8	4.03
865-780	840	1000	339	-2.7, +1.6	3.97
780-738	758	1000	53.3	-2.5, +1.3	0.62
738-695	713	1000	216	-2.7, +1.7	2.52
* 865-695	713	1000	607	-2.7, +1.6	7.05

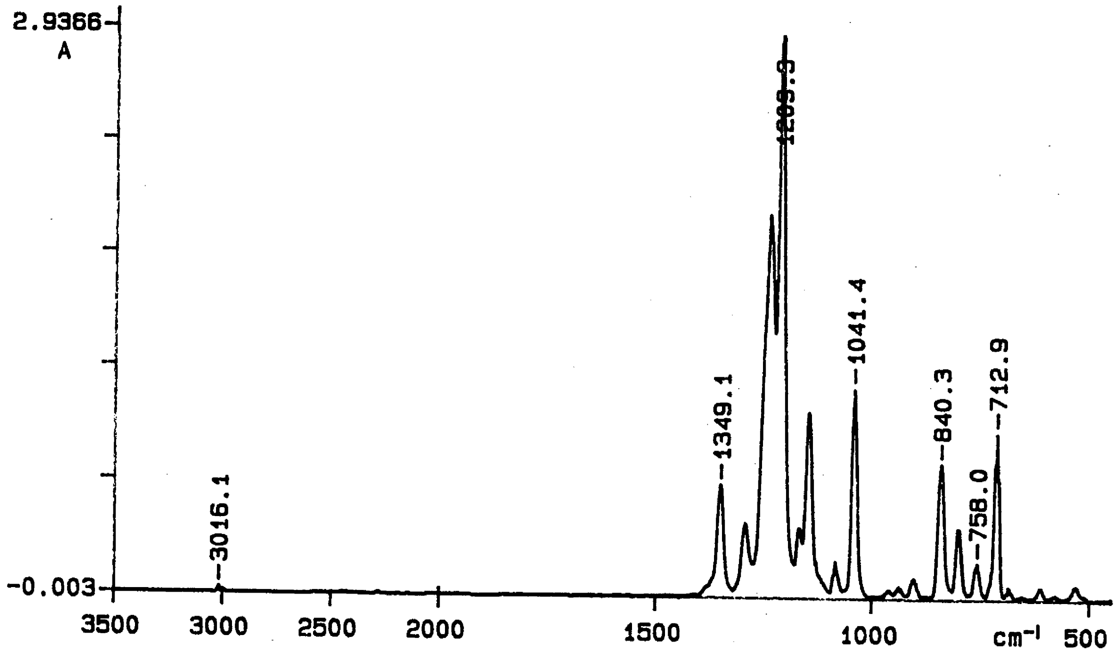


Figure 4.23. Infrared spectrum of HCFC225ca using 8.8torr and a 10cm cell.

Table 4.26. Band intensities of HCFC225cb, 1,3-dichloro-1,2,2,3,3-pentafluoropropane.

Band range (* group) cm^{-1}	Position of max. abs. cm^{-1}	Waveno. of baseline point cm^{-1}	Band Intensity $cm^{-2}atm^{-1}$	Max. % variation from average band intensity	Standard deviation $cm^{-2}atm^{-1}$
3040-2950	3008	3040-2950	12.1	-4.1, +2.4	0.23
1450-1330	1355	1600	46.4	-2.2, +1.7	0.53
1330-1010	1179	1600	2710	-1.0, +2.1	22.58
1010-890	960	1600	423	-0.9, +1.9	3.34
890-695	745	1600	785	-1.1, +2.1	7.04
695-626	670	1600	70.8	-1.0, +0.8	0.42
626-587	615	1600	38.5	-0.8, +0.5	0.17
* 1450-587	1179	1600	4074	-0.9, +2.0	32.31

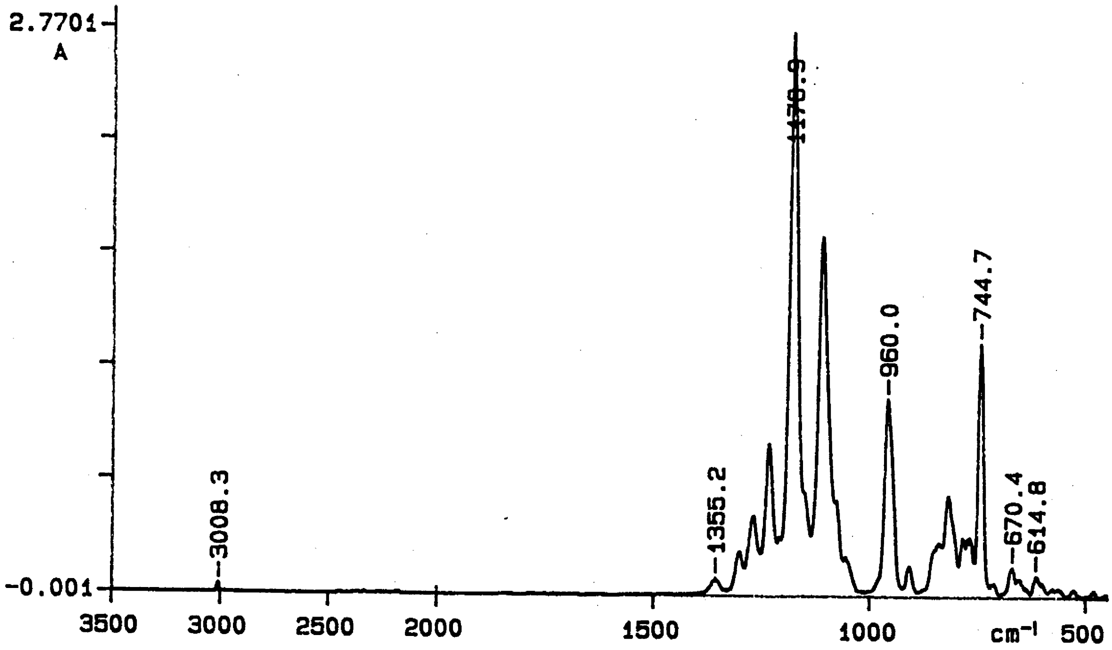


Figure 4.24. Infrared spectrum of HCFC225cb using 10.7torr and a 10cm cell.

Table 4.27. Band intensities of FC218, octafluoropropane.

Band range (* group) cm^{-1}	Position of max. abs. cm^{-1}	Waveno. of baseline point cm^{-1}	Band Intensity cm^{-2}atm^{-1}	Max. % variation from average band intensity	Standard deviation cm^{-2}atm^{-1}
1415-1329	1350	800	484	-2.8, +2.5	8.02
1287-1227	1262	800	3050	-3.3, +3.6	76.75
1227-1180	1209	800	590	-1.8, +1.6	6.93
* 1287-1180	1262	800	3640	-2.9, +3.2	77.90
1171-1110	1154	800	685	-2.0, +1.7	8.27
1022-960	1007	800	825	-1.9, +1.5	9.23
750-705	731	800	191	-2.5, +2.6	2.83
563-520	537	800	49.6	-10.5, +7.0	2.62

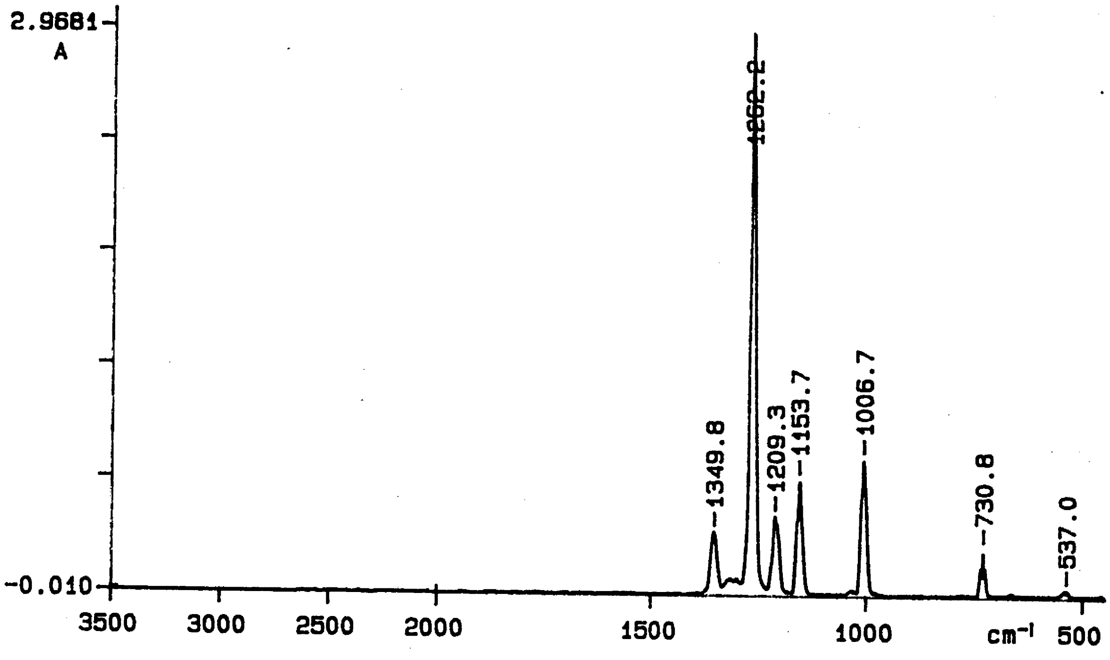


Figure 4.25. Infrared spectrum of FC218 using 7.0torr and a 3cm cell.

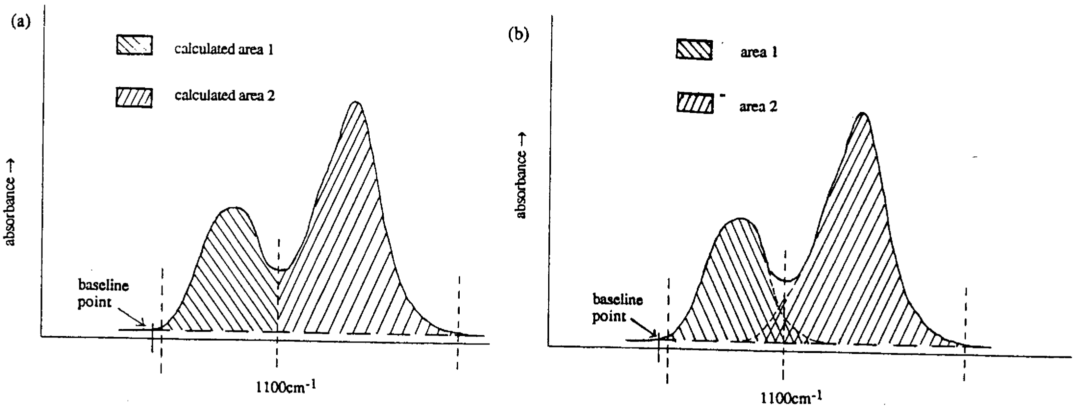


Figure 4.26. Discrepancies between (a) calculated areas and (b) 'true' areas.

The band intensities for a group of bands were obtained by adding the areas for all the bands in the spectra for the group, calculating the band intensity and averaging over all spectra for one compound. The 'errors' discussed here refer to the variation from the average band intensity. The individual sets of results are discussed below for each halocarbon.

CFC111. Results for CFC111 are presented in table 4.3 and figure 4.1. It is solid at room temperature, so only low pressures of vapour were obtained. The maximum percentage deviation from the average was +3.8% suggesting that all the results were satisfactory. The standard deviation for the group is slightly lower than that for the individual bands indicating that errors due to overlapping bands have been reduced.
CFC112. Results for CFC112 are presented in table 4.4 and figure 4.2. This substance is also solid at room temperature. The errors are all within the expected ±4%, except for the bands 645-612cm^{-1} and 498-462cm^{-1}. These bands are very weak, and with the pressures available for use, are very difficult to measure due to noise in the spectrum and the low absorbance. It is possible that there was some contamination of the sample by CFC112a, however, many of the bands are coincident and no large discrepancies were found in the areas.

CFC112a. Results for CFC112a are presented in table 4.5 and figure 4.3. As for CFC112, the substance is solid at room temperature, and the largest errors occurred in the weakest band.

CFC113 and CFC113a. Data for these compounds were taken from the publication by Olliff & Fischer (1992). The results are presented in tables 4.6 and 4.7 and figures 4.4 and 4.5.

CFC114. The results for CFC114 are presented in table 4.8 and figure 4.6. The largest errors are due to the very weak bands between 758 and 586cm^{-1}. In the case of the 1315-1253cm^{-1} band, one value was 4.6% less than the average. The other eleven values were all within 3%. Similarly, for the 862-820cm^{-1} band, one value was 4.3% less than the average, the other 11 values were all within 2%.

CFC114a. The results for CFC114a are presented in table 4.9 and figure 4.7. Several errors in the band intensities are apparent for this compound. While the large errors for the bands 1070-1024cm^{-1}, 861-822cm^{-1} and 603-543cm^{-1} may be attributed to the fact that the bands are very weak, the errors in the strong band 1266-1206cm^{-1} cannot be easily explained. The errors for the group including this band are acceptable, as some variations have been decreased by the grouping of bands as described above. It is possible however, that CFC114a is contaminated by CFC114, since the strongest bands of CFC114 are found at 1185, 1052, and 847cm^{-1}, and weak peaks can be seen at these positions in the spectrum in figure 4.7. Separation of the two gases was not possible in this work, so the results are reported as calculated at the given purity. The two compounds are isomeric, so it is possible that small amounts of CFC114 were formed during the manufacture of CFC114a.

CFC115. The results for CFC115 are presented in table 4.10 and figure 4.8. The error for the group 1273-1066cm^{-1} is considerably smaller than the individual band intensity errors suggesting that the choice of individual band ranges was not satisfactory. Again, the largest errors arose in the weakest bands.

FC116. The results for FC116 are presented in table 4.11 and figure 4.9. The very strong band between 1277-1222cm^{-1} made it necessary to measure the area using two sets of data, since maximum absorbance of the strong band exceeded 3.0 absorbance units when pressures high enough to bring the weak bands into the range 0.1 to 3.0 absorbance units were used.

HFC161. The results for HFC161 are presented in table 4.12 and figure 4.10. The errors for the band intensity data were well within the limit of ±4%, except for the weakest band from 1552-1433cm^{-1}. The strength of the band 3080-2820cm^{-1} and the lack of instrumental 'drift' observed in the spectrum, as described in chapter three, resulted in the choice of 3500cm^{-1} as the baseline point.

HFC152a. The results for HFC152a are presented in table 4.13 and figure 4.11. Since bands occurred at both ends of the spectrum, and that at 3100-2910cm^{-1} was relatively small, two different baseline points were selected. One adjacent to the 3100-2910cm^{-1} band and one at 700cm^{-1} for the remaining bands.

HFC143. The results for HFC143 are presented in table 4.14 and figure 4.12. Several of the spectra for this compound showed instrumental 'drift', so the area under the 3055-2866cm^{-1} band was calculated using a diagonal baseline drawn through the range limits. The remaining bands were calculated using a baseline through 800cm^{-1}. The errors were all small even for the weakest bands.

HFC143a. The results for HFC143a are presented in table 4.15 and figure 4.13. As for HFC143, two different baselines were used.

HFC134. The results for HFC134 are presented in table 4.16 and figure 4.14. Again two baselines were used. The errors were small, except for the very weak band at 1420-1369cm^{-1}.

HFC134a. The results for HFC134a are presented in table 4.17 and figure 4.15. Only one baseline point was used for the 3100-2750cm^{-1} band. The largest error was found in this band, suggesting that some baseline errors were apparent.

HFC125. The results for HFC125 are presented in table 4.18 and figure 4.16. Two baselines were used as for HFC143. Again the errors were all acceptable, except for those associated with the weakest bands.

HCFC141b. The results for HCFC141b are presented in table 4.19 and figure 4.17. Very consistent results were obtained for this compound, except for the very weak band at 2985-2914cm^{-1}. When combining the two bands at this end of the spectrum into the group 3054-2914cm^{-1}, the error in the band intensity was acceptable, suggesting that the bands should not have been divided.

HCFC142b. The results for HCFC142b are presented in table 4.20 and figure 4.18. Acceptable results were obtained, provided that the absorption due to C-H stretches between 3077-2936cm^{-1} are treated as a group.

HCFC123. The results for HCFC123 are presented in table 4.21 and figure 4.19. Despite the fact that these spectra were divided into many bands, the errors in the band intensities were small.

HCFC124. The results for HCFC124 are presented in table 4.22 and figure 4.20. The errors obtained from the data for this compound are acceptable, with slightly larger errors occurring for the very weak bands.

HCFC244ca. The results for HCFC244ca are presented in table 4.23 and figure 4.21. This compound was synthesised as part of this work, and although the product was purified as far as possible, the exact purity was not determined. The variations in the results are all within the expected range of ±4%, hence are acceptable.

HCFC235cb. The results for HCFC235cb are presented in table 4.24 and figure 4.22. This compound was also synthesised as part of this work, but as for HCFC244ca, the exact purity was not determined. The errors exceeded the 4% error range for the weaker bands, but the group results are acceptable.

HCFC225ca. The results for HCFC225ca are presented in table 4.25 and figure 4.23. The manufacturer specified a purity of only 88%, however, the errors in the band intensities show that the results were consistent. These values may still be valid when using the data for global warming predictions, since the compound will be used as a solvent at the purity supplied by the manufacturer.

HCFC225cb. The results for HCFC225cb are presented in table 4.26 and figure 4.24. This compound was available at a higher purity than HCFC225ca, and the band intensity errors are , in general, lower. As can be seen in the spectrum, many of the bands overlap, and so were not all separated for integration of absorbance under the bands.

FC218. The results for FC218 are presented in table 4.27 and figure 4.25. One baseline point was used for all of the bands, since no hydrogen is present in the molecule, and fundamental absorption occurs below 1500cm^{-1}. The errors are in the acceptable range, except for the weak band at 563-520cm^{-1}.

From the tables 4.3 to 4.27, it can be seen that the variations in the band intensities fall mostly within the acceptable error range of ±4%. The overall error obtained from pressure, pathlength and instrumental errors was found to be between ±2% and ±4% as defined in chapter three. This value is primarily dependent on pressure. The variations in errors between individual bands within one spectrum are due to errors in the choice of band range and baseline. In general, these variations are small, except in the case of the very weak bands, where, even at higher pressures, the maximum absorbance is still small and hence the effects of instrumental noise affect the integration of the absorbance under the bands.

Chapter 5

Data input for computer calculations.

The frequencies of molecular vibrations may be calculated by various methods. In this work, two approaches were used, a normal coordinate analysis using a Urey-Bradley force field and an *ab initio* electronic structure method, as described in section 1.6. The data required for the Urey-Bradley force field calculations are described in section 5.1, and the detailed computer input is given in appendix B. The data required for the *ab initio* calculations are described in section 5.2, and the detailed computer input is given in appendix C.

Nineteen halocarbons were selected for theoretical study. The halocarbons were divided into two groups, each group consisting of a series of two carbon compounds with increasing numbers of fluorine atoms. The first group includes the CFCs CFC110, CFC111, CFC112, CFC112a, CFC113, CFC113a, CFC114, CFC114a, CFC115, FC116. The second group includes the HFCs HFC170 (ethane), HFC161, HFC152, HFC152a, HFC143, HFC143a, HFC134, HFC134a, HFC125, FC116. Hexafluoroethane, FC116, is included in each group so that comparisons can be made between a fully fluorinated ethane and the partially fluorinated ethanes in both cases. In order to investigate changes in the infrared spectra with changes in the positions of the fluorine atoms within the molecule, all structural isomers were included.

5.1 Urey-Bradley force field calculations.

The programs NORCORD and OVER, when run consecutively, enable the fundamental vibrational frequencies for molecules of known geometry to be calculated. Using approximate values for initial force constants, the programs refine the force constants until calculated frequencies close to the observed values are obtained as described in section 1.6.1, using the techniques devised by Overend and Scherer (1960). The programs were made available for this work by Dr. Gad Fischer at the ANU, and had been written in Fortran and used on a VAX computer. Initially, considerable time was spent converting the programs to run on the SUN/UNIX computer system at the ANU, and to correct the previously undiagnosed errors due to problems with rounding of the Cartesian coordinates in NORCORD, and refining five or more force constants in OVER. An extra section was inserted into OVER to enable interactive changes of the force constants by the user between iterative calculations. This was useful when newly-refined force constants were deemed to be unsuitable. The fortran program CALST was written and run on a Macintosh computer to facilitate the construction of the Z matrix by calculating the force constant coefficients. It must be noted here that the Z matrix used by OVER, described in section 5.1.2, is entirely different to the Z matrix used by GAUSSIAN92. In order to carry out the two types of calculation independently, the optimised geometry from the *ab initio* calculations was not used for this part of the work. The molecular geometry used was that obtained from the literature and given in table 5.1.

5.1.1 Data input for the program NORCORD.

The program NORCORD uses Cartesian coordinates, internal coordinates and molecular symmetry to calculate moments of inertia, create a G matrix and hence a W matrix for use by the program OVER for a molecule of up to 30 atoms. The W matrix is obtained from the matrix calculation, UGU' , this procedure removes redundancies and introduces the molecular symmetry into the G matrix (Overend & Scherer 1960). The W matrix is output to disk by NORCORD for use by OVER in subsequent calculations for the same molecule.

Using the data in table 5.1, the Cartesian coordinates were easily calculated. For these 8 atom molecules, the number of fundamental vibrations is 18, as described in section 1.5.2. There are 22 internal coordinates hence 4 redundancies.
The redundancies occur because all the angles about the tetrahedral carbons are included. A general diagram of the internal coordinates used is shown in figure 5.1. Xn represents the atoms F, Cl, or H, depending on the molecule. The bond stretches are represented by r_n; the angle bends between the C-C backbone and a third atom by α_n; the angle bends between the atoms attached to the same carbon atom by β_n; and the torsion of the molecule about the C-C axis by γ_n.

A U matrix for each molecule was constructed, relating internal coordinates to symmetry coordinates. It was first necessary to determine the symmetry point group of each molecule, then, using the character tables given in Wilson et al. (1955), the irreducible representations were calculated giving the symmetry coordinates for the fundamental vibrations.

Table 5.1. Experimental geometries for the halocarbons used in the calculations. Bond lengths are given in Å, and angles in degrees. X represents the atom Cl for CFCs and H for HFCs, and T represents the tetrahedral angle 109.47°.

	C_1-C_2	C_1-F	C_2-F	C_1-X	C_2-X	C_2C_1F	C_1C_2F	C_2C_1X	C_1C_2X	FCF	FCX	XCX	ref.
CFC110	1.499			1.763	1.763			110.7	110.7			108.2	Tanabe & Saëki 1972
CFC111	1.54		1.37	1.77	1.77		T	T	T		T	T	Nielsen et al. 1953 (a)
CFC112	1.54	1.37	1.37	1.77	1.77	T	T	T	T		T	T	using CFC111 values.
CFC112a	1.55		1.33	1.76	1.74		108.0	110.7	110.6	108.0	110.5	108.2	Brown et al. 1967 *
CFC113	1.54	1.37	1.35	1.75	1.74	T	T	T	T	T	T	T	Brown et al. 1967
CFC113a	1.545	1.33			1.771	108.9			110.7	110.0		108.2	Bürger et al. 1980
CFC114	1.55	1.33	1.33	1.74	1.74	108.0	108.0	110.6	110.6	108.0	110.5		Brown et al. 1967 *
CFC114a	1.56	1.33	1.40		1.78	T	T		T	T	T	T	Brown et al. 1967
CFC115	1.555	1.33	1.33		1.74	110.9	108.0		110.6	108.0	110.5		Brown et al. 1967 *
FC116	1.545	1.326	1.326			109.8	109.8			109.1			Gallaher et al. 1974
HFC170	1.5324			1.1068	1.1068			111.0	111.0			107.9	Tanabe & Saëki 1972
HFC161	1.505		1.398	1.090	1.095		109.7	109.7	112.9		106.1	108.8	Chen et al. 1975
HFC152	1.5033	1.3892	1.3892	1.1034	1.1034	110.3	110.3	111.0	111.0		107.9	108.5	Huber-Wälchli et al. 1975
HFC152a	1.54		1.345	1.10	1.10		109.4	108.7	109.8	109.1	110.0	110.2	Chen et al. 1975
HFC143	1.500	1.3878	1.3534	1.0881	1.0881	109.1	109.1	108.9	108.9	106.9		120.9	Beagley & Brown 1979
HFC143a	1.530	1.335			1.085	111.0			108.3	107.9		110.6	Chen et al. 1975
HFC134	1.518	1.350	1.350	1.098	1.098	108.2	108.2	110.3	110.3	107.3	111.3		Brown & Beagley 1977
HFC134a	1.525	1.335	1.39		1.09	110.9	109.7		109.8	108.0	109.4	108.8	Chen et al. 1975
HFC125	1.52	1.335	1.345		1.10	110.8	109.6		110.0	109.1	109.3		Chen et al. 1975

* angles have been taken from Tanabe & Saëki 1972.

The symmetry point groups for the molecules studied here were found to be:

CFC110, FC116, HFC170	D_{3d}
CFC111, CFC112a, CFC114a, CFC115, HFC161, HFC152a, HFC134a, HFC125	C_s
CFC112, CFC114, HFC152, HFC134	C_{2h}
CFC113, HFC143	C_1
CFC113a, HFC143a	C_{3v}

assuming in all cases, a staggered configuration.

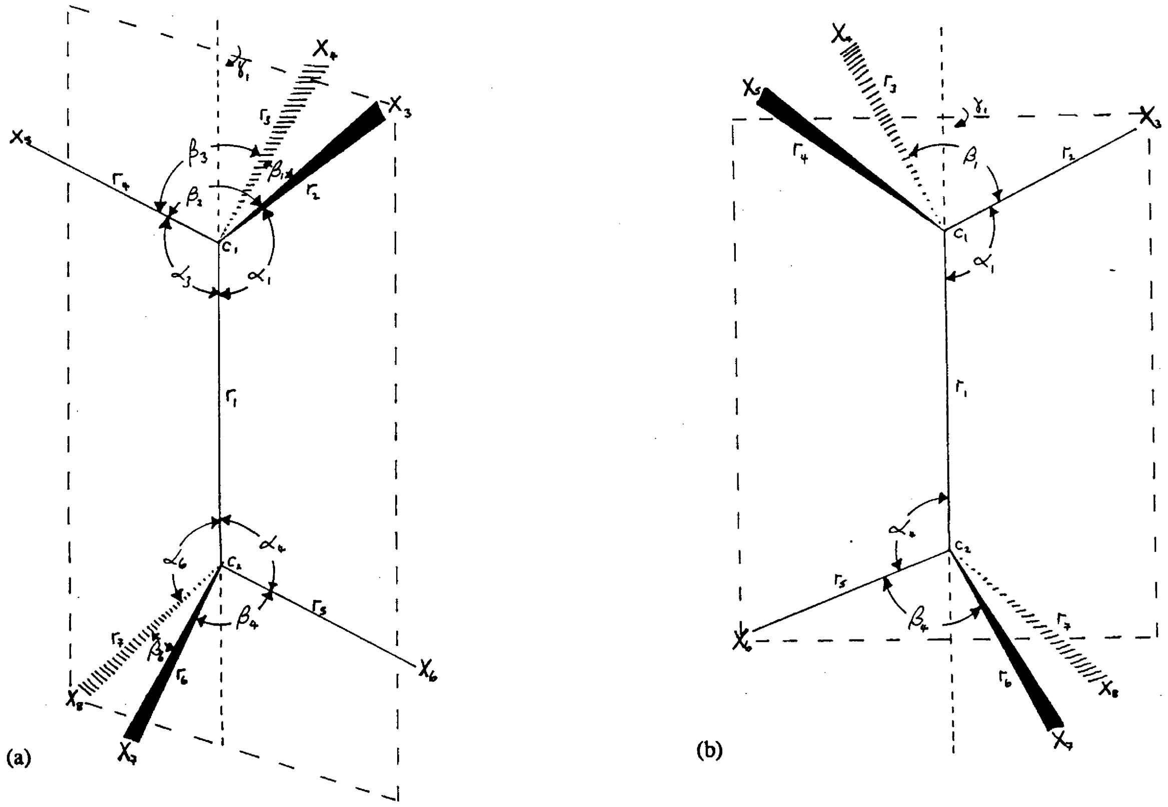


Figure 5.1. The internal coordinates of the molecule (a) used for the point groups D_{3d}, C_s, C_1, C_{3v} and (b) used for the point group C_{2h}, where atoms X_3 and X_6 are identical, as are X_4, X_5, X_7 and X_8.

To obtain the irreducible representations, the reducible representations were calculated. These were found by summing the coordinates of the atoms which do not move during a particular symmetry operation. For atoms which rotate, the change of direction of the x,y,z vectors must be noted. The symmetry operations from the character tables, as given by Wilson et al. (1955) with the corresponding reducible representations were found to be:

D_{3d}	E	$2C_3$	$3C_2$	i	$2S_6$	$3\sigma_d$
Γ_{rep}	24	0	0	0	0	4

C_s	E	σ_h
Γ_{rep}	24	4

C_{2h}	E	C_2	i	σ_h
Γ_{rep}	24	0	0	4

C_1	E
Γ_{rep}	24

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ_{rep}	24	0	4

E denotes the identity operation; C_n denotes an n-fold rotation about a symmetry axis; i denotes an inversion about the centre of symmetry; S_n denotes an improper rotation, such that $S_n = \sigma_h C_n$; and σ_x denotes a reflection in a plane of symmetry where x=h for a plane perpendicular to the principal axis, x=v for a plane containing the principal axis, and x=d for a plane containing the principal axis and bisecting the angles between the horizontal axes.

The number of fundamental vibrations for each species was then calculated using the formula , (Nakamoto 1986),

$$a_i = \frac{1}{h}\int n\chi(R)\chi_i(R)$$

where:

a_i is the species

h is the order of the group

$\chi(R)$ is a reducible representation element

$\chi_i(R)$ is the character of the operation R (an irreducible operation element.)

n is the number of times a particular class is present.

From this, the irreducible representations were found to be:

D_{3d} $3A_{1g} + 1A_{1u} + 2A_{2u} + 3E_g + 3E_u$

C_s $11A' + 7A''$

C_{2h} $6A_g + 4A_u + 3B_g + 5B_u$

C_1	18A
C_{3v}	$5A_1 + 1A_2 + 6E$

A_n, B_n are one-dimensional species. The suffix n is used when different irreducible representations of the same dimensions occur. A' is used for species symmetric under σ_h, and A" for species antisymmetric under σ_h.
E represents a two dimensional species.
For the groups D_{3d} and C_{2h}, where $D_{3d} = D_3 \times i$ and $C_{2h} = C_n \times i$, further notation is required since the number of irreducible representations is doubled. The species which are symmetric under inversion are subscripted g and the antisymmetric species are subscripted u (Schonland 1965)

Each row in the U matrix represents a symmetry species, including redundancies. Each column represents a particular internal coordinate. The sequence of these items is the same as that used for the symmetry block and internal coordinate vector data. Projection operators are used to calculate the magnitude of the contribution of each internal coordinate to each symmetry coordinate (Nakamoto 1978),

$$p_i = \frac{l}{h}\sum_n \chi_i(R_n)R_n$$

where,

p_i = projection operator
l_i = degeneracy, eg. l =1 for species A, B; l = 2 for species E
h = order of the group
$\chi_i(R_n)$ = character of R_n
R_n = symmetry operation n

The general form for the non-normalised U matrix for each point group was found to be as follows:

D_{3d}	(The bonds r_2 to r_7 are equivalent.)
A_{1g}	r_1
A_{1g}	$(r_2+r_3+r_4+r_5+r_6+r_7)/6$
A_{1g}	$(\alpha_1+\alpha_2+\alpha_3+\alpha_4+\alpha_5+\alpha_6)/6$
A_{1g}	$(\beta_1+\beta_2+\beta_3+\beta_4+\beta_5+\beta_6)/6$
A_{1u}	$(\gamma_1+\gamma_2+\gamma_3)/3$
A_{2u}	$(r_2+r_3+r_4-r_5-r_6-r_7)/6$
A_{2u}	$(\alpha_1+\alpha_2+\alpha_3-\alpha_4-\alpha_5-\alpha_6)/6$
A_{2u}	$(\beta_1+\beta_2+\beta_3-\beta_4-\beta_5-\beta_6)/6$

E_g	$(2r_2-r_3-r_4-r_5-r_6+2r_7)/12$,	$(r_3-r_4-r_5+r_6)/4$
E_g	$(2\alpha_1-\alpha_2-\alpha_3-\alpha_4-\alpha_5+2\alpha_6)/12$	$(\alpha_2-\alpha_3-\alpha_4+\alpha_5)/4$
E_g	$(2\beta_1-\beta_2-\beta_3-\beta_4-\beta_5+2\beta_6)/12$	$(\beta_2-\beta_3-\beta_4+\beta_5)/4$
E_u	$(2r_2-r_3-r_4+r_5+r_6-2r_7)/12$	$(r_3-r_4+r_5-r_6)/4$
E_u	$(2\alpha_1-\alpha_2-\alpha_3+\alpha_4+\alpha_5-2\alpha_6)/12$	$(\alpha_2-\alpha_3+\alpha_4-\alpha_5)/4$
E_u	$(2\beta_1-\beta_2-\beta_3+\beta_4+\beta_5-2\beta_6)/12$	$(-\beta_2+\beta_3-\beta_4+\beta_5)/4$
E_u	$(2\gamma_1-\gamma_2-\gamma_3)/6$	$(\gamma_2-\gamma_3)/2$

Showing redundancies as $1A_{1g}$, $1A_{2u}$ and $1E_u$

C_s (assuming the mirror plane bisects the angle between the bonds r_2 and r_3, and r_6 and r_7)

A'	r_1
A'	$(r_2+r_3)/2$
A'	r_4
A'	r_5
A'	$(r_6+r_7)/2$
A'	$(\alpha_1+\alpha_2)/2$
A'	α_3
A'	α_4
A'	$(\alpha_5+\alpha_6)/2$
A'	β_1
A'	$(\beta_2+\beta_3)/2$
A'	$(\beta_4+\beta_5)/2$
A'	β_6
A'	$(\gamma_2-\gamma_3)/2$
A"	$(r_2-r_3)/2$
A"	$(r_6-r_7)/2$
A"	$(\alpha_1-\alpha_2)/2$
A"	$(\alpha_5-\alpha_6)/2$
A"	$(\beta_2-\beta_3)/2$
A"	$(\beta_4-\beta_5)/2$
A"	γ_1
A"	$(\gamma_2+\gamma_3)/2$

Showing redundancies A' and A".

C_{2h} (assuming the bonds r_2 and r_5 are equivalent, see figure 5.1 (b).)

A_g	r_1
A_g	$(r_2+r_5)/2$

A_g	$(r_3+r_4+r_6+r_7)/4$
A_g	$(\alpha_1+\alpha_4)/2$
A_g	$(\alpha_2+\alpha_3+\alpha_5+\alpha_6)/4$
A_g	$(\beta_3+\beta_6)/2$
A_g	$(\beta_1+\beta_2+\beta_4+\beta_5)/4$
A_u	$(r_3-r_4-r_6+r_7)/4$
A_u	$(\alpha_2-\alpha_3-\alpha_5+\alpha_6)/4$
A_u	$(\beta_1-\beta_2-\beta_4+\beta_5)/4$
A_u	γ_1
A_u	$(\gamma_2+\gamma_3)/2$
B_g	$(r_3-r_4+r_6-r_7)/4$
B_g	$(\alpha_2-\alpha_3+\alpha_5-\alpha_6)/4$
B_g	$(\beta_1-\beta_2+\beta_4-\beta_5)/4$
B_u	$(r_2-r_5)/2$
B_u	$(r_3+r_4-r_6-r_7)/4$
B_u	$(\alpha_1-\alpha_4)/2$
B_u	$(\alpha_2+\alpha_3-\alpha_5-\alpha_6)/4$
B_u	$(\beta_3-\beta_6)/2$
B_u	$(\beta_1+\beta_2-\beta_4-\beta_5)/4$
B_u	$(\gamma_2-\gamma_3)/2$

Showing redundancies as $1A_g$, $1A_u$ and $2B_u$

C_1 This point group has no symmetry, so all coordinates are designated A.

C_{3v} (assuming the bonds r_2, r_3 and r_4 are equivalent, and r_5, r_6 and r_7 are equivalent.)

A_1	r_1	
A_1	$(r_2+r_3+r_4)/3$	
A_1	$(r_5+r_6+r_7)/3$	
A_1	$(\alpha_1+\alpha_2+\alpha_3)/3$	
A_1	$(\alpha_4+\alpha_5+\alpha_6)/3$	
A_1	$(\beta_1+\beta_2+\beta_3)/3$	
A_1	$(\beta_4+\beta_5+\beta_6)/3$	
A_2	$(\gamma_1+\gamma_2+\gamma_3)/3$	
E	$(2r_2-r_3-r_4)/6$	$(r_3-r_4)/2$
E	$(2r_5-r_6-r_7)/6$	$(r_6-r_7)/2$
E	$(2\alpha_1-\alpha_2-\alpha_3)/6$	$(\alpha_2-\alpha_3)/2$
E	$(2\alpha_4-\alpha_5-\alpha_6)/6$	$(\alpha_5-\alpha_6)/2$

E	$(2\beta_1-\beta_2-\beta_3)/6$	$(\beta_2-\beta_3)/2$
E	$(2\beta_4-\beta_5-\beta_6)/6$	$(\beta_5-\beta_6)/2$
E	$(\gamma_1+\gamma_2+\gamma_3)/3$	$(\gamma_1+\gamma_2+\gamma_3)/3$

Showing redundancies $2A_1$ and 1E.

The general format for the input records of NORCORD follows in bold type. The complete input to the program for each molecule is given in appendix B.

-09

This record indicates the start of a problem

1 1nnnbbbiiisssrrrvvvwgmut

The first two numbers indicate the problem number (1) and the number of isotopes (1). The number of atoms in the molecule is given in nnn, which is 8 for all the molecules studied here; bbb gives the no. of symmetry blocks in the molecule; iii gives the no. of internal coordinates (22); sss gives the no. of symmetry coordinates, inc. redundancies (22); rrr gives the number of redundancies (4), and vvv gives the number of internal coordinate vectors (22). The next 5 digits control the output from the program; w=1 for W matrix required; g=1 for G matrix eigenvalues required; m=1 for B matrix required; u=1 for U*B to be output and t=1 for U*U to be output.

xxxyyyxxxyyy.....

This record contains a pair of numbers for each symmetry block in the order they are presented in the rows of the U matrix. xxx is the number of symmetry coordinates, including redundancies and yyy is the number of redundancies for each block.

Molecular formula and name

date

Two records of descriptive information are given, usually used to identify the molecule and give the date.

cccaaaxxxx.xxxxxxx.....

A group of records containing the Cartesian coordinates for the molecule follows. Each coordinate is given in the format, ccc = 1 for x , 2 for y , 3 for z coordinate or -1 for end of coordinate input,

aaa = atom number within the molecule, (the atoms are numbered in the sequence of the atomic masses given in the last record), and xxxx.xxxxxxx is the value of the coordinate. Four coordinates are entered on each input line.

nnnccciiijjjkkklll

One line of input is entered for each internal coordinate, where; nnn = number assigned to the internal coordinate, this is the sequence of the internal coordinates used for the columns of the U matrix; ccc=1 for a bond stretch, 2 for an angle bend, or 4 for four atom torsion; iii , jjj , kkk , lll are the numbers of the atoms defining the coordinate (kkk=lll=0 for a simple bond stretch). The atom numbers must be the same as those used for the Cartesian coordinates.

rrrcccxxxx.xxxxxxx......

U matrix data are entered, four entries for each input line, where; rrr= row number (-3 for end of input of U matrix); ccc=column number and xxxx.xxxxxxx= non-normalised U matrix value. Zero elements need not be entered. It is important that the rows of the U matrix are in the same sequence as the symmetry block information given in input line 2, and the columns are in the same sequence as the internal coordinate vectors.

xxxxx.xxxxxx........

The masses of the atoms are entered next, up to six per line. The values must be entered in the same sequence of atoms as that used in the input of the Cartesian coordinates.

000

This is the last record in the input stream.

The name of the file to be used to hold the W matrix output is entered interactively at the start of the run.

5.1.2. Data input for the program OVER.

Approximate force constants are used by this program to calculate the fundamental vibrational frequencies and the potential energy distribution. The force constants may be refined in an attempt to fit the calculated frequencies to the observed frequencies. The input data includes the observed frequencies from an infrared spectrum of the molecule, a W matrix from NORCORD, a set of approximate force constants and a Z matrix. This Z matrix is a vector of the coefficients of contributions of each internal coordinate to each force constant, for each symmetry coordinate. For this work, Z matrix elements were calculated using the equations given in Overend & Scherer (1960).

The initial force constants, which need only be approximate values, were obtained from the data for similar molecules published by Bucker and Nielsen (1963) and Naito et al. (1955). These force constants were calculated using a Urey-Bradley force field for the molecules C_2H_6 (HFC170), CH_3CF_3 (HFC143a), and C_2F_6 (FC116) by Bucker and Nielsen (1963), and CCl_2HCCl_2H by Naito et al. (1955). The same initial force constants were used for all molecules and are given in table 5.2.

The values for the torsion were expected to be small and so were initially set to 0.01mdyneÅ^{-1}. The Urey-Bradley force field has four types of force constants, K for bond stretching, H for angle bending, F and F' for non-bonded or repulsive interactions as defined in section 1.6.1. F and F' are not independent as they are related to the Van der Waal's forces between non-bonded atoms, and F' is usually taken as -0.1F (Nakamoto 1986).

Table 5.2. Initial force constants for the UB calculations. Force constants are given in mdyneÅ^{-1}, taken from Bucker & Nielsen (1963) except for those indicated † which come from Naito et al. (1955) and * which are assumed approximate values.

Stretching force constants		bending force constants		non-bonded force constants	
K_{CC}	3.5	H_{CCF}	0.3	F_{FC}	0.4
K_{CF}	4.4	H_{CCH}	0.14	F_{HC}	0.4
K_{CH}	4.6	H_{CCCl}	0.10 †	F_{ClC}	0.6 †
K_{Cl}	1.8	H_{FCF}	0.1	F_{FF}	1.1
		H_{HCH}	0.43	F_{HH}	0.09
		H_{ClCCl}	0.10 †	F_{ClCl}	0.64 †
		H_{FCH}	0.1 *	F_{FH}	0.06
		H_{ClCH}	0.05 †	F_{HCl}	0.80 †
		H_{ClCF}	0.1 *	F_{FCl}	0.5 *

The initial values were adjusted by the program for subsequent runs of OVER, new frequencies calculated and compared to the observed frequencies. This process was repeated as many times as necessary to obtain a reasonable fit between calculated and observed frequencies. The required number of such perturbations was input to the program for each run. The number of cycles generally used was five, as it was more efficient to alter the input with updated force constants than allow a large number of perturbations to be run, as the adjusted force constants were sometimes given inappropriate values by the program. The decision as to whether or not the values were inappropriate was subjective and based on the following assumptions; stretching force constants were expected to be within the range 1 to 7 mdyneÅ^{-1}; stretching force constants were assumed to be larger than bending force constants; and bending force constants and non-bonded force constants were expected to be less than 2mdyneÅ^{-1}. Literature values from Bucker and Nielsen (1963), Shimanouchi (1963), Overend and Scherer (1960), and Naito et al. (1955) suggest that these are reasonable assumptions.

In order to compare calculated and observed frequencies, the observed frequencies must be assigned to the correct fundamental mode. The assignment of a frequency taken from an infrared spectrum is a difficult task, and the results from the literature may not always be correct. Complete assignments for all the molecules could not be found in the literature, and so some tentative assignments were made as part of this work and, initially, some observed frequencies were omitted.

Table 5.3. Initial values of the observed frequencies for the UB calculations, in symmetry group sequence.

Molecule		Observed frequencies cm^{-1}	Reference
CFC110	D_{3d}	978,432,169,-, 679,375, 858,858,341, 341,224,224, 780,780,278,278,115,115	Tanabe & Saëki 1972
CFC111	C_s	1101,1009,847,725,508,407,382,314,281,227,174, 883,796,395,314,266,174,77	Nielsen et al. 1953 a
CFC112	C_{2h}		not available
CFC112a	C_s	1111,1027,847,775,627,525,446,420,331,231,165, 1165,844,456,331,268,183,81	Nielsen et al. 1953 a
CFC113	C_1	1212,1119,1047,-,909,816,632,532,460, 442,391,350,309,288,240,203,168,80	Klaboe & Nielsen. 1961
CFC113a	C_{3v}	1255,909,714,430,260, 1225,1225,859,859,563, 563,366,366,265,265,182,182,-	Bürger et al. 1980
CFC114	C_{2h}		not available
CFC114a	C_s	1295,1232,1110,943,735,590,507,399,311,265,20 0,1232,897,560,399,330,181,-	Nielsen et al. 1953 b
CFC115	C_s	1351,1224,1133,982,762,648,560,441,362,314,18 6,1241,1185,596,454,331,186,-	Nielsen et al. 1953 b
FC116	D_{3d}	1417,808,348,-,1117,714, 1250,1250,619, 619,372,372, 1251,1251,523,523,216,216	Bucker& Nielsen 1963
HFC170	D_{3d}	2954,1388,995,289,2954,1379,2969,2969,1460, 1460,1190,1190,2996,2996,1486,1486,820,820	Tanabe & Saëki 1972
HFC161	C_s	3003,2941,2915,1479,1449,1395,1365,1108,1048, 880,415,3003,3003,1449,1277,1048,810,243	Chen et al. 1975
HFC152	C_{2h}	2962,1416,1079,1049,858,804,2994,1415,320,-, 2990,1285,450,2951,1376,1065,897,652	Klaboe & Nielsen 1960
HFC152a	C_s	3018,2978,2960,1460,1414,1372,1143,1129,868, 571,470,3001,1460,1360,1171,930,383,222	Chen et al. 1975
HFC143	C_1	3005,2986,2978,1465,1433,1379,1319,1249,1152, 1125,1076,-,905,577,476,426,247,117	Kalasinsky et al. 1982
HFC143a	C_{3v}	2975,1408,1280,830,602,220,3035,3035,1443,144 3,1233,1233,970,970,541,541,365,365	Chen et al. 1975
HFC134	C_{2h}	2995,1442,1149,1106,625,362, 1330,1136,212,82, 1365,1081,480, 2995,1320,1125,541,414	Kalasinsky et al. 1982
HFC134a	C_s	2984,1464,1427,1298,1103,972,842,665,549,408, 225, 3013,1374,1182,885,539,352,120	Chen et al. 1975
HFC125	C_s	3008,1393,1309,1218,1111,867,725,577,523,361, 246,1359,1198,1145,508,413,216,82	Chen et al. 1975

During subsequent runs of the program OVER, some assignments were altered when it was found that the calculated values were not in agreement with the observed values, and it was possible to interchange two or more observed values for a better fit. This could only be done if the constraints of matching the frequency to a particular mode were maintained, for example, in the case of C_{2h}, the A_g and B_g vibrations are infrared inactive and so could not be exchanged with observed values for the A_u and B_u modes. The initial values for the observed frequencies input to the program are given in table 5.3. The altered assignments, along with new assignments made in this part of the work are presented with the results of the calculations in chapter six. With new or altered assignments, experimental data from this work were used for the observed frequencies, however, this could only be done if the observed band was of a simple structure with no overlapping bands, since difficulties were encountered in locating the exact band centre of complex bands. For ambiguous results, the frequencies calculated using the *ab initio* methods were used to assist in assignments; appropriate changes made to the UB input data; and the UB calculations repeated.

The construction of the Z matrix was facilitated by the fortran program CALST, written specifically for use in this work. A listing of CALST is given in appendix D. Using the formulae given in the publication by Overend and Scherer (1960), values for the coefficients of Z were calculated. The input to CALST consisted of the bond lengths, and angles for each molecule, as given in table 5.1, and the non-bonded distances between two atoms i and j attached to an atom k. CALST computed all possible values for s and t where,

$$s_{ij} = \frac{r_i - r_j\cos\alpha_{ij}}{q_{ij}} \quad \text{and} \quad t_{ij} = \frac{r_j\sin\alpha_{ij}}{q_{ij}} \quad \text{(Overend \& Scherer 1960)}$$

for i=1 to 8 and j=1 to 8 representing all the atoms within the molecule. The coefficients for each of the atoms i and j bonded to a common atom k were calculated using definitions given in table 5.4 . For this work, it was assumed that the contribution to the force field by forces between atoms more than two bonds apart was negligible.

Table 5.4. Contributions to the UB Z matrix as given by Overend and Scherer (1960) for the atoms i and j bonded to the common atom k.

f vector	coefficients for F_{ij}	coefficients for F'_{ij}
$(\Delta r_i)^2$	s_{ij}^2	t_{ij}^2
$(\Delta r_j)^2$	s_{ji}^2	t_{ji}^2
$(r_i\Delta\alpha_{ij})^2$	$t_{ij}t_{ji}\left(\frac{r_j}{r_i}\right)$	$-s_{ij}s_{ji}\left(\frac{r_j}{r_i}\right)$
$(\Delta r_i\Delta r_j)$	$s_{ij}s_{ji}$	$-t_{ij}t_{ji}$
$(\Delta r_i r_i\Delta\alpha_{ij})$	$s_{ij}\sqrt{t_{ij}t_{ji}}\sqrt{\frac{r_j}{r_i}}$	$t_{ij}s_{ji}\left(\frac{r_j}{r_i}\right)$
$(\Delta r_j r_i\Delta\alpha_{ij})$	$s_{ji}\sqrt{t_{ij}t_{ji}}\sqrt{\frac{r_j}{r_i}}$	$t_{ji}s_{ij}$

The program CALST calculated each of the values given in table 5.4 for each s and t. The resultant Z matrix coefficients were then printed out for each molecule, and subsequently entered into the data input stream for OVER, as required by the Z matrix, relating each non-bonded interaction to each pair of coordinates in turn, for the F and F' force constants. The diagonal force constants K_i and H_{ij} are each represented by a coefficient of 1 in the Z matrix, in the appropriate diagonal element.

The general format of the input data for OVER follows, with the format of each input line given in bold type. In order to find a set of force constants which would give reasonable values for calculated frequencies across a group of molecules as well as for individual compounds, OVER was executed in two different ways. Initially, one set of force constants was used with the frequency data for all CFCs or HFCs and refined until the lowest possible errors in all the calculated frequencies for the group were obtained. Secondly, the same initial set of force constants was used for individual compounds and refined as before. In this way it was possible to see the changes in force constants across a group and to enable any trends in force constants with changes in the number or position of fluorine atoms to be detected. The compounds were divided into four groups, in ascending numbers of fluorine atoms.

Group 1. CFC110, CFC111, CFC112, CFC113, CFC114, CFC115, FC116
Group 2. CFC110, CFC111, CFC112a, CFC113a, CFC114a, CFC115, FC116
Group 3. HFC170, HFC161, HFC152, HFC143, HFC134, HFC125, FC116
Group 4. HFC170, HFC161, HFC152a, HFC143a, HFC134a, HFC125, FC116

The detailed input for the initial run of the program for the individual molecules is given in appendix B.

1 nfffaaaooopppp 1 1 1 0 0 1 0 0 0 1 0 1 0 0 0

The first line is known as the problem control record. The first digit, in column 6, is the number of the problem (1); n gives the number of different molecules to be used for the set of force constants given, n=7 for a group fit where the input stream includes the frequencies and Z matrices for all seven molecules or n =1 for an individual fit, and only one set of frequencies and one Z matrix follow; fff gives the total number of force constants supplied; aaa gives the number of force constants to be adjusted; ooo gives the number of observed frequencies (18); ppp gives the number of perturbations or cycles for this run; the remaining digits denote the following, in sequence; 1 - intermediate results to be printed; 1 - perturbation required; 1 - force constants to be adjusted; 0 - no weighting elements; 0 - use default convergence constants; 1 - output of FB matrix; 0 0 0 - no related force constants; 1 - F matrix output required; 0 follows; 1 - output new force constants; 0 - default convergence; 0 - no restarts; 0 - output to terminal.

Molecule name

date

Two comment lines, usually containing the molecule name and the date.

xxxxx.xxxxxxyyyyy.yyyyyy...

The next lines of input consist of a block of force constants in mdyneÅ^{-1}, six per line, in the sequence, all K's, all H's, then pairs of F,F'.

aaabbbcccddd......

A line of integers, denoting the force constants to be adjusted. The force constants are numbered in ascending order as they are input.

CX_3CX_3

This line gives the molecular formula.

1 22 18 ff s

This parameter line gives the following information; 1 = number of isotopes; 22 = number of internal coordinates; 18 = number of symmetry coordinates without redundancies; ff = number of force constants; s = number symmetry blocks.

aaabbbcccddd......

The dimension of each symmetry block is given in three column fields in the order of the symmetry blocks used in NORCORD.

aaabbbcccddd......

A line of three column field integers in ascending order from 1 to the number of force constants used.

xxxxx.xxxxxx.....
xxxxx.xxxxxx.....
xxxxx.xxxxxx.....

Three lines of input for the eighteen observed frequencies, six per line in decreasing order within each symmetry block. Unknown frequencies are entered as zero, in the correct position.

rrrcccfffxx.xxxxxx.....

Input lines for the Z matrix contain four entries per line in fixed format , as follows: rrr = F matrix row number; ccc = F matrix column number (ccc is not less than rrr since F is a symmetric matrix); fff = number of the force constant (from the sequence given above) and xx.xxxxxx = the relevant coefficient calculated by CALST. Termination of the Z matrix input is indicated by rrr = -4.

For group output, lines starting with the molecular formula input line are repeated for each molecule in the group, so that the same set of force constants is used for each set of frequencies and Z matrix. When OVER begins, the names of all the required W matrices are requested interactively.

The output from the program includes the refined force constants, calculated frequencies and potential energy distributions. The entire output for all four groups and nineteen individual molecules is not presented in this work, however, all relevant results are given in chapter six. The potential energy distributions in matrix form are presented in appendix E.

5.2. *Ab initio* calculations.

Many different methods of calculation are available when using the program GAUSSIAN92 (Foresman & Frisch 1993), however the choice of method used in this work was governed primarily by the availability of computer time. The Hartree-Fock theoretical method with the basis set 6-31G* was used on the RISC processor at ADFA, and the Møller-Plesset theoretical method with the basis set 6-31G* was used on the Fujitsu vector processor at the ANU, as the latter method takes considerably more computer time. A geometry optimisation was carried out for each molecule to locate minima on the potential energy surface and hence to predict the equilibrium structure for each molecule. *Ab initio* frequency calculations are only valid at stationary points on the potential energy surface (Foresman & Frisch 1993), thus it was necessary to optimise the molecular structure first.

Experimental bond lengths and angles were required for each molecule as a starting point for the optimisation, the values used are presented in table 5.1. Experimental geometries were obtained from a number of different sources, as indicated in table 5.1. When no data for an individual molecule were available, bond lengths and angles from similar molecules were used. When no values for angles were available, the tetrahedral angle was used, since both carbons may be considered to be approximately tetrahedral.

5.2.1. Data input for the program GAUSSIAN92

GAUSSIAN92 was run as a two step job, a geometry optimisation followed by frequency calculations. The computer input for each molecule was similar and followed the general description given here. The exact input for each molecule is given in appendix C. Computer input lines are shown in bold type. The general format of the input lines is as follows:

%chk=cfcxxx

This line initialises a checkpoint file to hold the output from the optimisation step, for use in the frequency calculation step. Checkpoint files have been named cfcxxx or hfcxxx where xxx is the halocarbon number of the molecule.

 # rhf/6-31G*   Opt test

This input line, known as the route section indicates to GAUSSIAN92 that a restricted Hartree-Fock calculation using the basis set 6-31G* for geometry optimisation is required. Full optimisation was not used as the molecules were taken as being in the 'trans' configuration, which sometimes forced them into a symmetry group different to that selected by the program for full optimisation. The parameter 'test' indicates to the program that the results are not to be stored in the GAUSSIAN92 archives. This input line must be followed by a blank line.

```
cfcxxx  optimisation
```

A comment line, followed by a blank line.

```
0 1
```

These values give the charge and spin multiplicity respectively. For a neutral molecule in a singlet state, which applies to all the molecules studied here, the charge is zero and the multiplicity is one.

```
C1
C2  C1   cc
X1  C1   cx1  C2   ccx1
X2  C1   cx2  C2   ccx2  X1   dx1
X3  C1   cx3  C2   ccx3  Xn   dx2
X4  C2   cx4       C1    ccx4  Xn   dx3
X5  C2   cx5       C1    ccx5  Xn   dx4
X6  C2   cx6       C1    ccx6  Xn   dx5
```

This is a list of approximate dimensions for the atoms within the molecules, known as the Z matrix. C1 and C2 represent the two carbon atoms, present in all the molecules, and Xn represents the remaining atoms F, H or Cl, depending on the molecule. The internuclear distances are given by cc for the distance C1 to C2, and cxn for the distances C1 to Xn, or C2 to Xn. From row three onwards, the third atom in the row allows the angle between the atoms to be input as ccxn, for example, ccx1 is the angle formed by X1-C1-C2. To complete the definition of the molecule, for line 4 onward, the dihedral angle must be entered, shown as dxn. This angle is defined as the angle between atom 1 and atom 4 in the input row, when viewed along the C1-C2 axis. Atom 4 may be any of the atoms X1 to X5 provided that it has already been defined in the Z matrix. Dihedral angles are shown in figure 5.2 using Newman projections. Positive dihedral angles correspond to a clockwise rotation in the Newman projection. It should be noted that for this work, all molecules are assumed to be in the 'trans' position, and the dihedral angles have been calculated accordingly. For some molecules, a different numbering sequence has been used for the atoms attached to the carbon atoms. This occurred as the numbering sequence was taken from the UB calculations, and not all the calculations were done at the same time. This has no effect on the results, as the correct dihedral angles for each case have been used.

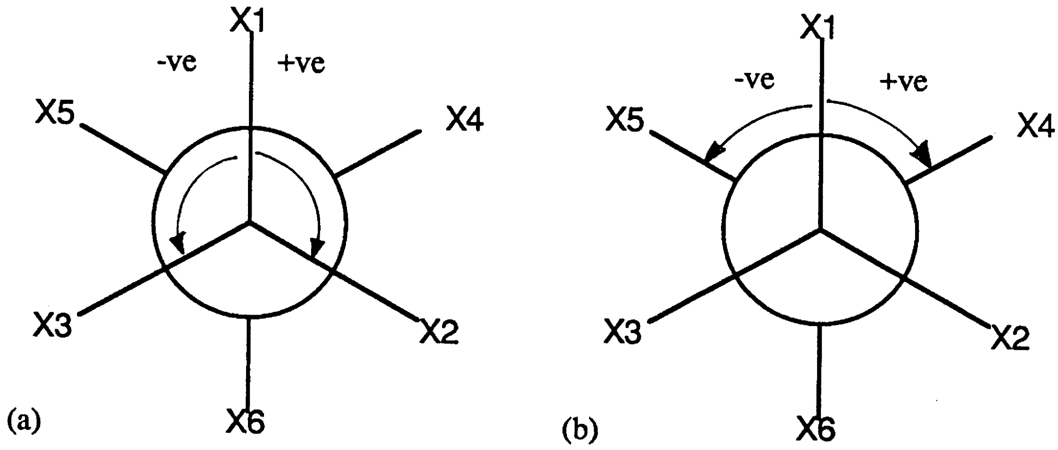


Figure 5.2. Dihedral angles when viewed along the C1-C2 axis (a) between atoms joined to the same carbon, and (b) between atoms joined to different carbons.

The variables cc, cxn, ccxn and dxn may be used as defined below, or may be numeric values. It is usual to omit '1' from X1, cx1, ccx1 and dx1. This block of information is followed by a blank line.

cc=x.x

cxn=x.x

ccxn=xxx.x

dxn=xxx.x

A list of variables is entered next, giving the initial value for each length in ångstroms or angle in degrees. More than one decimal place may be entered if available. For molecules with some symmetry, the same variable may be used on more than one input line of the Z matrix. In this way, the program can optimise the values and still retain the symmetry of the molecule, for example, if the bonds C1-X2, C1-X3 and C2-X4 are equivalent the variables cx2, cx3 and cx4 can be replaced by the one variable cx2 so that this length will apply to all the bonds for which cx2 was defined. When two different bonds or angles have the same value, it is necessary to slightly change the variables so that the program does not interpret such cases as imposing symmetry constraints (Foresman & Frisch 1993), for example, when using the tetrahedral angle for different bonds, it should be entered as ccx1=109.40, ccx2=109.45, ccx3=109.50 where cx1≠cx2≠cx3. The block of variables is followed by a blank line.

dxn=xxx.x

For the partial optimisation used, this section, known as the constants section, includes variables which remain constant throughout the optimisation. In particular, for ethane-type molecules used in the 'trans' position, it is usual for the dihedral angle between atom X1 and atom X6 to be 180.0 degrees as shown in figure 5.2. This block is followed by a blank line.

```
--Link1--
```

This line lets the program know that the second step follows.

```
%chk=cfcxxx
```

The checkpoint file created in the last step is identified for use by the frequency calculations.

```
# rhf/6-31G* freq geom=checkpoint  test
```

The second route section initiates the frequency calculation step. Geom=checkpoint indicates that the optimised geometry for input to the frequency calculation can be found in the checkpoint file.This line is followed by a blank line.

```
cfcxxx hf/6-31G* freq vibxxx
```

A comment line, followed by a blank line. The file vibxxx contains the data for input to GAUSSIAN92.

```
0 1
```

Again, the spin and multiplicity are entered, followed by a blank line to terminate the job.

For comparison, calculations for the first four of the HFCs listed were made using the Møller-Plesset theoretical method. Computer time was not available to compute the frequencies for the other molecules using this method. The first four HFCs were selected as they contain the least number of electrons and therefore use the least amount of computer time. The input data is the same, except for the two route sections (lines beginning with #). For the optimisation the route input line is

```
# mp2=fulldirect/6-31G* Opt test
```

and for the frequency step,

```
# mp2=fulldirect/6-31G* freq geom=checkpoint guess=checkpoint scf=
direct test
```

The parameters 'guess' and 'scf', and the parameter options 'fulldirect' and 'direct', are used to minimise time and disk space.

The entire output for all nineteen molecules from GAUSSIAN92 is not presented in this work, however, all relevant results are given in chapters six and seven.

Chapter 6

Assignments of frequencies and resultant force constants.

In this chapter, the final results of the calculations of fundamental vibrational frequencies and force constants are tabulated. Some tentative assignments of vibrational modes have been made for comparison with the calculated values. Changes in force constants with changes in the number and position of fluorine atoms are discussed in section 6.2.

6.1 Fundamental frequencies and assignments.

In order to carry out the *ab initio* calculations, only the experimental geometry for each molecule was required. The Urey-Bradley (UB) force field calculations needed, in addition, the values of observed fundamental frequencies. In some cases this caused difficulties, as complete assignments for all the molecules could not be found in the literature. Initially, the available assignments were used, as shown in tables 6.1 to 6.19, and these were amended, where possible, when large discrepancies between the UB results, the *ab initio* results and the literature values were found. In the case of the unassigned modes, frequencies were taken from the spectra recorded as part of this work or from literature sources, if it was possible to attribute them to fundamental modes. As reported in chapter four, a detailed investigation of the true centres of the bands was not carried out, so errors of a few wavenumbers may have been introduced by the use of the frequency at which maximum absorbance occurred within a band. In addition to the problem of correct assignments, initial force constants were required. The values used in the UB calculations are given in table 5.2. In order to refine the force constants to obtain the best agreement between the observed and calculated frequencies, the program OVER was executed repeatedly, both for the individual molecules and the groups of molecules discussed in section 5.1.2.

An average percentage difference for all the frequencies for each molecule was calculated. The overall percentage difference between the observed and calculated frequencies for all CFC molecules (including FC116) was 5.33% for the individual calculations and 6.41% for the group calculations. This was found when attempting to fit 170 of the possible 180 frequencies for the ten molecules involved. Similarly, for the nine HFC molecules, the overall difference was found to be 3.93% for the individual calculations and 4.98% for the group calculations. This was for 155 assigned frequencies out of a possible 162. It should be noted that the higher overall error for the CFCs is partly due to the fact that the frequency values are in the range 1500-10cm^{-1}, compared to the range 3100-10cm^{-1} for the HFCs, and a difference of 30 wavenumbers gives an error of 2% for 1500cm^{-1} compared to 1% for 3000cm^{-1}. The average difference for the same frequencies using the results from the Hartree-Fock *ab initio* calculations was 2.07% for the CFCs and 2.12% for the HFCs. *Ab initio* calculations using the theoretical method MP2 gave an average difference of 2.04% for the first four HFC molecules.

For the individual molecules, an exact fit using the UB force field was not sought since too few force constants were used to create the force field exactly. For example, forces for non-bonded interactions may be expected to vary slightly, depending on the neighbouring atoms. However, the number of force constants had to be kept to a minimum as the possibility of more than one solution existed for molecules with more force constants than frequencies. Instead, an individual fit was carried out to see if a better agreement could be found between observed and calculated frequencies by adjusting the group force constants by small amounts. It can be seen from the overall percentage differences that the improvement for the individual molecules was small. Errors may also have been introduced into the calculations by the imposition of symmetry constraints. The individual molecules were placed into a particular symmetry group by the assumption of a staggered configuration. Experimentally, the molecules freely rotate about the C-C axis, and while the staggered configuration may be preferred, some mixing of modes may occur due to the loss of symmetry on rotation.

6.1.1 Results and assignments for each compound.

A discussion of the assignments for each molecule accompanies the relevant table of frequency data given in this section. The columns of the tables 6.1 to 6.19 display the following information:

(a) Observed values with assignments from the literature, given in symmetry block sequence.

(b) Tentative assignments made in this work, or taken from alternative literature sources.

References to the literature used for columns (a) and (b) are given after each table.

Columns (c) to (g) are the same for all the tables, and give the following information:

(c) Calculated frequencies, using a UB force field, obtained by refining individual force constants for the molecule.

(d) Percentage difference between the observed and calculated frequencies using

$$\frac{\text{calc. freq. - obs. freq.}}{\text{obs.freq.}} * 100\%$$

The observed frequency is obtained from column (b) if there is an entry, or column (a) if not.

(e) Calculated frequencies using a UB force field with group force constants. Two sets of group force constants have been derived as part of this work, one for all the CFCs and one for all the HFCs. FC116 is present in all groups. Table 6.10, column (e) gives the results when FC116 is part of the CFC group and column (h) gives the results when it is part of the HFC group.

(f) Scaled calculated frequencies using *ab initio* methods, with the Hartree-Fock theoretical model and the basis set 6-31G*. The scaling factor used is 0.8953 (Scott 1994).

(g) Scaled calculated frequencies using *ab initio* methods, with the Møller-Plesset theoretical model and the basis set 6-31G*. The scaling factor used is 0.9427 (Scott 1994).

(h) Calculated frequencies using a UB force field for FC116 as part of the HFC group.

CFC110.

Table 6.1. Observed frequencies in symmetry group sequence with corresponding calculated values for CFC110. All frequencies are given in cm^{-1}.

Observed frequencies			Urey-Bradley force field calculations				Hartree-Fock/ 6-31G*	
	(a)	(b)	(c)	(d)	(e)	(d)	(f)	(d)
A_{1g}	978		980	0.20	1016	3.89	983	0.51
	432		417	-3.47	424	-1.85	423	-2.08
	169	228	181	-20.6	171	-25.0	218	-4.39
A_{1u}	-	77	77	0.00	77	0.00	83	7.79
A_{2u}	679		731	7.66	720	6.04	676	-0.44
	375		373	-0.53	380	1.33	372	-0.80
E_g	858		1026	19.6	1028	19.8	882	2.80
	858		1026	19.6	1028	19.8	882	2.80
	341		301	-11.7	302	-11.4	335	-1.76
	341		301	-11.7	302	-11.4	335	-1.76
	224		231	3.13	224	0.00	222	-0.89
	224		231	3.13	224	0.00	222	-0.89
E_u	780		787	0.90	802	2.82	793	1.67
	780		787	0.90	802	2.82	793	1.67
	278		294	5.76	297	6.83	276	-0.72
	278		294	5.76	297	6.83	276	-0.72
	115	167	149	-10.8	141	-15.6	163	-2.40
	115	167	149	-10.8	141	-15.6	163	-2.40

(a) Observed values with assignments from Tanabe & Saëki 1972.

(b) Tentative assignments made in this work using data from Woost & Bougeard 1986

The observed fundamental frequencies and the corresponding calculated values for CFC110 are given in table 6.1. The initial frequencies given by Tanabe & Saëki (1972) agreed well with the *ab initio* results except for the lowest A_{1g} and E_u modes. These modes have been attributed to the symmetric deformation and antisymmetric rocking of the CCl_3 groups respectively by Woost and Bougeard (1986), who suggest that the A_{1g} can be assigned to a frequency of 228cm^{-1}, and the E_u to 167cm^{-1}. While these assignments are in better agreement with the HF results, it was not possible to obtain similar values using the UB calculations. The torsional frequency of 77cm^{-1} observed by Woost and Bougeard (1986) is slightly lower than the HF value, but is in agreement with the UB result. Some calculated results were found in the literature (Carney et al. 1961) but are generally lower than the results given here, so they have not been included.

The largest discrepancy in the UB calculations was found in the highest E_g at 858cm^{-1} (Tanabe & Saëki 1972). The potential energy results, given in appendix E, suggest that this mode is due to a C-Cl stretch, with some contribution from a CCl_3 deformation. While this is essentially in agreement with Woost and Bougeard (1986), a considerable number of force constant refinements could not reduce the UB value without greatly increasing the errors in the other frequencies. The large difference between 858cm^{-1} and 1026cm^{-1} shown in table 6.1 may be attributed to the inadequacy of the UB potential as suggested by Bucker and Nielsen (1963), particularly as in this work, no consideration has been taken of the possible interaction between chlorine atoms attached to different carbon atoms.

CFC111.

The observed fundamental frequencies and the corresponding calculated values for CFC111 are given in table 6.2. The initial assignments used were taken from Nielsen et al. (1953 a) where frequencies were obtained using the compound as a solid glass and in CS_2 solution. This introduces discrepancies between the observed and calculated frequencies as the latter are calculated for an isolated molecule. Since no further literature references were found for the assignments, the spectrum of CFC111 recorded as part of this work was compared to that of Nielsen et al. (1953 a) and tentative values were obtained for the vapour phase.

For the fundamentals between 1120 and 500cm^{-1} the bands were well defined, except in the case of the band centred at 889cm^{-1}. This value may only be considered accurate within a few wavenumbers as a close inspection of the spectrum did not conclusively give the band centre.

Nielsen et al. (1953 a) expressed some doubt that 314cm^{-1} represented the coincidence of two fundamentals, and the HF results suggest that it may be due to the

A" CCl_3 deformation. This is confirmed by the UB results. The subsequent reassignment of the 266cm^{-1} rocking mode as A' and the possibility that 227cm^{-1} represents a superposition of A' and A" modes, leads to good agreement with the HF calculations. Comparatively large errors occur in the UB frequencies around 459cm^{-1}, 329cm^{-1}, 191cm^{-1}, 356cm^{-1} and 141cm^{-1} which cannot be satisfactorily explained, however, the difference in wavenumbers between the observed and calculated values is in the order of 30-50cm^{-1} which is acceptable for this level of calculations.

Table 6.2. Observed frequencies in symmetry group sequence with corresponding calculated values for CFC111. All frequencies are given in cm^{-1}.

	Observed frequencies		Urey-Bradley force field calculations				Hartree-Fock/ 6-31G*	
	(a)	(b)	(c)	(d)	(e)	(d)	(f)	(d)
A'	1101	1114†	1137	2.06	1203	7.99	1155	3.68
	1009	1018†	1015	-0.29	1038	1.96	1035	1.67
	847	856†	882	3.04	903	5.49	860	0.47
	725	731†	739	1.09	742	1.50	723	-1.09
	508	507†	459	-9.47	487	-3.94	493	-2.76
	407		397	-2.46	405	-0.49	401	-1.47
	382		329	-13.9	333	-12.8	378	-1.05
	314	281*	297	5.69	300	6.76	281	0.00
	281	266*	261	-1.88	263	-1.13	262	-1.50
	227		191	-15.9	186	-18.1	221	-2.64
	174		156	-10.3	152	-12.6	171	-1.72
A"	883	889†	1042	17.2	1063	19.6	919	3.37
	796	810†	820	1.23	837	3.33	816	0.74
	395		356	-9.87	383	-3.04	390	-1.27
	314		299	-4.78	298	-5.10	311	-0.96
	266	227*	239	5.29	235	3.52	229	0.88
	174		141	-19.0	137	-21.3	161	-7.47
	77		76	-1.30	72	-6.49	79	2.60

(a) Observed values with assignments from Nielsen et al. 1953 a.

(b) Tentative assignments using † experimental data obtained in this work, and * reassigned values from Nielsen et al. 1953 a.

A problem arises in the antisymmetric C-Cl stretch at 889cm^{-1}. The HF results confirm this assignment, but the UB values are very high at 1042cm^{-1} and 1063cm^{-1} for the individual and group results respectively. It is likely, as in the case for CFC110, that the UB potential used here is inadequate to fully account for the interaction of the heavy chlorine atoms.

CFC112.

The observed fundamental frequencies and the corresponding calculated values for CFC112 are given in table 6.3. A complete assignment of CFC112 could not be found in the literature, however, some Raman and infrared frequencies were given by

Kagarise and Daasch (1955) and were used with one experimental value from this work. Initially, no observed values were used for the UB calculations so no force constant refinement could be carried out, however, a rough comparison of calculated and observed values could be made. For the purpose of these calculations it was assumed that the molecule exists in the staggered configuration with the fluorine atoms in the 'trans' position, placing the molecule in the C_{2h} symmetry group. This assists with the assignments of the vibrational modes, as it is expected that the classes A_g and B_g are Raman active only, and A_u and B_u are infrared active only (Kagarise and Daasch 1955). Tentative assignments were made for some of the modes, and used in subsequent UB calculations to enable a force constant refinement to be carried out. A reasonable agreement was obtained between the observed and calculated values, although only 12 observed frequencies were used.

Table 6.3. Observed frequencies in symmetry group sequence with corresponding calculated values for CFC112. All frequencies are given in cm^{-1}.

Observed frequencies		Urey-Bradley force field calculations				Hartree-Fock /6-31G*	
(a)	(b)	(c)	(d)	(e)	(d)	(f)	(d)
A_g	1141†	1200	5.17	1245	9.11	1205	5.61
	1045†	1052	0.67	1061	1.53	1084	3.73
	587†	524	-10.7	535	-8.86	567	-3.41
	411†	361	-12.2	360	-12.4	406	-1.22
	297†	295	-0.67	295	-0.67	292	-1.68
		182		180		225	
A_u	844*	874	3.55	883	4.62	842	-0.24
	375†	378	0.80	382	1.87	373	-0.53
		135		134		160	
		73		77		72	
B_g		1074		1079		925	
	400†	377	-5.75	382	-4.50	388	-3.00
		248		246		254	
B_u	1136†	1064	-6.34	1120	-1.41	1173	3.26
	752†	761	1.20	760	1.06	749	-0.40
	473†	459	-2.96	465	-1.69	459	-2.96
	293†	304	3.75	303	3.41	291	-0.68
		199		198		198	

(a) No complete set of assigned frequencies was found in the literature.

(b) Tentative assignments from the results † given in Kagarise & Daasch 1955 , and * experimental values from this work.

Where no observed frequency was available, a comparison between the results for the two types of calculation shows a good agreement, except in the case of the highest B_g mode. The UB value of 1074cm^{-1} does not correspond well with the 925cm^{-1} from the HF calculations. No experimental data could be found to agree with either of these values.

CFC112a.

The observed fundamental frequencies and the corresponding calculated values for CFC112a are given in table 6.4. The initial assignments were taken directly from the publication by Nielsen et al. (1953 a). The observed frequencies given were obtained using a liquid sample, so the results are not expected to match exactly. Some doubt is expressed by Nielsen et al. (1953 a) about the weak band at 525cm^{-1}, and removal of this as a fundamental gives a good agreement between the observed and HF values, with the exception of the C-F stretching mode at 1111cm^{-1}. Nielsen et al. (1953 a) stated that the band at 1111cm^{-1} could be regarded as a combination band, which may account for the discrepancy, however, there is no band in the region of 1200cm^{-1} which could be assigned to this mode.

The UB results are somewhat lower than the newly assigned values, however, they are closer to these values than to the original frequencies suggested by Nielsen et al. (1953 a).

Table 6.4. Observed frequencies in symmetry group sequence with corresponding calculated values for CFC112a. All frequencies are given in cm^{-1}.

	Observed frequencies		Urey-Bradley force field calculations				Hartree-Fock /6-31G*	
	(a)	(b)	(c)	(d)	(e)	(d)	(f)	(d)
A'	1111		1170	5.31	1209	8.82	1202	8.19
	1027		1075	4.67	1085	5.65	1058	3.02
	847		894	5.55	898	6.02	870	2.72
	775		793	2.32	794	2.45	780	0.65
	627		589	-6.06	600	-4.31	612	-2.39
	525	446	416	-6.73	420	-5.83	435	-2.47
	446	420	391	-6.90	398	-5.24	412	-1.90
	420	331	304	-8.16	303	-8.46	326	-1.51
	331	-	261		259		258	
	231		211	-8.66	209	-9.52	227	-1.73
	165		143	-13.3	143	-13.3	160	-3.03
A"	1165		1218	4.55	1268	8.84	1227	5.32
	844		899	6.52	903	6.99	862	2.13
	456		416	-8.77	425	-6.80	447	-1.97
	331		333	0.60	333	0.60	327	-1.21
	268		285	6.34	282	5.22	265	-1.12
	183		180	-1.64	178	-2.73	179	-2.19
	81		80	-1.23	70	-13.6	81	0.00

(a) Observed values with assignments from Nielsen et al. 1953 a.

(b) Tentative assignments made in this work using observed frequencies from Nielsen et al. 1953 a.

CFC113.

The observed fundamental frequencies and the corresponding calculated values for CFC113 are given in table 6.5. The initial assignments were taken directly from the publication by Klaboe and Nielsen (1961). The UB calculations were carried out assuming a staggered configuration for the molecule such that there is no symmetry. Klaboe and Nielsen (1961) reported some difficulty in assigning the observed frequencies, however, they divided the frequencies into two groups, since the staggered molecule may exhibit either C_s or C_1 symmetry depending on the relative positions of the atoms about the C-C bond. They were unable to specify which of the two groups was C_1, however, by comparison with the HF results, one of the groups was selected and the assignments used in this work.

Table 6.5. Observed frequencies in symmetry group sequence with corresponding calculated values for CFC113. All frequencies are given in cm^{-1}.

	Observed frequencies		Urey-Bradley force field calculation				Hartree-Fock /6-31G*	
	(a)	(b)	(c)	(d)	(e)	(d)	(f)	(d)
A	1212	1214	1275	5.02	1292	6.43	1249	2.88
	1119	1180	1213	2.80	1214	2.88	1234	4.58
	1047	1119	1122	0.27	1130	0.98	1157	3.40
	-	1045	1111	6.32	1094	4.69	1080	3.35
	909		963	5.94	955	5.06	914	0.55
	816		826	1.23	816	0.00	811	-0.61
	632		613	-3.01	611	-3.32	640	1.27
	532		506	-4.89	502	-5.64	521	-2.07
	460		437	-5.00	434	-5.65	450	-2.17
	442		410	-7.24	407	-7.92	433	-2.04
	391		384	-1.79	379	-3.07	387	-1.02
	350		363	3.71	356	1.71	346	-1.14
	309		310	0.32	303	-1.94	306	-0.97
	288		293	1.74	286	-0.69	285	-1.04
	240		222	-7.50	217	-9.58	236	-1.67
	203		201	-0.99	196	-3.45	197	-2.96
	168		150	-10.7	147	-12.5	162	-3.57
	80		78	-2.50	70	-12.5	73	-8.75

(a) Observed values with assignments from Klaboe and Nielsen 1961.

(b) Tentative assignments made in this work using data from Varanasi and Chudamani 1988.

A good agreement was found between the HF and observed frequencies, except for the four highest values. Tentative assignments for these modes have been made using frequencies from Varanasi and Chudamani (1988), and while they are closer to the HF values, the percentage differences are still larger than expected.

The UB results show similar discrepancies to those for the other molecules under investigation, where some of the lower frequencies due to end group deformations are somewhat smaller than the observed and HF results.

CFC113a.

The observed fundamental frequencies and the corresponding calculated values for CFC113a are given in table 6.6. The assignments suggested by Bürger et al. (1980) agree well with the HF results, except in the case of the degenerate C-F stretching mode at 1225cm^{-1}. The calculated value was found to be higher for both types of calculation, however, from the spectrum shown in figure 4.5, it can be seen that the assignment of the very strong band at 1225cm^{-1} is most likely correct.

No observed frequency value for the torsional mode was found in the literature. The HF result of 83cm^{-1} is similar to the torsional frequencies for the other molecules, but the UB results are rather higher than might be expected.

Table 6.6. Observed frequencies in symmetry group sequence with corresponding calculated values for CFC113a. All frequencies are given in cm^{-1}.

	Observed frequencies		Urey-Bradley force field calculations				Hartree-Fock /6-31G*	
	(a)	(b)	(c)	(d)	(e)	(d)	(f)	(d)
A_1	1255		1208	-3.75	1170	-6.77	1266	0.88
	909		890	-2.09	884	-2.75	909	0.00
	714		656	-8.12	655	-8.26	698	-2.24
	430		417	-3.02	412	-4.19	418	-2.79
	260		235	-9.62	226	-13.1	255	-1.92
A_2	-		96		195		83	
E	1225		1309	6.86	1335	8.98	1277	4.24
	1225		1309	6.86	1335	8.98	1277	4.24
	859		905	5.36	901	4.89	865	0.70
	859		905	5.36	901	4.89	865	0.70
	563		547	-2.84	545	-3.20	547	-2.84
	563		547	-2.84	545	-3.20	547	-2.84
	366		343	-6.28	343	-6.28	360	-1.64
	366		343	-6.28	343	-6.28	360	-1.64
	265		282	6.42	276	4.15	262	-1.13
	265		282	6.42	276	4.15	262	-1.13
	182		185	1.65	181	-0.55	177	-2.75
	182		185	1.65	181	-0.55	177	-2.75

(a) Observed values with assignments from Bürger et al. 1980.

(b) No alternative assignments were made as part of this work.

CFC114.

The observed fundamental frequencies and the corresponding calculated values for CFC114 are given in table 6.7. As for CFC112, no complete set of assignments could be found in the literature. After an initial set of calculated frequencies were obtained using the UB method, an attempt was made to assign the frequencies given by Kagarise (1957), and Brown et al. (1967) by comparing values with both the UB and the HF results. When considering the staggered conformation, with the chlorine atoms in the 'trans' position, the molecule belongs to the symmetry group C_{2h}. This assists in the assignments as the A_g and B_g classes are exclusively Raman active, and the A_u and B_u classes are infrared active only.

Tentative assignments are given in column (b) in table 6.7. No observed Raman frequencies were found for the highest A_g and B_g modes. These modes can be attributed to the symmetric and antisymmetric C-F stretching modes respectively. The results for the two methods of calculation differ considerably for some modes, and in some cases the difference cannot be attributed to an incorrect assignment, for example, in the case of the observed band at 1112cm^{-1}, the UB result is higher at 1156cm^{-1}, whereas the HF result is lower at 1098cm^{-1}.

Table 6.7. Observed frequencies in symmetry group sequence with corresponding calculated values for CFC114. All frequencies are given in cm^{-1}.

Observed frequencies		Urey-Bradley force field calculations				Hartree-Fock /6-31G*	
(a)	(b)	(c)	(d)	(e)	(d)	(f)	(d)
A_g	-	1263		1236		1308	
	1112†	1156	3.96	1123	0.99	1098	-1.26
	700†	642	-8.29	631	-9.86	693	-1.00
	448‡	427	-4.69	413	-7.81	437	-2.46
	363‡	324	-10.7	319	-12.1	352	-3.03
	254‡	223	-12.2	215	-15.4	250	-1.57
A_u	1241†	1185	-4.51	1181	-4.83	1233	-0.64
	382‡	412	7.85	408	6.81	365	-4.45
	230‡	240	4.35	246	6.96	212	-7.83
	67‡	69	2.99	76	13.4	67	0.00
B_g	-	1303		1307		1228	
	543‡	459	-15.5	461	-15.1	534	-1.66
	326‡	343	5.21	343	5.21	318	-2.45
B_u	1185*	1137	-4.05	1123	-5.23	1158	-2.28
	847*	854	0.83	836	-1.30	849	0.24
	616*	586	-4.87	580	-5.84	594	-3.57
	438‡	409	-6.62	394	-10.1	429	-2.05
	167‡	160	-4.19	156	-6.59	166	-0.60

(a) No complete set of assigned frequencies were found in the literature.

(b) Tentative assignments using data from † Kagarise 1957 ,

‡ Brown et al. 1967 and * experimental results obtained in this work.

It is possible that some assignments are incorrect, for example, the observed frequency at 616cm^{-1} is higher than both the UB result at 586cm^{-1} and the HF result at 594cm^{-1}. Since the HF results have corresponded reasonably well for many of the other molecules, the assignments of observed frequencies which differ substantially from the HF results must be in doubt. This applies particularly to the observed frequencies at 382cm^{-1} and 230cm^{-1} with percentage differences of -4.45% and -7.83% respectively. However, since the assignment of lower frequencies to these two modes would increase the error for the UB calculations, the tentative assignments given in column (b) table 6.7 have been retained.

CFC114a.

The observed fundamental frequencies and the corresponding calculated values for CFC114a are given in table 6.8.

Table 6.8. Observed frequencies in symmetry group sequence with corresponding calculated values for CFC114a. All frequencies are given in cm^{-1}.

Observed frequencies		Urey-Bradley force field calculations				Hartree-Fock /6-31G*	
(a)	(b)	(c)	(d)	(e)	(d)	(f)	(d)
A' 1295		1320	1.93	1340	3.47	1322	2.08
1232		1249	1.38	1203	-2.35	1282	4.06
1110		1131	1.89	1138	2.52	1148	3.42
943		911	-3.39	900	-4.56	943	0.00
735		658	-10.5	664	-9.66	720	-2.04
590		545	-7.63	550	-6.78	577	-2.20
507		506	-0.20	498	-1.78	492	-2.96
399		378	-5.26	375	-6.02	395	-1.00
311		314	0.96	304	-2.25	304	-2.25
265		259	-2.26	256	-3.40	259	-2.26
200		202	1.00	197	-1.50	194	-3.00
A" 1232		1312	6.49	1327	-7.71	1276	3.57
897		975	8.70	964	7.47	918	2.34
560		542	-3.21	547	-2.32	546	-2.50
399		384	-3.76	379	-5.01	390	-2.26
330		332	0.61	340	3.03	323	-2.12
181		180	-0.55	174	-3.87	178	-1.66
-		64		64		74	

(a) Observed values with assignments from Nielsen et al. 1953 b.

(b) No changes in the assignments were made in this work.

A good agreement was obtained between the HF results and the assignments by Nielsen et al. (1953 b), although the calculated frequencies for the C-F stretching modes are again somewhat higher than expected.

The large discrepancies in the UB results for the C-Cl stretching modes, identified by Nielsen et al. (1953 b) at 735cm^{-1} and 897cm^{-1} cannot readily be explained. In order to keep the total number of force constants less than the number of frequencies, the same non-bonded interaction force constants were associated with the fluorines at both ends of the molecule. This may well have introduced errors, since three fluorine atoms are bonded to one carbon, and the fourth fluorine atom shares the other carbon with the two chlorine atoms, hence forces associated with the fourth fluorine atom may be somewhat different to those for the other fluorine atoms.

CFC115.

The observed fundamental frequencies and the corresponding calculated values for CFC115 are given in table 6.9. A reasonable agreement is obtained between the assigned frequencies from the work by Nielsen et al. (1953 (b)) and the HF results. Brown et al. (1967) suggested that the bands at 222cm^{-1} and 185cm^{-1} for the CF_2Cl rocking modes should be designated A' and A" respectively. This is not in agreement with the HF results, hence for the purpose of refining the force constants, the frequencies 222cm^{-1} and 185cm^{-1} were interchanged.

Table 6.9. Observed frequencies in symmetry group sequence with corresponding calculated values for CFC115. All frequencies are given in cm^{-1}.

	Observed frequencies		Urey-Bradley force field calculation				Hartree-Fock /6-31G*	
	(a)	(b)	(c)	(d)	(e)	(d)	(f)	(d)
A'	1351		1327	-1.78	1329	-1.63	1386	2.59
	1224		1270	3.76	1241	1.39	1278	4.41
	1133		1164	2.74	1145	1.06	1147	1.24
	982		977	-0.51	967	-1.53	981	-0.10
	762		682	-10.5	681	-10.6	746	-2.10
	648		617	-4.78	613	-5.40	631	-2.62
	560		541	-3.39	542	-3.21	541	-3.39
	441		441	0.00	418	-5.22	430	-2.49
	362		353	-2.49	360	-0.55	356	-1.66
	314		291	-7.32	295	-6.05	304	-3.18
	186	185	184	-0.54	183	-1.08	179	-3.24
A"	1241		1339	7.90	1356	9.27	1283	3.38
	1185		1211	2.19	1206	1.77	1234	4.14
	596		544	-8.72	546	-8.39	583	-2.18
	454		449	-1.10	452	-0.44	441	-2.86
	331		365	10.3	370	11.8	327	-1.21
	186	222	239	7.66	255	14.9	211	-4.95
	-	70	70	0.00	66	-5.71	68	-2.86

(a) Observed values with assignments from Nielsen et al. 1953 b.

(b) Tentative assignments made in this work using data from Brown et al.1967 .

Raman depolarisation has been frequently used as an aid in the assignment of fundamental frequencies. Totally symmetric modes are expected to have low Raman depolarisation ratios, however, since the molecule is freely rotating about the C-C axis, the symmetry may be reduced, resulting in some mixing of the A' and A" character. This problem occurs for the highest frequencies, since Brown et al. (1967) designated 1241cm^{-1} as A' and 1351cm^{-1} as A". This has been taken from the publication by Risgin and Taylor (1959) which reported Raman depolarisation for the higher frequency only and consequently assigned 1351cm^{-1} as an A" stretching mode. The results for the HF calculations give Raman depolarisation ratios of 0.5778 for 1386cm^{-1} and 0.7500 for 1283cm^{-1}, assigning them to A' and A" respectively. (It should be noted here that the Raman depolarisation values given by the HF calculations are relative, not absolute (Foresman and Frisch 1993)). The UB results do not assist in this assignment, as the two frequencies obtained from the calculations at 1327cm^{-1} and 1339cm^{-1} are relatively close together.

FC116.

The observed fundamental frequencies and the corresponding calculated values for FC116 are given in table 6.10. The assigned frequencies reported by Bucker and Nielsen (1963) are in reasonable agreement with the HF results. The normal vibrations for molecules belonging to the D_{3d} symmetry group are Raman active for the A_{1g} and E_g modes, infrared active for the A_{2u} and E_u modes, and inactive for the A_{1u} torsional mode. The value of 68cm^{-1} for the torsional mode was taken from the calculations by Carney et al. (1961).

Table 6.10. Observed frequencies in symmetry group sequence with corresponding calculated values for FC116. All frequencies are given in cm^{-1}.

Observed freq.		Urey-Bradley force field calculations						Hartree-Fock /6-31G*	
(a)	(b)	(c)	(d)	(e)	(d)	(h)	(d)	(f)	(d)
A_{1g} 1417		1391	-1.83	1424	0.49	1263	-10.9	1458	2.89
808		717	-11.3	745	-7.80	713	-11.8	795	-1.61
348		319	-8.33	336	-3.45	310	-10.9	338	-2.87
A_{1u} -	68	68	0.00	71	4.41	68	0.00	63	-7.35
A_{2u} 1117		1051	-5.91	1111	-0.54	1070	-4.21	1113	-0.36
714		631	-11.6	661	-7.42	644	-9.80	693	-2.94
E_g 1250		1359	8.72	1451	16.1	1388	11.0	1277	2.16
1250		1359	8.72	1451	16.1	1388	11.0	1277	2.16
619		553	-10.7	567	-8.40	554	-10.5	603	-2.58
619		553	-10.7	567	-8.40	554	-10.5	603	-2.58
372		375	0.81	420	12.9	405	8.87	371	-0.27
372		375	0.81	420	12.9	405	8.87	371	-0.27
E_u 1251		1248	-0.24	1299	3.84	1241	-0.80	1283	2.56
1251		1248	-0.24	1299	3.84	1241	-0.80	1283	2.56
523		548	4.78	556	6.31	546	4.40	505	-3.44
523		548	4.78	556	6.31	546	4.40	505	-3.44
216		230	6.48	268	24.1	257	19.0	206	-4.63
216		230	6.48	268	24.1	257	19.0	206	-4.63

(a) Observed values with assignments from Bucker and Nielsen 1963 .

(b) Torsional value calculated by Carney et al. 1961.

(e) Results for FC116 as part of the CFC group.

(h) Results for FC116 as part of the HFC group.

The most significant error arising from the UB calculations is that for the highest E_g mode, where a difference of over 100 wavenumbers occurs. This vibration may be attributed to a C-F symmetric bond stretch, and may be higher than expected due to the omission of forces relating to the interaction between the fluorine atoms bonded to different carbon atoms. The UB results for the individual molecule are not very satisfactory, mainly due to the constraints used when refining the force constants. By attempting to use similar force constants to those for the other molecules in the group, no satisfactory fit could be obtained. It can be seen from both sets of group results that the UB calculated frequencies did not fit well for either group.

HFC170.

The observed fundamental frequencies and the corresponding calculated values for HFC170 are given in table 6.11. The assignments reported by Tanabe & Saëki (1972) are in good agreement with the results from the *ab initio* calculations. For HFC170, both the HF and MP2 theoretical methods of calculation were available, enabling a comparison between the two different methods to be made.

Table 6.11. Observed frequencies in symmetry group sequence with corresponding calculated values for HFC170. All frequencies are given in cm^{-1}.

Obs. frequencies		Urey-Bradley force field calcs.				HF/6-31G*		MP2/6-31G*	
(a)	(b)	(c)	(d)	(e)	(d)	(f)	(d)	(g)	(d)
A_{1g} 2954		2907	-1.59	2920	-1.15	2870	-2.84	2933	-0.71
1388		1433	3.24	1429	2.95	1415	1.95	1406	1.30
995		1005	1.01	1009	1.41	951	-4.42	990	-0.50
A_{1u} 289		289	0.00	245	-15.2	292	1.04	312	7.96
A_{2u} 2954		2933	-0.17	2943	-0.37	2864	-3.05	2934	-0.68
1379		1402	1.67	1379	0.00	1386	0.51	1381	0.15
E_g 2969		2995	0.88	3007	1.28	2909	-2.02	3006	1.25
2969		2995	0.88	3007	1.28	2909	-2.02	3006	1.25
1460		1447	-0.89	1396	-4.38	1472	0.82	1479	1.30
1460		1447	-0.89	1396	-4.38	1472	0.82	1479	1.30
1190		1007	-15.4	1009	-15.2	1198	0.67	1198	0.67
1190		1007	-15.4	1009	-15.2	1198	0.67	1198	0.67
E_u 2996		3006	0.33	3017	0.70	2931	-2.17	3024	0.93
2996		3006	0.33	3017	0.70	2931	-2.17	3024	0.93
1486		1490	0.27	1434	-3.50	1477	-0.61	1483	-0.20
1486		1490	0.27	1434	-3.50	1477	-0.61	1483	-0.20
820		835	1.83	834	1.71	796	-2.93	801	-2.32
820		835	1.83	834	1.71	796	-2.93	801	-2.32

(a) Observed values with assignments from Tanabe & Saëki 1972.

(b) No new assignments were made in this work.

It can be seen from table 6.11 that the percentage difference between the calculated and observed frequencies is generally lower for the MP2 results than the HF results, although overall, the difference is small. The largest error occurs for the torsional mode, where the MP2 result at $312cm^{-1}$ is considerably higher than expected. The UB results also agree well with the observed values, except in the case of the lowest E_g mode which is calculated to be at 1007cm^{-1}. The calculations by Bucker and Nielsen (1963) give a frequency of 1004cm^{-1}, which agrees well with the result obtained here. Smith et al. (1952) reported that the value 1190cm^{-1} was derived from overtone or combination bands and was not observed directly, suggesting that the assignment may not be correct.

HFC161.

The observed fundamental frequencies and the corresponding calculated values for HFC161 are given in table 6.12.

Table 6.12. Observed frequencies in symmetry group sequence with corresponding calculated values for HFC161. All frequencies are given in cm^{-1}.

Obs. frequencies		Urey-Bradley force field calcs.				HF/6-31G*		MP2/6-31G*	
(a)	(b)	(c)	(d)	(e)	(d)	(f)	(d)	(g)	(d)
A' 3003		3000	-0.10	3013	0.33	2940	-2.10	3031	0.93
2941		2955	0.48	2965	0.82	2904	-1.26	2942	0.03
2915		2911	-0.14	2923	0.27	2877	-1.30	2941	0.89
1479		1502	1.56	1489	0.68	1507	1.89	1504	1.69
1449		1450	0.07	1455	0.41	1473	1.66	1476	1.86
1395		1399	0.29	1406	0.79	1421	1.86	1403	0.57
1365		1370	0.37	1322	-3.15	1385	1.47	1370	0.37
1108		1037	-6.41	1030	-7.04	1110	0.18	1102	-0.54
1048		998	-4.77	966	-7.82	1046	-0.19	1052	0.38
880		887	0.80	881	0.11	869	-1.25	874	-0.68
415		426	2.65	375	-9.64	393	-5.30	389	-6.27
A" 3003		3008	0.17	3020	0.57	2954	-1.63	3034	1.03
3003	2967†	2997	1.01	3010	1.45	2931	-1.21	2994	0.91
1449		1456	0.48	1467	1.24	1456	0.48	1460	0.76
1277		1178	-7.75	1123	-12.1	1272	-0.39	1260	-1.33
1048	1171*	978	-16.5	958	-18.2	1172	0.09	1162	-0.77
810		799	-1.36	752	-7.16	787	-2.84	790	-2.47
243		243	0.00	226	-7.00	244	0.41	262	7.82

(a) Observed values with assignments from Chen et al. 1975.

(b) Tentative assignments made in this work using data from † Crowder and Mao 1973, and * Smith et al. 1952.

Initially, the assigned frequencies given in Chen et al. (1975) were used. Reasonable agreement was obtained with both the HF and MP2 calculations, except in the case of one of the antisymmetric A" stretches at 3003cm^{-1}, and the A" mode at 1048cm^{-1}. In both cases, the observed values were derived by assuming the superposition of two or more frequencies.

The results given by Crowder and Mao (1973) suggested that one of the antisymmetric C-H stretches occurred at a frequency of 2967cm^{-1}. Smith et al. (1952) designated a strong band at 1171cm^{-1} as an A' mode, but the Raman depolarisation ratio was not measured. The HF results give a Raman depolarisation ratio of 0.7500 for a frequency at 1172cm^{-1} which may well correspond to the observed frequency at 1171cm^{-1} suggesting it could be assigned to an A" mode. The MP2 calculations did not report Raman depolarisation ratios. In contrast, the UB results give a much lower value for this fundamental at 978cm^{-1} which does not correlate well with either assignment.

From the potential energy matrix, the lower than expected UB results of 1037cm^{-1}, 1178cm^{-1} and 978cm^{-1} are all partly associated with rocking of the CFH_2 group. Shimanouchi (1963) reported that calculated rocking frequencies for several RCH_2X (X=halogen) molecules were too low without the inclusion of an angle interaction constant between H and X as well as the standard UB bending and repulsive force constants.

HFC152.

The observed fundamental frequencies and the corresponding calculated values for HFC152 are given in table 6.13. The initial assignments were taken from the publication by Klaboe and Nielsen (1960).

Table 6.13. Observed frequencies in symmetry group sequence with corresponding calculated values for HFC152. All frequencies are given in cm^{-1}.

Obs. frequencies		Urey-Bradley force field calcs.				HF/6-31G*		MP2/6-31G*	
(a)	(b)	(c)	(d)	(e)	(d)	(f)	(d)	(g)	(d)
A_g 2962		2945	-0.57	2954	-0.27	2921	-1.38	2955	-0.24
1416	1456†	1460	0.27	1461	0.34	1506	3.43	1502	3.16
1079	1416†	1377	-2.75	1382	-2.40	1450	2.40	1424	0.56
1049	1079‡	1054	-2.32	1040	-3.61	1070	-0.83	1070	-0.83
858	1049‡	957	-8.77	931	-11.3	1048	-0.10	1043	-0.57
804	450‡	412	-8.44	374	-16.9	445	-1.11	440	-2.22
A_u 2994		3005	0.37	3019	0.84	2978	-0.53	3028	1.14
1415	-	1146		1089		1213		1189	
320	-	754		714		786		789	
-		129		125		130		133	
B_g 2990		2997	0.23	3010	0.67	2954	-1.20	3007	0.57
1285		1186	-7.70	1135	-11.7	1271	-1.09	1260	-1.95
450	-	871		820		1158		1145	
B_u 2951		2961	0.34	2971	0.68	2922	-0.98	2960	0.30
1376	1415†	1424	0.64	1469	3.82	1513	6.93	1510	6.71
1065	1376†	1325	-3.71	1269	-7.78	1343	-2.40	1318	-4.22
897	1065†	983	-7.70	960	-9.86	1073	0.75	1053	-1.13
652	320‡	338	5.63	305	-4.69	275	-14.1	263	-17.8

(a) Observed values with assignments from Klaboe and Nielsen 1960.

(b) Tentative assignments were taken from †Beagley and Brown 1979, and, ‡ made in this work using data from Klaboe and Nielsen 1960.

Several large discrepancies were found between the calculated and observed frequencies. In an attempt to obtain a better agreement, some assignments suggested by

Beagley and Brown (1979) were substituted and a further four tentative assignments were made using values from Klaboe and Nielsen (1960) for alternative modes. HFC152 has C_{2h} symmetry, where the A_g and B_g modes are Raman active and the A_u and B_u modes are infrared active. No sample of HFC152 was available for experimental use as part of this work.

Using the data presented in column (b) table 6.13, a better agreement is obtained between the *ab initio* and observed frequencies. In the case of the B_u mode observed at 1415cm^{-1} by Beagley and Brown (1979) however, the results from the *ab initio* calculations are 100 wavenumbers higher, suggesting an incorrect assignment, although the UB result does not confirm this.

The presence of two CH_2F groups and the lack of angle interaction constants, as described by Shimanouchi (1963), may well account for the lower than expected UB values at 957cm^{-1} and 983cm^{-1}. The reassignment of 320cm^{-1} to the torsional mode may be incorrect, although the actual value observed by Klaboe and Nielsen (1960) was said to be approximate. The four unassigned frequencies do not agree for the two types of calculation, possibly suggesting that the UB force field is not adequate for this type of molecule.

HFC152a.

The observed fundamental frequencies and the corresponding calculated values for HFC152a are given in table 6.14. A good agreement was obtained between the observed frequencies and the *ab initio* calculated values, except in the case of the lower frequencies observed at 571cm^{-1}, 470cm^{-1}, 383cm^{-1} and 222cm^{-1}. The percentage differences shown are high, however, as has been noted previously, the difference is in the order of 20-30 wavenumbers which is comparable with the difference for some of the higher frequencies. A better fit has been obtained from the UB calculations for this molecule than for HFC152, suggesting that the angle interaction constant is not so significant without the -CH_2F end group.

Guirgis and Crowder (1984) have suggested alternative assignments for the observed frequencies at 1143cm^{-1}, 1129cm^{-1}, 1360cm^{-1}, and 1171cm^{-1}, giving the values 1171cm^{-1}, 1142cm^{-1}, 1164cm^{-1}, and 1149cm^{-1} respectively. These new assignments are not in agreement with the results calculated here, except in the case of the exchange of 1171cm^{-1} for the new value of 1149cm^{-1}. Guirgis and Crowder (1984) also indicate that by force constant adjustment alternative assignments can be made to fit, however, when attempting to determine transferable force constants for use with similar molecules, as is the case in this work, large changes in force constants are not desirable.

Table 6.14. Observed frequencies in symmetry group sequence with corresponding calculated values for HFC152a. All frequencies are given in cm^{-1}.

Obs. frequencies		Urey-Bradley force field calcs.				HF/6-31G*		MP2/6-31G*	
(a)	(b)	(c)	(d)	(e)	(d)	(f)	(d)	(g)	(d)
A' 3018		3016	-0.07	3015	-0.10	2976	-1.39	3051	1.09
2978		2995	0.57	2991	0.44	2956	-0.74	2981	0.10
2960		2924	-1.22	2920	-1.35	2891	-2.33	2953	-0.24
1460		1451	-0.62	1481	1.44	1459	-0.07	1461	0.07
1414		1435	1.49	1418	0.28	1435	1.49	1412	-0.14
1372		1359	-0.95	1349	-1.68	1380	0.58	1363	-0.66
1143		1104	-3.41	1084	-5.16	1149	0.52	1133	-0.87
1129		1045	-7.44	1024	-9.30	1121	-0.71	1120	-0.80
868		882	1.61	869	0.12	849	-2.19	853	-1.73
571		540	-5.43	528	-7.53	549	-3.85	537	-5.95
470		477	1.49	459	-2.34	450	-4.26	440	-6.38
A" 3001		3016	0.50	3014	0.43	2959	-1.40	3047	1.53
1460		1523	4.32	1486	1.78	1462	0.14	1463	0.21
1360		1426	4.85	1449	6.54	1395	2.57	1370	0.74
1171		1136	-2.99	1102	-5.89	1162	-0.77	1137	-2.90
930		916	-1.51	903	-2.90	961	3.33	942	1.29
383		422	10.2	391	2.09	365	-4.70	363	-5.22
222		221	-0.45	236	6.31	231	4.05	252	13.5

(a) Observed values with assignments from Chen et al. 1975.

(b) No changes in the assignments were made for this compound.

HFC143.

Table 6.15. Observed frequencies in symmetry group sequence with corresponding calculated values for HFC143. All frequencies are given in cm^{-1}.

Observed frequencies		Urey-Bradley force field calculations				Hartree-Fock /6-31G*	
(a)	(b)	(c)	(d)	(e)	(d)	(f)	(d)
A 3005		3035	1.00	3033	0.93	2994	-0.37
2986		2993	0.23	2992	0.20	2977	-0.30
2978		2946	-1.07	2938	-1.34	2929	-1.65
1465		1527	4.23	1553	6.01	1491	1.77
1433		1491	4.05	1484	3.56	1460	1.88
1379		1442	4.57	1428	3.55	1403	1.74
1319		1341	1.67	1305	-1.06	1339	1.52
1249		1175	-5.92	1139	-8.81	1240	-0.72
1152		1110	-3.65	1094	-5.03	1152	0.00
1125		1093	-2.84	1075	-4.44	1132	0.62
1076		992	-7.81	973	-9.57	1117	3.81
-		964		951		1086	
905		860	-4.97	835	-7.73	897	-0.88
577		538	-6.76	524	-9.19	558	-3.29
476		491	3.15	475	-0.21	474	-0.42
426		404	-5.16	389	-8.69	411	-3.52
247		265	7.29	258	4.45	234	-5.26
117		117	0.00	112	-4.27	120	2.56

(a) Observed values with assignments from Kalasinsky et al. 1982.

(b) No changes were made in the assignments for this compound.

The observed fundamental frequencies and the corresponding calculated values for HFC143 are given in table 6.15. The results for the HF calculations are in good agreement with the assignments reported by Kalasinsky et al. (1982), except for the observed value at 1076cm^{-1}. The HF results suggest that the omitted observed frequency should be switched with the frequency of 1076cm^{-1}, which would then correspond well to the calculated frequency at 1086cm^{-1}. This does not, however, concur with the UB results, which are considerably lower for both frequencies.

Difficulties in obtaining comparable UB results may arise from the use of only one force constant for the fluorine atoms, since one of the fluorine atoms is in a different environment to the other two. In addition, the presence of a CH_2F group may require an angle interaction constant to be incorporated into the UB potential.

HFC143a.

The observed fundamental frequencies and the corresponding calculated values for HFC143a are given in table 6.16. The overall difference between the HF calculated values and the observed frequencies is somewhat higher than for the other molecules studied, with an average value of 2.17%. The calculated results suggest that the observed frequency at 602cm^{-1} may be high, since the UB value is 558cm^{-1} and the HF value is 579cm^{-1}.

Table 6.16. Observed frequencies in symmetry group sequence with corresponding calculated values for HFC143a. All frequencies are given in cm^{-1}.

Observed frequencies		Urey-Bradley force field calculations				Hartree-Fock /6-31G*	
(a)	(b)	(c)	(d)	(e)	(d)	(f)	(d)
A_1 2975		2957	-0.61	2918	-1.92	2906	-2.32
1408		1421	0.92	1423	1.07	1433	1.78
1280		1292	0.94	1302	1.72	1280	0.00
830		790	-4.82	790	-4.82	813	-2.05
602		558	-7.31	566	-5.98	579	-3.82
A_2 220		249	13.2	252	14.6	225	2.27
E 3035		3035	0.00	3015	-0.66	2981	-1.78
3035		3035	0.00	3015	-0.66	2981	-1.78
1443		1445	0.14	1491	3.33	1457	0.97
1443		1445	0.14	1491	3.33	1457	0.97
1233		1360	10.3	1364	10.6	1266	2.68
1233		1360	10.3	1364	10.6	1266	2.68
970		932	-3.92	920	-5.15	980	1.03
970		932	-3.92	920	-5.15	980	1.03
541		536	-0.92	542	0.18	524	-3.14
541		536	-0.92	542	0.18	524	-3.14
365		422	15.6	433	18.6	351	-3.84
365		422	15.6	433	18.6	351	-3.84

(a) Observed values with assignments from Chen et al. 1975.

(b) No changes in assignments have been made for this molecule.

However, the spectrum in figure 4.13 shows an obviously PQR shaped band centred at 602.9cm^{-1} confirming the assignment given by Chen et al. (1975). The UB calculated frequency at 1360cm^{-1} is considerably higher than expected. The potential energy matrix gives a 63% contribution to this vibrational mode from the C-F stretching force constant, however, reduction of this force constant would affect the other vibrational modes associated with a C-F stretch, calculated at 1292cm^{-1}, 790cm^{-1}, 932cm^{-1}. Although all three fluorine atoms belonging to this molecule are attached to the same carbon atom, and therefore should require only one force constant, no interaction between atoms more than two bonds apart has been included in the calculation which may account for this discrepancy.

HFC134.

The observed fundamental frequencies and the corresponding calculated values for HFC134 are given in table 6.17. For all but one of the frequencies, there is a good agreement between the HF results and the observed values. The spectrum given by Kalasinsky et al. (1982) for the region 300-50cm^{-1} distinctly shows the band centred around 216-204cm^{-1}, although the exact centre is difficult to determine. The difference in wavenumbers between the observed frequency at 212cm^{-1} and the HF frequency at 194cm^{-1} is relatively small, compared to the difference for the other frequencies.

Table 6.17. Observed frequencies in symmetry group sequence with corresponding calculated values for HFC134. All frequencies are given in cm^{-1}.

Observed frequencies		Urey-Bradley force field calculations				Hartree-Fock /6-31G*	
(a)	(b)	(c)	(d)	(e)	(d)	(f)	(d)
A_g 2995		2989	-0.20	2988	-0.23	3002	0.23
1442		1478	2.50	1455	0.90	1480	2.64
1149		1101	-4.18	1101	-4.18	1145	-0.35
1106		1011	-8.59	1018	-7.96	1098	-0.72
625		563	-9.92	561	-10.2	613	-1.92
362		332	-8.29	330	-8.84	352	-2.76
A_u 1330		1429	7.44	1457	9.55	1358	2.11
1136		1050	-7.57	1056	-7.04	1158	1.94
212		236	11.3	237	11.8	194	-8.49
82		82	0.00	83	1.22	85	3.66
B_g 1365		1477	8.21	1499	9.82	1385	1.47
1081		1090	0.83	1104	2.13	1131	4.63
480		425	-11.5	425	-11.5	478	-0.42
B_u 2995		2997	0.07	3000	0.17	3011	0.53
1320		1332	0.91	1322	0.15	1304	-1.21
1125		1068	-5.07	1064	-5.42	1125	0.00
541		520	-3.88	519	-4.07	530	-2.03
414		456	10.1	457	10.4	412	-0.48

(a) Observed values with assignments from Kalasinsky et al. 1982.

(b) No changes in assignments have been made in this work.

The UB results are not very satisfactory, it can be seen in table 6.17 that little improvement was made when refining the force constants for the individual fit. Again, the problem of one antisymmetric C-F stretching mode having a calculated value too high at 1477cm^{-1} compared to 1365cm^{-1} for the observed frequency occurs. Other modes influenced by a C-F stretch are too low, 1011cm^{-1} compared to 1106cm^{-1} and 1050cm^{-1} compared to 1136cm^{-1}. For HFC134, the fluorine atoms are all in the same environment, so the problems must partly arise from the omission of interaction between the two ends of the molecule in the UB potential.

HFC134a.

The observed fundamental frequencies and the corresponding calculated values for HFC134a are given in table 6.18. Since large differences have been found between several of the observed and calculated frequencies, three of the original assignments made by Chen et al. (1975) have been amended in this work. The assignments suggested by Nielsen and Halley (1965) and Edgell et al. (1963) were not in agreement, however, Chen et al. (1975) used the observed frequencies reported in these publications, with the torsional frequency of 120cm^{-1} observed by Dante and Wood (1959), to derive the set of assignments given in table 6.18.

Table 6.18. Observed frequencies in symmetry group sequence with corresponding calculated values for HFC134a. All frequencies are given in cm^{-1}.

	Observed frequencies		Urey-Bradley force field calculations				Hartree-Fock /6-31G*	
	(a)	(b)	(c)	(d)	(e)	(d)	(f)	(d)
A'	2984		2985	0.03	2960	-0.80	2942	-1.41
	1464		1437	-1.84	1503	2.66	1490	1.78
	1427		1405	-1.54	1425	-0.14	1451	1.68
	1298		1346	3.70	1361	4.85	1302	0.31
	1103	-	1244		1256		1233	
	972	1103†	960	-13.0	967	-12.3	1104	0.09
	842		791	-6.06	799	-5.11	831	-1.31
	665		586	-11.9	600	-9.77	648	-2.56
	549		541	-1.46	546	-0.55	530	-3.46
	408		400	-1.96	414	1.47	395	-3.19
	225		222	-1.33	236	4.89	210	-6.67
A"	3013		3027	0.46	3014	0.03	2997	-0.53
	1374		1366	-0.58	1378	0.29	1313	-4.44
	1182		1077	-8.88	1081	-8.54	1201	1.61
	885	968‡	823	-15.0	827	-14.6	983	1.55
	539		541	0.37	546	1.30	518	-3.90
	352		405	15.1	419	19.0	346	-1.70
	120		119	-0.83	113	-5.83	107	-10.8

(a) Observed values with assignments from Chen et al. 1975.

(b) Tentative assignments made in this work using data from †Nielsen and Halley 1965 and ‡Edgell et al. 1963.

In order to reach a closer agreement between the observed and calculated values, the observed value from Nielsen and Halley's work (1965) of 1103cm^{-1} was assigned to ν_6, and ν_5 was omitted. Edgell et al. (1963) assigned 968cm^{-1} to the ν_{15} A" mode, which is in reasonable agreement with the HF results. Edgell et al.(1963) also suggested 201cm^{-1} in place of the observed 225cm^{-1}, and 407cm^{-1} in place of the observed 352cm^{-1} A" mode. The former is in closer agreement to the HF results, and the latter corresponds to the UB results. Changes in assignments have not been made to fit with the UB results at the expense of agreement with the HF results because, although the HF calculations are based on approximations and therefore do not exactly replicate the observed frequencies, they have been seen to be more reliable in this work than frequencies obtained from the UB calculations.

HFC125.

The observed fundamental frequencies and the corresponding calculated values for HFC125 are given in table 6.19.

Table 6.19. Observed frequencies in symmetry group sequence with corresponding calculated values for HFC125. All frequencies are given in cm^{-1}.

	Observed frequencies		Urey-Bradley force field calculations				Hartree-Fock/6-31G*	
	(a)	(b)	(c)	(d)	(e)	(d)	(f)	(d)
A'	3008		3002	-0.20	2993	-0.50	3002	-0.20
	1393	1447	1437	-0.69	1541	6.50	1470	1.59
	1309		1344	2.67	1376	5.12	1318	0.69
	1218		1219	0.08	1283	5.34	1222	0.33
	1111		1017	-8.46	1054	-5.13	1133	1.98
	867		800	-7.73	829	-4.38	861	-0.69
	725		629	-13.2	654	-9.79	708	-2.34
	577		542	-6.07	555	-3.81	560	-2.95
	523		531	1.53	541	3.44	506	-3.25
	361		349	-3.32	362	0.28	351	-2.77
	246		262	6.50	278	13.0	239	-2.85
A"	1359		1430	5.22	1496	10.1	1389	2.21
	1198	1224	1314	7.35	1353	10.5	1267	3.51
	1145		1046	-8.65	1087	-5.1	1173	2.45
	508	-	543		554		571	
	413		411	-0.48	431	4.36	407	-1.45
	216		234	8.33	250	15.7	201	-6.94
	82		82	0.00	81	-1.22	73	-11.0

(a) Observed values with assignments from Chen et al. 1975.

(b) Tentative assignments made in this work using data from Nielsen et al. 1955 .

Three observed frequencies assigned by Chen et al (1975) differed from the HF results by more than 60 wavenumbers. This led to the tentative assignments listed in column (b) of table 6.19. Nielsen et al. (1955) suggested that 1447cm^{-1} could be used as an alternative to 1393cm^{-1}, and reported a strong band centred around 1224cm^{-1}, but did not identify it. From the spectrum of HFC125 in figure 4.16, a strong, broad band occurs between 1255cm^{-1} and 1171cm^{-1}, which may include both an A' and an A" mode. The tentative assignments of 1447cm^{-1} to ν_2 and 1224cm^{-1} to ν_{13} have been made in this work.

Nielsen et al. (1955) expressed uncertainty about the assignment of 508cm^{-1}, and it has been omitted here as it is not in agreement with the calculated results. The UB results exhibit the same problems here as for the other HFCs, with the calculated frequency for a C-F stretch at 1314cm^{-1} being too large, and the other frequencies affected by C-F stretching being too low. Tipton et al. (1967) report a torsional frequency of 74cm^{-1} which is in agreement with the HF results, however, Kinumaki and Kozuka (1968) reported an observed torsional band centred at 82cm^{-1}. Kinumaki and Kozuka (1968) referred to the band around 216cm^{-1} as being weak, diffuse and structureless, indicating that the position of the band centre is uncertain, suggesting that the HF result of 201cm^{-1} may be close to the true centre of the band.

6.1.2 Discussion of assignments.

When comparing observed and calculated frequencies, many factors need to be considered. Problems arise with inaccuracies in the observed values, incorrect assignments, and the inadequacies of the theoretical models used for the calculations.

Most of the assignments of the vibrational fundamentals found in the literature may be considered reliable, since they were made using both Raman and infrared spectra, and the study and identification of the combination bands. However, the observed values may vary by a few wavenumbers, due to inaccuracies in the recording of the spectra and the difficulties in the selection of the correct centre of a band when two or more bands overlap. The assignment of inactive modes is difficult, and was usually based on the interpretation of combination bands. Further misinterpretation of the spectra may have been caused by the presence of weak bands due to contamination of the samples used.

It can be seen from tables 6.1 to 6.19 that reasonable agreement is obtained between the *ab initio* results and the observed frequencies. It should be noted however, that the *ab initio* calculations are based on several approximations as described in section 1.6.2. The neglect of electron correlation by the HF method will result in errors in the computation, however, comparison of the results obtained from the HF and MP2 levels of theory indicate that at least for the lighter HFCs the differences were small. It is possible that the results for the heavier molecules may be improved by the use of a higher level of theory, however, considerable computer time would have been required to complete these calculations, and generally the HF results seem acceptable for this work.

The scaling factors used to adjust the frequencies have been determined from a large number of *ab initio* calculations (Pople et al. 1993). Another source of error may arise from the calculation of the equilibrium geometry of the molecule. Fogarasi and Pulay (1985) state that SCF wave functions (as used for the HF calculations) generally yield bond lengths which are too short. This is confirmed by the results for CF_4 and C_2F_6 calculated by Cooper et al. (1989). The effects of anharmonicity for the C-H stretching modes may increase the error for the calculated values, but even with errors in the range of 20-30cm^{-1}, Fogarasi and Pulay (1985) suggest that the results are suitable for checking vibrational assignments.

The Urey-Bradley calculations have not agreed as well as the *ab initio* calculations with the fundamental assignments. The programs used in this work allow only the simple Urey-Bradley potential field to be used. Shimanouchi (1963) divided various molecules into three groups, those for which the simple UB field was successful, such as CX_4 (X=halogen); those for which the UB field was successful, but the resultant force constants were not transferable to similar molecules, such as the halomethanes with at least one hydrogen atom; and those for which the force field had to be modified, such as the dichloroethanes. The modification of the UB force field includes the incorporation of a 'trans' interaction constant, a 'gauche' interaction constant and an angle interaction constant. The 'trans' and 'gauche' interaction constants given by Shimanouchi (1963) involve interactions between atoms attached to adjacent carbon atoms, and the angle interaction constant involves interactions between atoms attached to the same carbon, but not directly affected by the rocking or twisting motions involved. The use of the same force constants for bonded atoms in different environments may also have introduced errors, for example, the C-F stretching force constants for fluorine atoms sharing the same carbon atom may not all be the same if the atoms on the other carbon atom are not identical to each other. For example, the C-F stretching force constants for CFC115, shown in table 6.23, are not all the same, even for the three fluorines attached to the same carbon atom.

Errors in the experimental geometry will have introduced errors in the frequencies, since a small change in bond length or angle results in a change of frequency by a few wavenumbers.

The most time-consuming problem arose from the difficulty of starting with two sets of 'approximate' values, the initial force constants and the assigned frequencies. While most of the assigned frequencies may be considered to be accurate within a few wavenumbers, the force constants, in particular for the non-bonded interactions were not reliable. The assumption was made that the assignments given in tables 6.1 to 6.19

were correct, and the force constants adjusted accordingly. Difficulties arose for those frequencies where the assignments were doubtful or missing, as, a change in a particular force constant may change the calculated frequency to correspond to any specified value within a range of approximately 100 wavenumbers. This problem was also encountered by Guirgis and Crowder (1984) when they were calculating the frequencies for HFC152a.

Further refinements of the force constants could have been carried out, however, the possible reduction of the overall errors by tenths of a percent was not considered to be beneficial, since it is the trends in force constants that are of more interest here, as the simple UB force field used will not give exact values.

6.2 Force constants.

Force constants derived from calculations using the UB force field have clear physical meanings in that they are associated directly with stretches, bends or non-bonded interactions between atoms within the molecule. When a set of transferable force constants has been determined, they may be used to calculate the vibrational frequencies for a compound which is not available for experimental studies. The resultant frequencies may also be used to assist in the assignment of fundamentals when experimental results are available. In this work it has been found that, for the simple UB force field used by the programs NORCORD and OVER, some of the calculated frequencies are not close enough to the observed values to confirm assignments. However, the group force constants obtained still provide a useful starting point for the calculation of frequencies for similar molecules.

The *ab initio* models calculate force constants for the internal coordinates input via the Z matrix for GAUSSIAN92. These internal coordinates are different to those used for the UB calculations, since they consist of seven stretches, six bends between the F, Cl or H atoms and the C-C axis, and five dihedral angles. It is possible therefore, to compare only the stretching force constants. The bending and non-bonded interaction force constants for the UB force field are some combination of the force constants for the internal coordinates used in the *ab initio* calculations.

6.2.1. Force constants calculated using a UB force field.

Tables 6.20 and 6.21 present the UB force constants for the CFCs and HFCs respectively. UB force constants for stretches and bends appear lower than those from other force fields. This is due to the fact that the F matrix diagonal elements used in the calculation of frequencies are a combination of the UB stretches and bending force constants and the relevant non-bonded interactions. The number and magnitude of the non-bonded interaction force constants incorporated in the F matrix is determined by the Z matrix entries input to the program OVER.

From table 6.20 and 6.21 it can be seen that the C-C , C-H and C-Cl stretching force constants increase as the number of fluorine atoms increases. A strengthening of the C-C bond with fluorine substitution has been reported in the literature by Bucker and Nielsen (1963). This has been observed here with both the CFCs and HFCs suggesting that the trend does not directly depend on the type of atom replaced. Conversely, the C-F stretching force constant increases with fluorine substitution of the CFCs and decreases when fluorine atoms replace hydrogen atoms. It would be expected that the presence of the chlorine atoms affect the fluorine atoms to a greater extent than the hydrogen atoms, and this is shown by the non-bonded interaction force constant of 0.5316mdyneÅ^{-1} for the F...Cl interaction and 0.0602mdyneÅ^{-1} for the F...H interaction. The bending force constants are smaller than the stretching force constants as would be expected, with stronger interactions between the halogen atoms in the ClCCl, FCCl, and FCF bends than the halogen and carbon atoms in the XCC bends. In contrast, in the case of the HFCs, the force constants for the FCH and HCH bends are very small.

The force constants relating to the torsion of the molecules (designated by X~X) are relatively small, with the magnitude increasing in the sequence H~H<F~H<F~F<F~Cl<Cl~Cl, although there is some doubt about the sequence of F~Cl and F~H as these values had to be decreased substantially for the individual refinement of the force constants for the C_{3v} molecules CFC113a and HFC143a.

Some values for UB force constants relating to halogenated alkanes were found in the literature, and are given in table 6.22, together with the force constants obtained in this work. There is a reasonable agreement between the literature values and the values calculated as part of this work, except in the case of the bending force constants between like atoms bonded to the same carbon atom. From this work, H_{HCH} is much smaller than the literature values, and both H_{ClCCl} and H_{FCF} are much larger. The non-bonded interactions between like atoms show a good agreement with the literature values, so it cannot be argued that these force constants compensate for the discrepancy found in the bending force constants. The calculations were repeated using the values for H_{FCF}, H_{ClCCl} and H_{HCH} given by Shimanouchi (1963), but despite refining the other force constants, no reasonable set of calculated frequencies could be obtained. It should be noted, however, that the results obtained by Shimanouchi (1963) were calculated using a modified UB force field including additional interaction constants.

Table 6.20. Force constants in mdyneÅ^{-1}, from a Urey-Bradley force field for the CFCs. X~X signifies atoms 1 and 4 in a 4-atom torsion.

Force	CFC	Force constants for individual CFCs and CFCas									
constant	group	110	111	112	113	114	115	116	112a	113a	114a
C-C	1.9021	1.4734	1.6921	1.8018	2.1162	2.1801	2.3154	3.3740	1.8123	2.3067	2.5145
C-F	4.3106	-	3.5868	3.7842	4.0983	4.3445	4.3506	4.3810	3.8219	4.0122	4.1844
C-Cl	1.8365	1.6365	1.6946	1.7834	1.8365	2.1103	2.2535	-	1.8047	1.8318	1.9022
CCF	0.2944	-	0.3267	0.3134	0.2620	0.2055	0.1549	0.1117	0.3044	0.2539	0.2037
CCCl	0.2863	0.2433	0.2633	0.2748	0.2846	0.3381	0.3427	-	0.2663	0.2919	0.3102
FCF	0.6037	-	-	-	0.5975	0.6190	0.6237	0.6282	0.5537	0.5830	0.5965
FCCl	0.5891	-	0.4947	0.5645	0.5784	0.5963	0.6327	-	0.5134	-	0.5235
ClCCl	0.4555	0.4085	0.4385	0.4634	0.5233	-	-	-	0.4832	0.4936	0.5334
F~F	0.0397	-	-	0.0386	0.0594	0.0323	0.0444	0.0402	-	-	0.0397
F~Cl	0.0507	-	0.1045	-	0.0932	-	0.0673	-	0.0974	0.0139	0.0570
Cl~Cl	0.1692	0.1692	0.1652	0.1544	0.1692	0.1364	-	-	0.1692	-	-
C..F	0.3797	-	0.3937	0.3895	0.3784	0.3734	0.3524	0.3459	0.3784	0.3576	0.3526
C..Cl	0.1901	0.3523	0.3001	0.2201	0.2144	0.2023	0.1621	-	0.2301	0.2293	0.2113
F..F	0.6339	-	-	-	0.6847	0.6561	0.6273	0.6097	0.6944	0.6888	0.6347
F..Cl	0.5316	-	0.3524	0.5016	0.5394	0.6214	0.6408	-	0.4646	-	0.5493
Cl..Cl	0.7518	0.6947	0.7247	0.7747	0.8873	-	-	-	0.7422	0.7630	0.9964

Table 6.21. Force constants in mdyne$Å^{-1}$, from a Urey-Bradley force field for the HFCs. X~X signifies atoms 1 and 4 in a 4-atom torsion.

Force	HFC	Force constants for individual HFCs and HFCas.									
constant	group	170	161	152	143	134	125	116	152a	143a	134a
C-C	3.2300	2.8992	3.0592	3.1239	3.2943	3.3265	3.3318	3.3740	3.2792	3.3104	3.3278
C-F	4.8070	-	4.9227	4.9002	4.8993	4.8539	4.6111	4.3810	4.9168	4.8411	4.7643
C-H	4.6447	4.5887	4.5937	4.6056	4.6723	4.6847	4.7254	-	4.6478	4.7083	4.7101
CCF	0.3763	-	0.5597	0.5304	0.3973	0.3573	0.2914	0.1117	0.5208	0.3131	0.2936
CCH	0.2244	0.1874	0.1985	0.2298	0.2594	0.2668	0.2824	-	0.2384	0.2421	0.2507
FCF	0.6321	-	-	-	0.5684	0.6098	0.6232	0.6882	0.5432	0.5657	0.6098
FCH	0.0422	-	0.0671	0.0522	0.0447	0.0272	0.0268	-	0.0632	-	0.0496
HCH	0.0848	0.0848	0.0567	0.0302	0.0159	-	-	-	0.0443	0.0423	0.404
F~F	0.0435	-	-	0.0435	0.0487	0.0435	0.0454	0.0402	-	-	0.0489
F~X	0.0418	-	0.0443	-	0.0464	-	0.0427	-	0.0353	0.0042	0.0473
X~X	0.0190	0.0264	0.0241	0.0224	0.0197	0.0154	-	-	0.0190	-	-
C..F	0.4078	-	0.5582	0.5381	0.5094	0.4428	0.3712	0.3459	0.4528	0.3901	0.3783
C..H	0.3813	0.4249	0.3970	0.3744	0.3394	0.3121	0.3058	-	0.3824	0.3525	0.3271
F..F	0.6262	-	-	-	0.6652	0.6349	0.6152	0.6097	0.6562	0.6427	0.6312
F..H	0.0602	-	0.0715	0.0554	0.0548	0.0501	0.0481	-	0.0702	-	0.0682
H..H	0.0372	0.0343	0.0388	0.0494	0.0534	-	-	-	0.0418	0.0643	0.0734

Table 6.22. A comparison of some UB force constants for halogenated alkanes. All force constants are given in mdyneÅ^{-1}.

	This work	(a)	(b)	(c)
K_{CC}	1.5 - 3.4	2.9 - 4.0		2.0 - 2.3
K_{CF}	3.6 - 4.9		5.15	4.2
K_{CCl}	1.6 - 2.6			1.8 - 2.1
K_{CH}	4.5 - 4.7		4.698	3.9 - 4.8
H_{FCC}	0.11 - 0.56	0.3		0.1
H_{HCC}	0.19 - 0.28	0.14		0.19 - 0.21
H_{FCF}	0.57 - 0.69	0.1		0.3
H_{ClCCl}	0.41 - 0.52			0.08
H_{HCH}	0.02 - 0.08	0.43		0.34 - 0.44
F_{FC}	0.35 - 0.56	0.4	0.14	
F_{ClC}	0.16 - 0.35			0.60
F_{HC}	0.31 - 0.42	0.4		0.48 - 0.54
F_{FF}	0.60 - 0.69	1.1		-
F_{ClCl}	0.69 - 1.0			0.6 - 0.7
F_{HH}	0.03 - 0.07	0.09	0.03	0.04 - 0.10

(a) UB force constants for C_2H_6, CF_3CH_3, and C_2F_6 reported by Bucker and Nielsen (1963).

(b) UB Force constants from Crowder and Mao (1973).

(c) UB force constants for a range of hydrocarbons, excluding the CFCs and HFCs used here, reported by Shimanouchi (1963).

The final force constants for the isomeric pairs of molecules (CFC112, CFC112a; CFC113, CFC113a; CFC114, CFC114a; HFC152, HFC152a; HFC143, HFC143a; HFC134, HFC134a) do not differ by large amounts, and fit the trends of the overall groups.

6.2.2. Force constants calculated using *ab initio* methods.

Tables 6.23 and 6.24 present the unscaled stretching force constants obtained from both the HF and MP2 calculations. In order to confirm the trends in changes of the stretching force constants, comparisons have been made between the UB force constants and those obtained from the *ab initio* calculations. Direct comparison is not possible, since the UB force constants as shown in tables 6.20 and 6.21 are not the same as the final force constants found in the F matrix diagonal elements used for

Table 6.23. Unscaled stretching force constants in mdyneÅ^{-1}, from the Hartree-Fock calculations for the CFCs.

Force constant	Force constants for individual CFCs and CFCas.									
	110	111	112	113	114	115	116	112a	113a	114a
C_1-C_2	4.3266	4.5430	4.7548	4.9634	5.1476	5.3360	5.4956	4.7710	5.0048	5.1824
C_1-F_1	-	-	7.7595	-	-	8.3041	8.2922	-	8.2451	8.2552
C_1-F_2	-	-	-	-	7.9398	8.2574	8.2922	-	8.2451	8.3132
C_1-F_3	-	-	-	7.6107	7.9398	8.3041	8.2922	-	8.2451	8.2552
C_2-F_4	-	7.5006	7.7595	7.9538	7.9398	-	8.2922	-	-	7.5552
C_2-F_5	-	-	-	7.9313	7.9398	7.9520	8.2922	7.8869	-	-
C_2-F_6	-	-	-	-	-	7.9520	8.2922	7.8869	-	-
C_1-Cl_1	3.9019	3.9449	-	4.1454	4.3464	-	-	4.0004	-	-
C_1-Cl_2	3.9019	3.9728	4.0459	4.1431	-	-	-	3.9762	-	-
C_1-Cl_3	3.9019	3.9449	4.0459	-	-	-	-	4.0004	-	-
C_2-Cl_4	3.9019	-	-	-	-	4.3538	-	4.2642	4.0163	-
C_2-Cl_5	3.9019	4.0773	4.0459	-	-	-	-	-	4.0163	4.1906
C_2-Cl_6	3.9019	4.0773	4.0459	4.2774	4.3464	-	-	-	4.0163	4.1906

Table 6.24. Unscaled stretching force constants in mdyneÅ^{-1}, from the HF (MP2) calculations for the HFCs.

Force constant	Force constants for individual HFCs and HFCas.									
	170	161	152	143	134	125	116	152a	143a	134a
C_1-C_2	5.0262(4.9080)	5.1965(5.0026)	5.2559(4.9491)	5.3830	5.4339	5.4430	5.4956	5.3862(5.1303)	5.5190	5.4479
C_1-F_1	-	-	6.9276(6.0069)	-	-	8.1414	8.2922	-	7.6847	7.9136
C_1-F_2	-	-	-	-	7.5855	8.0955	8.2922	-	7.6847	7.9567
C_1-F_3	-	-	-	7.1534	7.5855	8.1414	8.2922	-	7.6847	7.9136
C_2-F_4	-	6.6784(5.7926)	6.9276(6.0069)	7.4295	7.5855	-	8.2922	-	-	7.3709
C_2-F_5	-	-	-	7.3822	7.5855	7.8371	8.2922	7.1706(6.0797)	-	-
C_2-F_6	-	-	-	-	-	7.8371	8.2922	7.1706(6.0797)	-	-
C_1-H_1	5.7988(5.5406)	5.8669(5.5918)	-	5.9936	6.1862	-	-	5.9338(5.6440)	-	-
C_1-H_2	5.7988(5.5406)	5.8645(5.5916)	5.9507(5.5270)	6.0079	-	-	-	5.9452(5.6549)	-	-
C_1-H_3	5.7988(5.5406)	5.8669(5.5918)	5.9507(5.5270)	-	-	-	-	5.9338(5.6440)	-	-
C_2-H_4	5.7988(5.5406)	-	-	-	-	6.1717	-	6.0427(5.4958)	6.0111	-
C_2-H_5	5.7988(5.5406)	5.8754(5.4608)	5.9507(5.5270)	-	-	-	-	-	6.0111	6.0525
C_2-H_6	5.7988(5.5406)	5.8754(5.4608)	5.9507(5.5270)	6.1179	6.1862	-	-	-	6.0111	6.0525

calculating the fundamental frequencies. The F matrix diagonals include contributions from the non-bonded interactions. In addition, the HF and MP2 force constants need to be scaled to account for systematic errors. The determination of the scaling factors requires reliable assignments of all vibrational fundamentals followed by refinement of individual scaling factors until an optimised set can be obtained (Fogarasi and Pulay 1985). It has been found that several scaling factors may be required, depending on the nature of the stretch or bend, for example, six scaling factors were used when calculating the vibrational frequencies for benzene, ranging in magnitude from 0.690 to 0.919 (Fogarasi and Pulay 1985). At present, research is being carried out by Zhou et al. (1993) on the compilation of force constants using suitable scaling factors in order to obtain accurate scaled quantum mechanical force fields for a range of molecules. The values in tables 6.23 and 6.24 are therefore unscaled.

For the first four HFCs, the results from the MP2 calculations have been included in tables 6.23 and 6.24 . These force constants are somewhat smaller than the HF values, which may be due in part to the fact that the scaling factors for the two theoretical methods are not likely to be identical. Since electron correlation is included in the MP2 calculations, it might be expected that the MP2 force constants are more accurate. However, some other discrepancies are apparent, for example, the C-C stretching force constant for the MP2 results does not increase for HFC152 from that for HFC161, and some of the C-H stretching force constants are not as expected. The differences are small however, and until further information on scaling factors is available, reasons for the discrepancies cannot be determined.

6.2.3. Comparisons between the UB and HF force constants.

The C-C stretching force constants obtained by the HF method of calculation increase with an increasing number of fluorine atoms, in agreement with the UB results. For the CFCs there is a larger increase than for the HFCs, from 4.3266 to 5.4956mdyneÅ^{-1} compared to 5.0262 to 5.4956mdyneÅ^{-1} for the HF results and 1.4734 to 3.3740mdyneÅ^{-1} compared to 2.8992 to 3.3740mdyneÅ^{-1} for the UB results.

The C-Cl and C-H stretching force constants also increase with increasing numbers of fluorine atoms, however, for the HFCs, the HF force constant for the C-F stretch increases, unlike that for the UB force field. Table 6.23 and 6.24 illustrate the problem of using only one UB force constant for similar stretches. For example, for CFC115, there is not only a difference between the stretching force constants for the C-F bond belonging to the CF_2Cl end and that from the CF_3 end, but also between the force constants associated with the three stretches at the CF_3 end alone. This is due to the fact that the chlorine atom is not equidistant from all three fluorine atoms in that group. The UB force field will allow for the difference in the stretching force constants for the two ends of the molecule, by incorporating some non-bonded interactions between atoms attached to the same carbon when creating the F matrix, but no difference will be seen between the C-F stretches at the CF_3 end, as non-bonded interactions between atoms more than two bonds apart are not included in the construction of the force field.

By comparing the stretching force constants from table 6.20 and 6.21 to those of table 6.23 and 6.24 respectively, it can be concluded that by allowing for small non-bonded contributions to the UB results, and with scaling factors in the range 0.6 to 0.8 for the HF results, the force constants for both types of calculations are similar.

Chapter 7.

Infrared absorbance intensities and optimised geometries.

Comparisons have been made between the calculated infrared absorbance intensities from the *ab initio* calculations and the experimental integrated intensities reported in chapter four of this work. The change in intensity with increasing numbers of fluorine atoms in the molecule is investigated. It was necessary to optimise the geometry using *ab initio* methods before calculating frequencies. The optimised bond lengths and angles are given in tables 7.4 and 7.5, and compared to the experimental values used in the initial calculations.

7.1 Infrared absorption intensities.

Although infrared intensities are determined by *ab initio* methods at HF level when the frequency calculations are requested these values have always been seen as qualitative rather than quantitative (Foresman and Frisch 1993). The intensity calculations involve the determination of the dipole moment and Fogarasy and Pulay (1985) report that basis sets without polarisation and diffuse functions only produce semi-quantitative results. In this work the polarised basis set 6-31G*, which allows orbitals to change shape, is used. However, the basis set 6-31G* does not include diffuse functions, which allow orbitals to occupy a large region of space (Foresman and Frisch 1993). Calculated intensities are considered to be correct qualitatively, in that they correctly differentiate between strong, medium and weak bands (Fogarasy & Pulay 1985), however, in this work, comparisons between the total intensities from both the calculated and experimental results show a reasonable quantitative agreement when a scaling factor is used. Individual intensities and corresponding frequencies for all 19 molecules are given in appendix F. The units for the HF results are km mole^{-1}, whereas the experimental results are given in cm^{-2}atm^{-1}, the commonly used unit for experimental methods. The conversion factor 0.245 (Person and Zerbi 1982) is used to convert from cm^{-2}atm^{-1} to km mole^{-1} since it can be assumed that the results obtained in this work are valid for a temperature of 298K. Table 7.1 shows the total experimental and calculated infrared intensities for the region 3500cm^{-1} to 450cm^{-1}. Intensities below

450cm^{-1} were not measured experimentally, and, as can be seen from the individual calculated results in appendix F, these intensities are relatively very small.

Table 7.1. Comparison of experimental and calculated intensities for the range 3500-450cm^{-1}.

	Expt. intens. cm^{-2}atm^{-1}	Expt. intens. km mole^{-1}	HF intens. km mole^{-1}	Scaled† HF km mole^{-1}	% diff.‡
CFC110	1781*	436.3	471.09	345.78	-20.8
CFC111	2015	493.7	693.70	509.18	3.13
CFC112	2708	663.5	902.84	662.68	-0.12
CFC112a	2622	642.4	922.37	677.02	5.39
CFC113	3402	833.5	1132.44	831.21	-0.27
CFC113a	3177	778.4	1119.15	821.46	5.53
CFC114	3979	974.9	1313.57	964.16	-1.10
CFC114a	3803	931.7	1340.89	984.21	5.64
CFC115	4588	1124.1	1545.16	1134.15	0.89
FC116	5049	1237.0	1677.91	1231.59	-0.44
HFC170	793*	194.3	292.48	214.68	10.5
HFC161	1064	260.7	392.83	288.34	10.6
HFC152	-	-	459.47	377.25	
HFC152a	1746	427.8	660.79	485.02	13.4
HFC143	2043	500.5	715.59	525.24	4.94
HFC143a	3210	786.5	994.15	729.71	-7.22
HFC134	2802	686.5	904.91	664.20	-3.25
HFC134a	3481	852.8	1068.30	784.13	-8.05
HFC125	4224	1034.9	1322.07	970.40	-6.23

* Values taken from Tanabe & Saëki 1972.

† Scaling Factor = 0.734, as described in text.

‡ % diff. = [(scaled HF value - experimental value)/experimental value]*100.

The scaling factor of 0.734 was derived by calculating the ratio of the experimental total intensities to the HF total intensities for each molecule, and then averaging this value over all the compounds, excluding HFC152 for which no experimental results were available. The intensities of CFC110 and HFC170 were not measured in this work, and so intensity values were taken from Tanabe & Saëki (1972). The percentage differences between the experimental and the calculated values are less than 6% for the CFCs, with the exception of that for CFC110. The large discrepancy for CFC110 may be due to the fact that the intensities measured by Tanabe & Saëki

(1972) were not obtained using the same criteria as those used in the measurements taken in this work. It is possible that if all the intensities had been measured using the method followed by Tanabe & Saëki (1972), a different scaling factor would be required overall. The intensities for the HFCs are not in such good agreement, although the percentage differences between the experimental and calculated results are not large, considering that the experimental values have an error margin of ±4%.

The results for the MP2 theoretical level of calculations are not included here, as there are only two experimental results to compare with the four molecules investigated. The MP2 results are given in appendix F and are , in general, lower than the HF results, therefore needing a larger scaling factor. It should be noted that the calculated frequencies required a larger scaling factor for the MP2 level of theory than for the HF calculations.

It is not possible to attribute individual bands to C-F stretching modes, since there is considerable mixing of modes between the C-F and C-C stretches and some of the higher CH bending vibrations, as can be seen from the potential energy distributions given in appendix E. However, C-F stretching frequencies dominate the region of approximately 1350-1000cm^{-1}, and so this area has been investigated more closely. Table 7.2 lists the intensities in this region, and using the scaling factor 0.734 derived for the total intensities, comparisons have been made between the experimental and calculated values. CFC110 and HFC170 have been excluded from this table, as they do not contain fluorine atoms, and do not absorb in the region of interest. Experimental results for the HCFCs are also included in the table, although time did not permit theoretical studies of these molecules to be carried out. The percentage differences between the experimental and calculated results for this region are generally larger than those for the total region, however, they are still less than 10% for the CFCs.

Changes in intensities with changes in the number of fluorine atoms have been plotted and displayed in figures 7.1 for the CFCs, 7.2 for the HFCs and 7.3 for the HCFCs. From the graphs, the increase in intensities for the CFCs and the HFCs with increasing numbers of fluorine atoms can be seen. For interest, lines were fitted for all the points on each graph, using the commercial package CA-Cricket Graph™. Attempts were made to find a line of best fit using linear, polynomial and exponential functions. In each case, the line of best fit was found to be a polynomial of order 2, suggesting that the intensity increases proportionally with the square of the number of fluorine atoms in the molecule. No references were found in the literature suggesting such a quantitative relationship. The HCFCs are not directly comparable, as the change in the number of the fluorine atoms is not the only difference between the molecules.

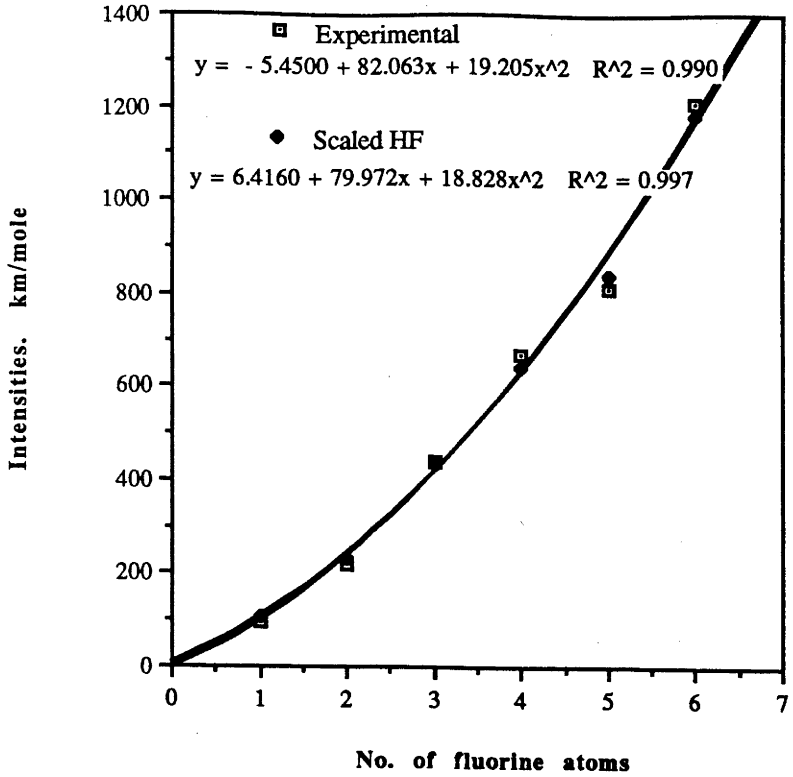
Table 7.2. Comparison of intensities for the approximate C-F stretching region of 1350-1000cm^{-1}.

	Expt. intens. cm^{-2}atm^{-1}	Expt. intens. km mole^{-1}	HF intens. km mole^{-1}	Scaled† HF km mole^{-1}	% diff. ‡
CFC111	392	96.0	142.15	104.34	8.69
CFC112	885	216.8	316.13	232.04	7.03
CFC112a	1267	310.4	460.09	338.71	8.80
CFC113	1788	438.1	589.83	432.94	-1.18
CFC113a	2005	491.2	687.03	504.27	2.66
CFC114	2722	666.9	875.50	642.62	-3.64
CFC114a	2474	606.1	833.59	611.86	0.95
CFC115	3313	811.7	1142.04	838.26	3.27
FC116	4934	1208.8	1609.05	1181.04	-2.30
HFC161	434	106.3	125.97	92.46	-13.02
HFC152	-	-	288.35	211.65	-
HFC152a	1093	267.8	312.23	229.18	-14.42
HFC143	1425	349.1	440.15	323.07	-7.46
HFC143a	2325	569.6	741.36	544.16	-4.47
HFC134	2269	555.9	684.25	502.24	-9.65
HFC134a	2766	677.7	854.72	627.36	-7.43
HFC125	3538	866.8	1122.24	823.72	-4.97
HCFC141b	911	223.2			
HCFC142b	1666	408.2			
HCFC123	2418	592.4			
HCFC124	2751	674.0			
HCFC244ca	2059	504.5			
HCFC235cb	3286	805.1			
HCFC225ca	2824	691.9			
HCFC225cb	2710	664.0			
FC218	5150	1261.8			

† Scaling factor = 0.734, as described in text.

‡ % diff. = [(scaled HF value - experimental value)/experimental value]*100.

(a) CFC vibrational intensities for the region 1350-1000cm-1.



(b) CFCa vibrational intensities for the region 1350-1000cm-1

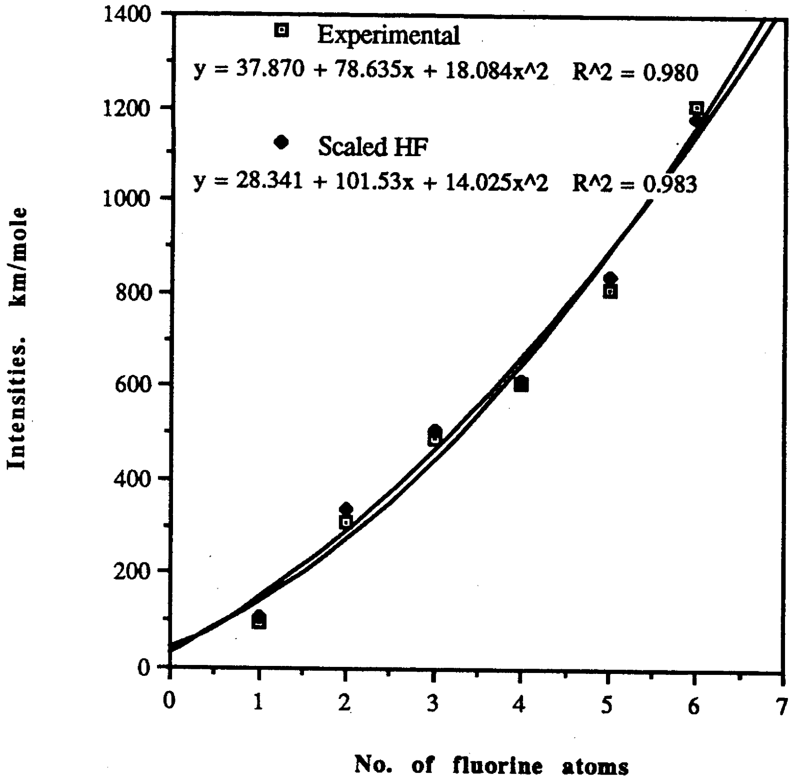
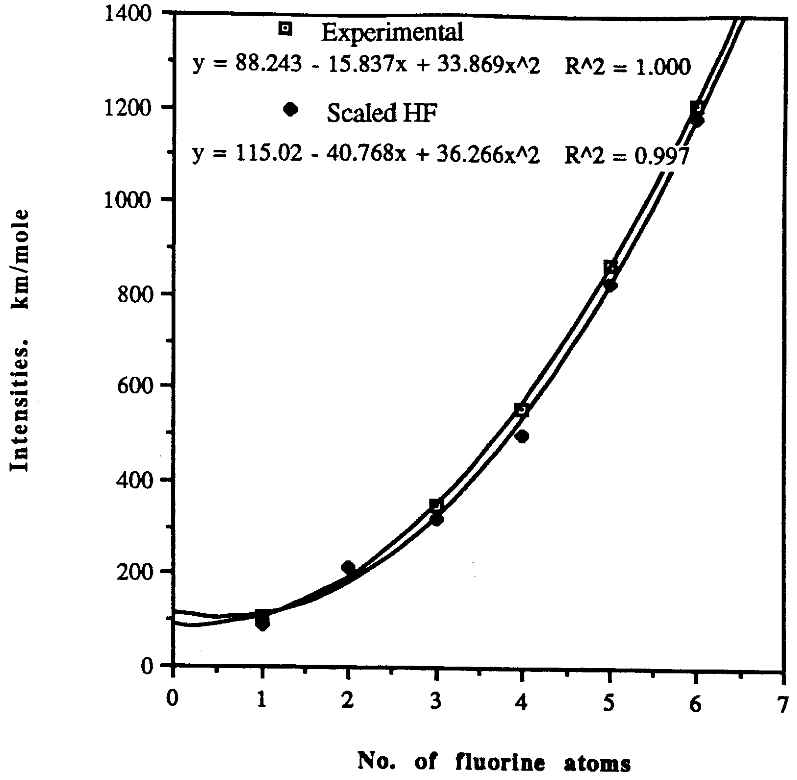


Figure 7.1. Changes in intensities with changing numbers of fluorine atoms for the (a) CFCs and (b) CFCas.

(a) HFC vibrational intensities for the region 1350-1000cm-1



(b) HFCa vibrational intensities for the region 1350-1000cm-1

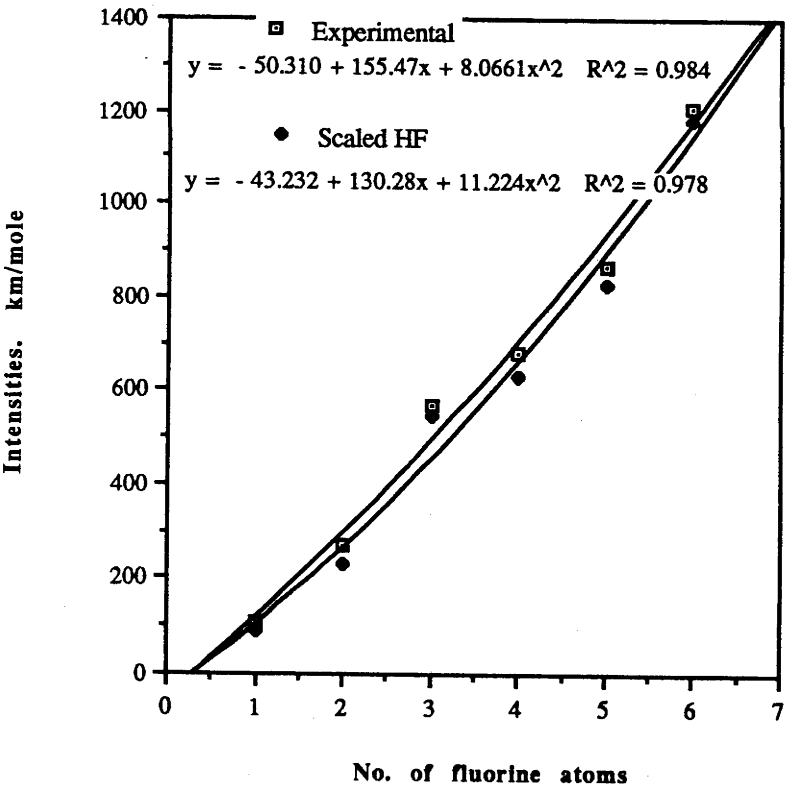


Figure 7.2. Changes in intensities with changing numbers of fluorine atoms for the (a) HFCs and (b) HFCas.

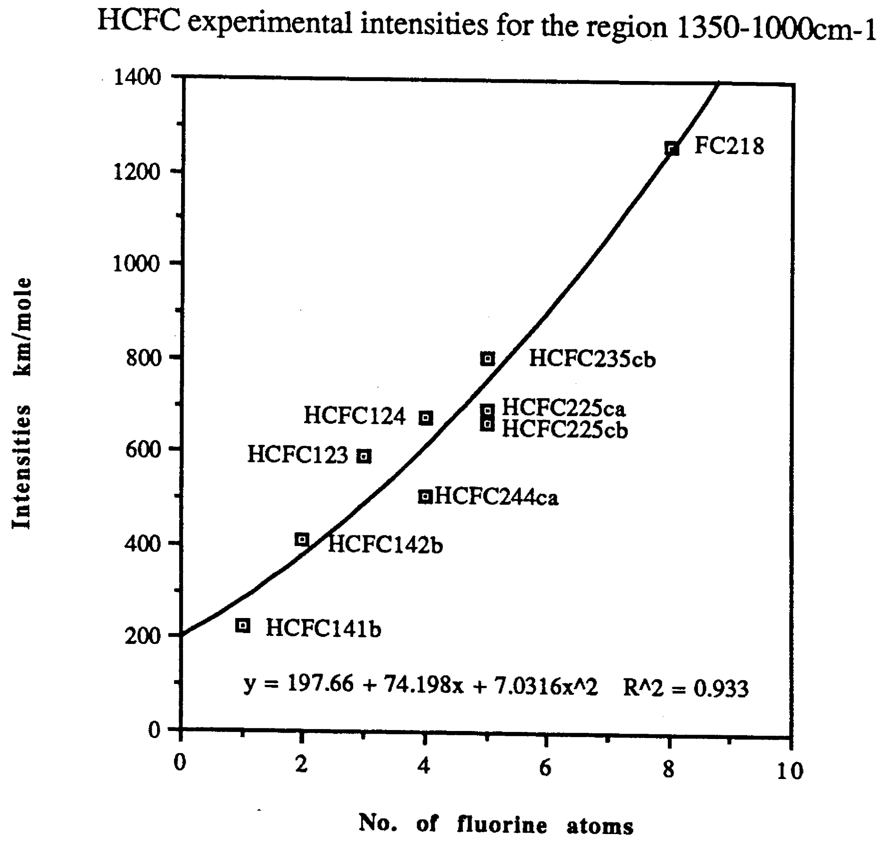


Figure 7.3. Change in intensities with changing numbers of fluorine atoms for the HCFCs.

For the CFCs, the differences between intensities of the isomeric pairs of molecules are relatively small. For the experimental values of the 'a' type molecules, where the fluorine atoms preferentially share the same carbon atom, the intensities are lower than for the molecules with a more even distribution of fluorine atoms within the molecule. This is reversed for the calculated intensities of CFC112, CFC112a and CFC114, CFC114a, however, the differences are small. For the HFCs, the differences are much larger, and in all cases the 'a' type molecules have higher total intensities. This suggests that the intensity of a C-F stretching mode may be less when the fluorine atom shares a carbon atom with a hydrogen atom, than when the fluorine atom shares the carbon atom with another fluorine atom. However, since only five experimental values and six theoretical values are available, any conclusion from these results must be tentative.

In contrast, the C-H stretching region intensities do not agree well. These values are given in table 7.3. This is due, in part, to the fact that the experimental intensities are weak and therefore may include large errors. The calculated frequencies for the C-H stretching region show generally larger errors than for the other regions for both the HF and MP2 calculations. This has been attributed to the use of the harmonic approximation in the calculations (Fogarasy and Pulay 1985).This may also be a contributing factor to the larger percentage differences obtained for the calculated intensities involving a C-H stretch. It can be seen from table 7.3, however, that the calculated intensities could be used to give the relative strengths of the bands.

Table 7.3. Intensities for the C-H stretching region, approximately 3200-2800cm^{-1}.

	Expt. intens. cm^{-2}atm^{-1}	Expt. intens. km mole^{-1}	HF intens. km mole^{-1}	Scaled† HF km mole^{-1}
HFC170	698*	171.0	275.94	202.54
HFC161	437	107.1	203.89	149.66
HFC152	-	-	167.01	122.59
HFC152a	195	47.8	113.20	83.09
HFC143	186	45.6	102.76	75.43
HFC143a	27.7	6.79	24.45	17.95
HFC134	128	31.4	59.75	43.86
HFC134a	80.4	19.7	40.91	30.03
HFC125	51.2	12.5	30.39	22.31

* Value taken from Tanabe and Saëki 1972.

† Scaling Factor = 0.734, as described in text.

A more difficult problem arose in the comparison of intensities attributed to individual bands. For example, for CFC111, shown in figure 4.1, the individual intensities for the bands centred around 1114, 1018, 856 and 810cm^{-1} are 70.3, 25.7, 82.3 and 173km mole^{-1} respectively. When compared to the HF results, the corresponding bands at 1135, 1035, 860 and 816cm-1 have unscaled intensities of 113, 30.0, 136 and 245km mole^{-1} respectively, and scaled intensities of 82.9, 22.0, 100 and 180km mole^{-1} respectively. While these results are in reasonable agreement, those for HFC143 , shown in figure 4.12, are not. For HFC143, experimental bands at 1433, 1379, 1319 and 1249cm^{-1} have intensities 17.2, 16.9, 10.2 and 13.7km mole^{-1} respectively. These do not compare well with the corresponding calculated bands at 1460, 1403, 1339 and 1240cm^{-1} , having unscaled intensities of 15.8, 40.1, 41.2 and 15.7km mole^{-1} respectively, and scaled intensities of 11.6, 29.4, 30.3 and 11.5km mole^{-1} respectively. These discrepancies may be attributed to several different problems: the experimental intensities are relatively weak, and therefore may include large errors in absorbance measurements; the spectral bands are adjacent to one another and errors in areas at the band limits may have occurred; and the presence of , as yet, uninvestigated errors in the calculations of small intensities.

7.2. Optimised molecular geometries.

Comparisons between experimental values used for the UB calculations and the optimised geometries from the HF *ab initio* calculations are given in tables 7.4 and 7.5. Only bond lengths and angles between fluorine, chlorine or hydrogen atoms attached to a carbon atom and the C-C axis are compared. Comparisons of angles between fluorine, chlorine and hydrogen atoms attached to the same carbon atom and the dihedral angles used in the *ab initio* results have not been made, as conversions between the results for the two methods of calculation would have had to be carried out.

The lengths of the C-C bonds obtained from the literature vary considerably, as do the optimised results. However, for the CFCs, the optimised C-C bond length decreases with a decreasing number of chlorine atoms, corresponding to the increase in the C-C stretching force constants calculated using both the UB force field and *ab initio* methods. The C-C bond lengths for the HFCs show a smaller and more random variation. This again is expected since these calculated force constants show only small variations.

For all the molecules, whether CFCs or HFCs, a trend can be seen in the lengths of the C-F bonds, where the bond lengths increase with fewer fluorines in the end group such that, C-F (CF_3 group) < C-F (CF_2H group) < C-F (CFH_2 group). The changes in the bond lengths between atoms in the same end group but with a different total number of fluorine atoms in the molecule are very small. C-Cl bond lengths increase with an increasing number of chlorines in the group. This corresponds to the changes in the C-Cl stretching force constants shown in tables 6.20 and 6.23. The same trend can be seen for the C-H bond lengths, although overall, the variations in bond lengths for the C-Cl and C-H bonds are smaller than those for the C-C and C-F bonds.

The CCX angles are variable, however, a small decrease in the CCF angle for fewer fluorine atoms in the group can be detected. The CCCl angle increases for fewer chlorines in the group and the CCH angle increases for fewer hydrogens. A change in one CCX angle will affect the other angles between the atoms in the same group, so no conclusion has been drawn here.

The optimised geometries are determined from the calculations when searching for a stationary point on the energy surface, and thus are calculated using the approximations described in section 1.6.2.

Table 7.4. Experimental values from table 5.1* and HF optimised values for the geometry of the CFCs. Bond lengths are given in Å, and angles in degrees.

Stretch or bend†	CFC110		CFC111		CFC112		CFC112a		CFC113	
	Expt.	Opt.	Expt.	Opt.	Expt.	Opt.	Expt.	Opt.	Expt.	Opt.
C-C	1.499	1.582	1.54	1.570	1.54	1.558	1.55	1.559	1.54	1.549
C-F (CF_3)										
C-F (CF_2Cl)							1.33	1.318	1.35	1.317
C-F ($CFCl_2$)			1.37	1.328	1.37	1.321			1.37	1.327
C-Cl (CCl_3)	1.763	1.769	1.77	1.767			1.76	1.765		
C-Cl (CCl_2F)			1.77	1.760	1.77	1.762			1.75	1.757
C-Cl ($CClF_2$)							1.74	1.753	1.74	1.752
CCF (CF_3)										
CCF (CF_2Cl)							108.0	108.50	109.5	108.69
CCF ($CFCl_2$)			109.5	106.69	109.5	108.51			109.5	107.25
CCCl (CCl_3)	110.7	110.12	109.5	109.57			110.7	109.11		
CCCl (CCl_2F)			109.5	112.07	109.5	110.43			109.5	110.53
CCCl ($CClF_2$)							110.6	114.01	109.5	112.54

	CFC113a		CFC114		CFC114a		CFC115		FC116	
	Expt.	Opt.	Expt.	Opt.	Expt.	Opt.	Expt.	Opt.	Expt.	Opt.
C-C	1.545	1.549	1.55	1.540	1.56	1.540	1.555	1.532	1.545	1.525
C-F (CF_3)	1.33	1.310			1.33	1.310	1.33	1.311	1.326	1.311
C-F (CF_2Cl)			1.33	1.319			1.33	1.319		
C-F ($CFCl_2$)					1.40	1.330				
C-Cl (CCl_3)	1.771	1.764								
C-Cl (CCl_2F)					1.78	1.754				
C-Cl ($CClF_2$)			1.74	1.748			1.74	1.748		
CCF (CF_3)	108.9	110.29			109.5	110.07	110.9	109.9	109.8	109.8
CCF (CF_2Cl)			108.0	108.59			108.0	108.1		
CCF ($CFCl_2$)					109.5	106.33				
CCCl (CCl_3)	110.7	108.76								
CCCl (CCl_2F)			110.6	111.88	109.5	110.58				
CCCl ($CClF_2$)							110.6	112.30		

† The stretches and bends define the atoms involved. The atoms belong to the end group shown in the brackets.

* Literature references for the experimental geometries are given in table 5.1.

Table 7.5. Experimental values from table 5.1* and HF optimised values for the geometry of the HFCs. Bond lengths are given in Å, and angles in degrees.

Stretch or bend†	HFC170		HFC161		HFC152		HFC152a		HFC143	
	Expt.	Opt.	Expt.	Opt.	Expt.	Opt.	Expt.	Opt.	Expt.	Opt.
C-C	1.5324	1.527	1.505	1.512	1.5033	1.512	1.54	1.502	1.500	1.506
C-F (CF_3)										
C-F (CF_2H)							1.345	1.346	1.3534	1.341
C-F (CFH_2)			1.398	1.373	1.3892	1.367			1.3878	1.361
C-H (CH_3)	1.1068	1.086	1.090	1.085			1.10	1.083		
C-H (CH_2F)			1.095	1.083	1.1034	1.082			1.0881	1.081
C-H (CHF_2)							1.10	1.079	1.0881	1.078
CCF (CF_3)										
CCF (CF_2H)							109.4	110.07	109.1	108.99
CCF (CFH_2)			109.7	109.5	110.3	108.10			109.1	108.23
CCH (CH_3)	111.0	111.2	109.7	110.4			108.7	109.81		
CCH (CH_2F)			112.9	111.5	111.0	110.81			108.9	109.97
CCH (CHF_2)							109.8	113.71	108.9	113.22

	HFC143a		HFC134		HFC134a		HFC125		FC116	
	Expt.	Opt.	Expt.	Opt.	Expt.	Opt.	Expt.	Opt.	Expt.	Opt.
C-C	1.53	1.500	1.518	1.510	1.525	1.508	1.52	1.518	1.545	1.525
C-F (CF_3)	1.335	1.325			1.335	1.320	1.335	1.315	1.326	1.311
C-F (CF_2H)			1.350	1.337			1.345	1.330		
C-F (CFH_2)					1.39	1.355				
C-H (CH_3)	1.085	1.082								
C-H (CH_2F)					1.09	1.080				
C-H (CHF_2)			1.098	1.077			1.10	1.077		
CCF (CF_3)	111.0	111.64			110.9	110.84	110.8	110.22	109.8	109.79
CCF (CF_2H)			108.2	108.25			109.6	108.42		
CCF (CFH_2)					109.7	108.26				
CCH (CH_3)	108.3	109.40								
CCH (CH_2F)					109.8	109.44				
CCH (CHF_2)			110.3	112.57			110.0	111.41		

† The stretches and bends define the atoms involved. The atoms belong to the end group shown in the brackets.

* Literature references for the experimental geometries are given in table 5.1.

The force constants are directly related to the molecular geometries and so any errors introduced by optimisation are carried over into the force constant calculations (Fogarasy and Pulay 1985). Initially, the *ab initio* calculations were carried out using the experimental geometries with no optimisation, as it was thought that it would be more meaningful to compare the two types of calculations when identical molecular geometries had been used. Fogarasy and Pulay (1985) suggested that this may be done, provided that corrections to the frequencies were made to compensate for the fact that the molecule, when constructed using the experimental geometries, is not necessarily at a potential minimum. It was not possible to calculate the corrections required for the energies, and so the frequency calculations were preceded by an optimisation step, as suggested by Foresman and Frisch (1993).

Chapter 8.

Conclusion.

The aim of this work has been to measure the integrated absorption intensities of both halocarbons of topical interest and a range of chloroethanes and ethanes to observe the effects of fluorination. Difficulties were encountered in obtaining new halocarbons thought to have commercial applications, resulting in the syntheses of two halopropanes. 1-Chloro-2,2,3,3-tetrafluoropropane (HCFC244ca) and 1-chloro-2,2,3,3,3-pentafluoropropane (HCFC235cb) were synthesised and used in subsequent spectroscopic measurements. The consistency of the resultant integrated band intensities confirmed that the compounds were of a purity comparable with the other halocarbons used.

In an attempt to obtain reproducible results for the absorption intensities, the errors in FTIR spectroscopy were examined closely, and results from different instruments were compared. A comprehensive set of procedures for recording and analysing infrared spectra was determined in an attempt to reduce errors and discrepancies in the data. Band intensities in the ranges 3500-450cm^{-1}, 1250-833cm^{-1}, and 1300-700cm^{-1} were measured for 25 compounds with an estimated error of ±4%.

In order to investigate the effects on the vibrational absorbance of fluorine atoms in a molecule, 19 ethane-type compounds were selected for theoretical studies. Several different methods of modelling chemical substances may be found in the literature, and in order to compare experimental and theoretical results, two approaches were used in this work: a normal coordinate analysis using a Urey-Bradley force field; and *ab initio* calculations. The UB force field gives a relatively simple mechanistic model, without reference to quantum theories and methods. In contrast, *ab initio* methods are based on Schrödinger's wave equation and a number of mathematical approximations.
The calculations enabled some comparisons of fundamental frequencies, force constants, intensities and molecular geometries to be made. The results from three different sources were combined; those from both experiments reported in the literature and experiments carried out as part of this work; from the normal coordinate analyses; and from *ab initio* methods. Using these results, literature assignments of the fundamental frequencies have been confirmed and some new assignments tentatively made for the 19 compounds studied.

While the discrepancies between the experimental frequencies and the UB force field were larger than those for the *ab initio* results, the errors were such that the resultant force constants may be considered reasonable, and the group force constants may be used as a starting point for frequency calculations for similar molecules. As far as possible, the UB and *ab initio* force constants were compared and found to be in reasonable agreement, in that the trends across a group of molecules with increasing numbers of fluorine atoms were generally consistent. C-H stretching force constants from the two methods of calculation were not in agreement, however, variation was also seen in the geometries. Problems occur when using the simple UB force field for the C-H group (Shimanouchi 1963), and have been reported for C-H stretching frequencies and force constants when using *ab initio* methods (Fogarasy and Pulay 1985).

The theoretical methods and basis set used for *ab initio* calculations were the most sophisticated available for this work, and have produced satisfactory results. Comparisons of HF and MP2 calculations using the basis set 6-31G* show similar results with the judicious use of scaling factors.

It was not possible to calculate intensities as part of the UB force field, however, intensity calculations were obtained from the *ab initio* calculations. Comparison between the experimental and theoretical results have shown surprisingly good agreement, considering that calculated intensities have been assumed to be only qualitative (Foresman and Frisch 1993). The derivation of a scaling factor of 0.734 for intensities in the range 3500-450cm^{-1} has enabled comparisons to be made between the experimental and calculated results for the C-F stretching region of approximately 1350-1000cm^{-1} and the C-H stretching region of 3200-2800cm^{-1}. A satisfactory agreement was found in the results for the C-F stretching region, but not for the C-H region, due, in part, to the problems associated with calculating frequencies and force constants for the C-H bond.

A relationship has been observed between the number of fluorine atoms and the absorption intensity of the molecule in the mid-infrared region. Initially, the calculations for the HCFCs were not carried out as there is insufficient relationship between the HCFC molecules used in the experimental part of this work. However, the usefulness of combining experimental and theoretical results has become apparent for studies of frequencies and intensities, and so it would be of interest to complete calculations for the HCFCs used. Barton et al. (1993) suggested that the combination of theoretical calculations and experimental measurements in the study of vibrational spectroscopy is much more powerful than if either technique is used alone. This has proved to be the case in this work, where the assignment of fundamental modes has been made easier by the use of both observed and calculated values. Calculations involving all halopropanes containing fluorine, chlorine and hydrogen atoms would enable further investigation of the effects on intensities of the position of the fluorine atoms within the molecules, as well as facilitate the assignments of fundamental frequencies should the relevant spectra become available.

The experimental results of this work may be useful in the calculations of global warming potentials. The frequencies, force constants and intensity calculations carried out suggest that these methods of calculation, when applied to fluorocarbons thought to have commercial uses, may be used to predict infrared spectra with an accuracy suitable for use in climate modelling techniques. Should further studies of the relationship between the intensities and the number of fluorine atoms be undertaken to confirm the findings made in chapter seven, it may be possible to estimate the intensity of new halopropanes in the C-F stretching region using graphs such as those in figures 7.1, 7.2 and 7.3, without recourse to synthesis or expensive *ab initio* calculations.

Appendix A

Nomenclature of Chlorofluorocarbons.

Chlorofluorocarbons have been collectively named 'freonXYZ', where,

X is the number of carbon atoms minus 1, if X=0, it is omitted.

Y is the number of hydrogen atoms plus one.

Z is the number of fluorine atoms. (Selinger 1989)

The number of chlorine atoms required to complete the compound can be easily calculated. 'Freon' is usually replaced by CFC for compounds containing carbon, fluorine and chlorine only, HFC for compounds containing carbon, fluorine and hydrogen only, and HCFC for compounds containing carbon, fluorine, chlorine and hydrogen.

For example, $CHCl_2F$ is known as freon21 or HCFC21

CH_2FCHF_2 is known as freon143 or HFC143

Molecules exhibiting isomerism are further designated with lower case letters. In the case of the 2-carbon molecules, the difference between the sum of the atomic weights of the atoms at each carbon is calculated. The isomer with the smallest difference has no letter, the next smallest is designated 'a', the next 'b' and so on. For example $C_2Cl_3F_3$ has two isomers; CCl_2FCF_2Cl, where the difference between the atomic weights at the two ends is 90-73=17, so it is designated CFC113; and CCl_3CF_3 , where the difference is 106-57=49 hence CFC113a. In the case of 3-carbon molecules, two letters are used. The first relates to the central carbon atom , $-CCl_2-$ 'a', -CFCl- 'b', $-CF_2-$ 'c', -CHCl- 'd', -CHF-'e', $-CH_2-$ 'f'. The second letter follows the logic of the 2-carbon molecule numbering system, except that it cannot be omitted, hence 'a' denotes the smallest difference, 'b' the next smallest and so on. (Dudman et al.1990)

Appendix B

Data input for the Urey-Bradley force field calculations.

Data input for the program NORCORD.

CFC110

```
-09
   1  1  8  5 22 22  4 2211111
  4  1  1  0  3  1  6  0  8  2
CCl3CCl3  hexachloroethane
October 1992
  1  1    0           2  1   1.564        3  1   0.0          1  2   0.0
  2  2   0.0          3  2   0.0          1  3   0.8312       2  3   2.1690
  3  3   1.4396       1  4   0.8312       2  4   2.1690       3  4  -1.4396
  1  5  -1.66232      5   2.1690          3  5   0.0          1  6   1.6623
  2  6  -0.6050       3  6   0.0          1  7  -0.8312       2  7  -0.6050
  3  7   1.4396       1  8  -0.8312       2  8  -0.6050       3  8  -1.4396
-1
  1  1  1  2
  2  1  1  3
  3  1  1  4
  4  1  1  5
  5  1  2  6
  6  1  2  7
  7  1  2  8
  8  2  2  1  3
  9  2  2  1  4
 10  2  2  1  5
 11  2  1  2  6
 12  2  1  2  7
 13  2  1  2  8
 14  2  3  1  4
 15  2  3  1  5
 16  2  4  1  5
 17  2  6  2  7
 18  2  6  2  8
 19  2  7  2  8
 20  4  5  1  2  6
 21  4  3  1  2  8
 22  4  4  1  2  7
  1  1   1.000000     2  2   0.166667     2  3  0.166667      2  4   0.166667
  2  5   0.166667     2  6   0.166667     2  7   0.166667     3  8   0.166667
  3  9   0.166667     3 10   0.166667     3 11   0.166667     3 12   0.166667
  3 13   0.166667     4 14   0.166667     4 15   0.166667     4 16   0.166667
  4 17   0.166667     4 18   0.166667     4 19   0.166667     5 20   0.333333
  5 21   0.333333     5 22   0.333333     6  2   0.166667     6  3   0.166667
  6  4   0.166667     6  5  -0.166667     6  6  -0.166667     6  7  -0.166667
  7  8   0.166667     7  9   0.166667     7 10   0.166667     7 11  -0.166667
  7 12  -0.166667     7 13  -0.166667     8 14   0.166667     8 15   0.166667
  8 16   0.166667     8 17  -0.166667     8 18  -0.166667     8 19  -0.166667
  9  2   0.166667     9  3  -0.083333     9  4  -0.083333     9  5  -0.083333
  9  6  -0.083333     9  7   0.166667    10  3   0.25        10  4  -0.25
 10  5  -0.25        10  6   0.25        11  8   0.166667    11  9  -0.083333
 11 10  -0.083333    11 11  -0.083333    11 12  -0.083333    11 13   0.166667
```

```
 12  9   0.25        12 10  -0.25        12 11  -0.25        12 12   0.25
 13 14   0.166667    13 15  -0.083333    13 16  -0.083333    13 17  -0.083333
 13 18  -0.083333    13 19   0.166667    14 15   0.25        14 16  -0.25
 14 17  -0.25        14 18   0.25        15  2   0.166667    15  3  -0.083333
 15  4  -0.083333    15  5   0.083333    15  6   0.083333    15  7  -0.166667
 16  3   0.25        16  4  -0.25        16  5   0.25        16  6  -0.25
 17  8   0.166667    17  9  -0.083333    17 10  -0.083333    17 11   0.083333
 17 12   0.083333    17 13  -0.166667    18  9   0.25        18 10  -0.25
 18 11   0.25        18 12  -0.25        19 14   0.166667    19 15  -0.083333
 19 16  -0.083333    19 17   0.083333    19 18   0.083333    19 19  -0.166667
 20 15  -0.25        20 16   0.25        20 17  -0.25        20 18   0.25
 21 20   0.333333    21 21  -0.166667    21 22  -0.166667    22 21   0.5
 22 22  -0.5         -3
   12.01       12.01        35.45        35.45        35.45        35.45
   35.45       35.45
000
```

CFC111

```
-09
   1  1  8  2 22 22  4 2211111
 14  3  8  1
CFCl2CCl3  1,1,1,2,2-pentachlorofluoroethane
September 1992
  1  1   0.0          2  1   1.54         3  1   0.0          1  2   0.0
  2  2   0.0          3  2   0.0          1  3   0.8343       2  3   2.1308
  3  3   1.4455       1  4   0.8343       2  4   2.1308       3  4  -1.4455
  1  5  -1.6685       2  5   2.1308       3  5   0.0          1  6   1.2914
  2  6  -0.4573       3  6   0.0          1  7  -0.8343       2  7  -0.5908
  3  7   1.4455       1  8  -0.8343       2  8  -0.5908       3  8  -1.4455
-1
  1  1  1  2
  2  1  1  3
  3  1  1  4
  4  1  1  5
  5  1  2  6
  6  1  2  7
  7  1  2  8
  8  2  2  1  3
  9  2  2  1  4
 10  2  2  1  5
 11  2  1  2  6
 12  2  1  2  7
 13  2  1  2  8
 14  2  3  1  4
 15  2  3  1  5
 16  2  4  1  5
 17  2  6  2  7
 18  2  6  2  8
 19  2  7  2  8
 20  4  5  1  2  6
 21  4  3  1  2  8
 22  4  4  1  2  7
  1  1   1.000000     2  2   0.5          2  3   0.5          3  4   1.0
  4  5   1.0          5  6   0.5          5  7   0.5          6  8   0.5
  6  9   0.5          7 10   1.0          8 11   1.0          9 12   0.5
  9 13   0.5         10 14   1.0         11 15   0.5         11 16   0.5
 12 17   0.5         12 18   0.5         13 19   1.0         14 21   0.5
 14 22  -0.5         15  2   0.5         15  3  -0.5         16  6   0.5
```

```
 16 7   -0.5       17 8    0.5       17 9   -0.5       18 12   0.5
 18 13   -0.5      19 15    0.5      19 16   -0.5      20 17   0.5
 20 18   -0.5      21 20    1.0      22 21    0.5      22 22   0.5
-3
  12.01      12.01      35.45      35.45      35.45      19.00
  35.45      35.45
000
```

CFC112

```
-09
   1  1  8  4 22 22  4 2211111
  7  1  5  1  3  0  7  2
CFCl2CFCl2  1,1,2,2-tetrachlorodifluoroethane
October 1992
  1  1   0.0       2  1   1.54       3  1   0.0        1  2   0.0
  2  2   0.0       3  2   0.0        1  3   1.2914     2  3   1.9973
  3  3   0.0       1  4  -0.8333     2  4   2.1308     3  4  -1.4455
  1  5  -0.8333    2  5   2.1308     3  5   1.4455     1  6  -1.2914
  2  6  -0.4573    3  6   0.0        1  7   0.8333     2  7  -0.5908
  3  7   1.4455    1  8   0.8333     2  8  -0.5908     3  8  -1.4455
-1
  1  1  1  2
  2  1  1  3
  3  1  1  4
  4  1  1  5
  5  1  2  6
  6  1  2  7
  7  1  2  8
  8  2  2  1  3
  9  2  2  1  4
 10  2  2  1  5
 11  2  1  2  6
 12  2  1  2  7
 13  2  1  2  8
 14  2  3  1  4
 15  2  3  1  5
 16  2  4  1  5
 17  2  6  2  7
 18  2  6  2  8
 19  2  7  2  8
 20  4  3  1  2  6
 21  4  4  1  2  7
 22  4  5  1  2  8
  1  1    1.000000    2  2    0.5       2  5    0.5       3  3    0.25
  3  4    0.25        3  6    0.25      3  7    0.25      4  8    0.5
  4 11    0.5         5  9    0.25      5 10    0.25      5 12    0.25
  5 13    0.25        6 14    0.25      6 15    0.25      6 17    0.25
  6 18    0.25        7 16    0.5       7 19    0.5       8  3    0.25
  8  4   -0.25        8  6   -0.25      8  7    0.25      9  9    0.25
  9 10   -0.25        9 12   -0.25      9 13    0.25     10 14    0.25
 10 15   -0.25       10 17   -0.25     10 18    0.25     11 20    1.0
 12 21    0.5        12 22    0.5      13  3    0.25     13  4   -0.25
 13  6    0.25       13  7   -0.25     14  9    0.25     14 10   -0.25
 14 12    0.25       14 13   -0.25     15 14    0.25     15 15   -0.25
 15 17    0.25       15 18   -0.25     16 21    0.5      16 22   -0.5
 17  2    0.5        17  5   -0.5      18  3    0.25     18  4    0.25
 18  6   -0.25       18  7   -0.25     19  8    0.5      19 11   -0.5
 20  9    0.25       20 10    0.25     20 12   -0.25     20 13   -0.25
```

```
 21 14   0.25          21 15   0.25          21 17  -0.25          21 18  -0.25
 22 16   0.5           22 19  -0.5           -3
  12.01      12.01      19.00      35.45      35.45      19.00
  35.45      35.45
000
```

CFC112a

```
-09
   1  1  8  2 22 22  4 2211111
 14  3  8  1
CF2ClCCl3  1,1,1,2-tetrachlorodifluoroethane
October 1992
  1  1   0.0           2  1   1.55           3  1   0.0            1  2   0.0
  2  2   0.0           3  2   0.0            1  3   0.8232         2  3   2.1721
  3  3   1.4258        1  4   0.8232         2  4   2.1721         3  4  -1.4258
  1  5  -1.6464        2  5   2.1721         3  5   0.0            1  6   1.6284
  2  6  -0.6131        3  6   0.0            1  7  -0.6650         2  7  -0.4110
  3  7   1.0760        1  8  -0.6650         2  8  -0.4110         3  8  -1.0760
-1
  1  1  1  2
  2  1  1  3
  3  1  1  4
  4  1  1  5
  5  1  2  6
  6  1  2  7
  7  1  2  8
  8  2  2  1  3
  9  2  2  1  4
 10  2  2  1  5
 11  2  1  2  6
 12  2  1  2  7
 13  2  1  2  8
 14  2  3  1  4
 15  2  3  1  5
 16  2  4  1  5
 17  2  6  2  7
 18  2  6  2  8
 19  2  7  2  8
 20  4  5  1  2  6
 21  4  3  1  2  8
 22  4  4  1  2  7
  1  1    1.000000     2  2    0.5           2  3    0.5           3  4    1.0
  4  5    1.0          5  6    0.5           5  7    0.5           6  8    0.5
  6  9    0.5          7 10    1.0           8 11    1.0           9 12    0.5
  9 13    0.5         10 14    1.0          11 15    0.5          11 16    0.5
 12 17    0.5         12 18    0.5          13 19    1.0          14 21    0.5
 14 22   -0.5         15  2    0.5          15  3   -0.5          16  6    0.5
 16  7   -0.5         17  8    0.5          17  9   -0.5          18 12    0.5
 18 13   -0.5         19 15    0.5          19 16   -0.5          20 17    0.5
 20 18   -0.5         21 20    1.0          22 21    0.5          22 22    0.5
-3
  12.01      12.01      35.45      35.45      35.45      35.45
  19.00      19.00
000
```

CFC113

```
-09
   1  1  8  1 22 22  4 2211111
```

```
 22  4
CFCl2CF2Cl  1,1,2-trichlorotrifluoroethane
October 1992
  1  1   0.0           2  1   1.54          3  1   0.0           1  2   0.0
  2  2   0.0           3  2   0.0           1  3   0.8248        2  3   2.1242
  3  3   1.4286        1  4   0.8248        2  4   2.1242        3  4  -1.4286
  1  5  -1.2886        2  5   1.9963        3  5   0.0           1  6   1.2726
  2  6  -0.4506        3  6   0.0           1  7  -0.6363        2  7  -0.4506
  3  7   1.1021        1  8  -0.8201        2  8  -0.5808        3  8  -1.4205
-1
  1  1  1  2
  2  1  1  3
  3  1  1  4
  4  1  1  5
  5  1  2  6
  6  1  2  7
  7  1  2  8
  8  2  2  1  3
  9  2  2  1  4
 10  2  2  1  5
 11  2  1  2  6
 12  2  1  2  7
 13  2  1  2  8
 14  2  3  1  4
 15  2  3  1  5
 16  2  4  1  5
 17  2  6  2  7
 18  2  6  2  8
 19  2  7  2  8
 20  4  5  1  2  6
 21  4  3  1  2  8
 22  4  4  1  2  7
  1  1    1.000000     2  2    1.0        3  3    1.0         4  4    1.0
  5  5    1.0          6  6    1.0        7  7    1.0         8  8    1.0
  9  9    1.0         10 10    1.0       11 11    1.0        12 12    1.0
 13 13    1.0         14 14    1.0       15 15    1.0        16 16    1.0
 17 17    1.0         18 18    1.0       19 19    1.0        20 20    1.0
 21 21    1.0         22 22    1.0       -3
   12.01      12.01    35.45      35.45  19.00      19.00
   19.00      35.45
000
```

CFC113a

```
-09
    1  1  8  3 22 22  4 2211111
  7  2 12  0  3  2
CF3CCl3  1,1,1-trichlorotrifluoroethane
May 1992
  1  1   0.0           2  1   0.0           3  1   0.0           1  2   0.0
  2  2   0.0           3  2   1.545         1  3   1.2583        2  3   0.0
  3  3  -0.4308        1  4  -0.6292        2  4   1.0897        3  4  -0.4308
  1  5  -0.6292        2  5  -1.0897        3  5  -0.4308        1  6  -1.6567
  2  6   0.0           3  6   2.1710        1  7   0.8284        2  7   1.4347
  3  7   2.1710        1  8   0.8284        2  8  -1.4347        3  8   2.1710
-1
  1  1  1  2
  2  1  1  3
  3  1  1  4
```

```
 4 1 1 5
 5 1 2 6
 6 1 2 7
 7 1 2 8
 8 2 3 1 2
 9 2 4 1 2
10 2 5 1 2
11 2 6 2 1
12 2 7 2 1
13 2 8 2 1
14 2 3 1 4
15 2 3 1 5
16 2 4 1 5
17 2 6 2 7
18 2 6 2 8
19 2 7 2 8
20 4 3 1 2 6
21 4 4 1 2 8
22 4 5 1 2 7
 1 1   1.000000     2 2   0.333333     2 3   0.333333     2 4   0.333333
 3 5   0.333333     3 6   0.333333     3 7   0.333333     4 8   0.333333
 4 9   0.333333     4 10   0.333333    5 11   0.333333    5 12   0.333333
 5 13   0.333333    6 14   0.333333    6 15   0.333333    6 16   0.333333
 7 17   0.333333    7 18   0.333333    7 19   0.333333    8 2   0.333333
 8 3  -0.166667     8 4  -0.166667     9 3   0.5          9 4  -0.5
10 5   0.333333    10 6  -0.166667    10 7  -0.166667    11 6   0.5
11 7  -0.5         12 8   0.333333    12 9  -0.166667    12 10  -0.166667
13 9   0.5         13 10  -0.5        14 11   0.333333    14 12  -0.166667
14 13  -0.166667   15 12   0.5        15 13  -0.5        16 14   0.333333
16 15  -0.166667   16 16  -0.166667   17 15   0.5        17 16  -0.5
18 17   0.333333   18 18  -0.166667   18 19  -0.166667   19 18   0.5
19 19  -0.5        20 20   0.333333   20 21   0.333333   20 22   0.333333
21 20   0.333333   21 21   0.333333   21 22   0.333333   22 20   0.333333
22 21   0.333333   22 22   0.333333   -3
  12.01       12.01      19.00       19.00     19.00       35.45
  35.45       35.45
000
```

CFC114

```
-09
   1 1 8 4 22 22 4 2211111
 7 1 5 1 3 0 7 2
CF2ClCF2Cl 1,2-dichlorotetrafluoroethane
October 1992
 1 1  0.0           2 1  1.55          3 1  0.0           1 2  0.0
 2 2  0.0           3 2  0.0           1 3  1.6284        2 3  2.1622
 3 3  0.0           1 4 -0.6650        2 4  1.9610        3 4 -1.0760
 1 5 -0.6650        2 5  1.9610        3 5  1.0760        1 6 -1.6284
 2 6 -0.6122        3 6  0.0           1 7  0.6650        2 7 -0.4110
 3 7  1.0760        1 8  0.6650        2 8 -0.4110        3 8 -1.0760
-1
 1 1 1 2
 2 1 1 3
 3 1 1 4
 4 1 1 5
 5 1 2 6
 6 1 2 7
 7 1 2 8
```

```
 8 2 2 1 3
 9 2 2 1 4
10 2 2 1 5
11 2 1 2 6
12 2 1 2 7
13 2 1 2 8
14 2 3 1 4
15 2 3 1 5
16 2 4 1 5
17 2 6 2 7
18 2 6 2 8
19 2 7 2 8
20 4 3 1 2 6
21 4 4 1 2 7
22 4 5 1 2 8
 1 1   1.000000    2 2   0.5       2 5   0.5       3 3   0.25
 3 4   0.25        3 6   0.25      3 7   0.25      4 8   0.5
 4 11  0.5         5 9   0.25      5 10  0.25      5 12  0.25
 5 13  0.25        6 14  0.25      6 15  0.25      6 17  0.25
 6 18  0.25        7 16  0.5       7 19  0.5       8 3   0.25
 8 4  -0.25        8 6  -0.25      8 7   0.25      9 9   0.25
 9 10 -0.25        9 12 -0.25      9 13  0.25     10 14  0.25
10 15 -0.25       10 17 -0.25     10 18  0.25     11 20  1.0
12 21  0.5        12 22  0.5      13 3   0.25     13 4  -0.25
13 6   0.25       13 7  -0.25     14 9   0.25     14 10 -0.25
14 12  0.25       14 13 -0.25     15 14  0.25     15 15 -0.25
15 17  0.25       15 18 -0.25     16 21  0.5      16 22 -0.5
17 2   0.5        17 5  -0.5      18 3   0.25     18 4   0.25
18 6  -0.25       18 7  -0.25     19 8   0.5      19 11 -0.5
20 9   0.25       20 10  0.25     20 12 -0.25     20 13 -0.25
21 14  0.25       21 15  0.25     21 17 -0.25     21 18 -0.25
22 16  0.5        22 19 -0.5      -3
  12.01     12.01   35.45     19.00   19.00     35.45
  19.00     19.00
000
```

CFC114a

```
-09
   1  1  8  2 22 22  4 2211111
 14  3  8  1
CFCl2CF3  1,1-dichlorotetrafluoroethane
October 1992
 1 1   0.0         2 1   1.56        3 1   0.0         1 2   0.0
 2 2   0.0         3 2   0.0         1 3   0.626857    2 3   2.00396
 3 3   1.085747    1 4   0.626857    2 4   2.00396     3 4  -1.085747
 1 5  -1.25371     2 5   2.00396     3 5   0.0         1 6   1.3197
 2 6  -0.4673      3 6   0.0         1 7  -0.8390      2 7  -0.5942
 3 7   1.4531      1 8  -0.8390      2 8  -0.5942      3 8  -1.4531
-1
1 1 1 2
2 1 1 3
3 1 1 4
4 1 1 5
5 1 2 6
6 1 2 7
7 1 2 8
8 2 2 1 3
9 2 2 1 4
```

```
10  2  2  1  5
11  2  1  2  6
12  2  1  2  7
13  2  1  2  8
14  2  3  1  4
15  2  3  1  5
16  2  4  1  5
17  2  6  2  7
18  2  6  2  8
19  2  7  2  8
20  4  5  1  2  6
21  4  3  1  2  8
22  4  4  1  2  7
 1  1    1.000000     2  2    0.5       2  3    0.5       3  4    1.0
 4  5    1.0          5  6    0.5       5  7    0.5       6  8    0.5
 6  9    0.5          7 10    1.0       8 11    1.0       9 12    0.5
 9 13    0.5         10 14    1.0      11 15    0.5      11 16    0.5
12 17    0.5         12 18    0.5      13 19    1.0      14 21    0.5
14 22   -0.5         15  2    0.5      15  3   -0.5      16  6    0.5
16  7   -0.5         17  8    0.5      17  9   -0.5      18 12    0.5
18 13   -0.5         19 15    0.5      19 16   -0.5      20 17    0.5
20 18   -0.5         21 20    1.0      22 21    0.5      22 22    0.5
-3
  12.01       12.01       19.00       19.00       19.00       19.00
  35.45       35.45
000
```

CFC115

```
-09
   1  1  8  2 22 22  4 2211111
 14  3  8  1
CF2ClCF3  chloropentafluoroethane
October 1992
 1  1   0.0          2  1   1.555        3  1   0.0          1  2   0.0
 2  2   0.0          3  2   0.0          1  3   0.6213       2  3   2.0295
 3  3   1.0760       1  4   0.6213       2  4   2.0295       3  4  -1.0760
 1  5  -1.2425       2  5   2.0295       3  5   0.0          1  6   1.6287
 2  6  -0.6122       3  6   0.0          1  7  -0.6325       2  7  -0.4110
 3  7   1.0760       1  8  -0.6325       2  8  -0.4110       3  8  -1.0760
-1
 1  1  1  2
 2  1  1  3
 3  1  1  4
 4  1  1  5
 5  1  2  6
 6  1  2  7
 7  1  2  8
 8  2  2  1  3
 9  2  2  1  4
10  2  2  1  5
11  2  1  2  6
12  2  1  2  7
13  2  1  2  8
14  2  3  1  4
15  2  3  1  5
16  2  4  1  5
17  2  6  2  7
18  2  6  2  8
```

```
19  2  7  2  8
20  4  5  1  2  6
21  4  3  1  2  8
22  4  4  1  2  7
 1  1   1.000000     2  2   0.5        2  3   0.5        3  4   1.0
 4  5   1.0          5  6   0.5        5  7   0.5        6  8   0.5
 6  9   0.5          7 10   1.0        8 11   1.0        9 12   0.5
 9 13   0.5         10 14   1.0       11 15   0.5       11 16   0.5
12 17   0.5         12 18   0.5       13 19   1.0       14 21   0.5
14 22  -0.5         15  2   0.5       15  3  -0.5       16  6   0.5
16  7  -0.5         17  8   0.5       17  9  -0.5       18 12   0.5
18 13  -0.5         19 15   0.5       19 16  -0.5       20 17   0.5
20 18  -0.5         21 20   1.0       22 21   0.5       22 22   0.5
-3
  12.01      12.01      19.00      19.00      19.00      35.45
  19.00      19.00
000
```

FC116

```
-09
  1  1  8  5 22 22  4 2211111
 4  1  1  0  3  1  6  0  8  2
CF3CF3  hexafluoroethane
October 1992
 1  1   0.0          2  1   1.5450     3  1   0.0        1  2   0.0
 2  2   0.0          3  2   0.0        1  3   0.6238     2  3   1.9942
 3  3   1.08045      1  4   0.6238     2  4   1.9942     3  4  -1.08045
 1  5  -1.2476       2  5   1.9942     3  5   0.0        1  6   1.2476
 2  6  -0.4492       3  6   0.0        1  7  -0.6238     2  7  -0.4492
 3  7   1.08045      1  8  -0.6238     2  8  -0.4492     3  8  -1.08045
-1
 1  1  1  2
 2  1  1  3
 3  1  1  4
 4  1  1  5
 5  1  2  6
 6  1  2  7
 7  1  2  8
 8  2  2  1  3
 9  2  2  1  4
10  2  2  1  5
11  2  1  2  6
12  2  1  2  7
13  2  1  2  8
14  2  3  1  4
15  2  3  1  5
16  2  4  1  5
17  2  6  2  7
18  2  6  2  8
19  2  7  2  8
20  4  5  1  2  6
21  4  3  1  2  8
22  4  4  1  2  7
 1  1   1.000000     2  2   0.166667   2  3   0.166667   2  4   0.166667
 2  5   0.166667     2  6   0.166667   2  7   0.166667   3  8   0.166667
 3  9   0.166667     3 10   0.166667   3 11   0.166667   3 12   0.166667
 3 13   0.166667     4 14   0.166667   4 15   0.166667   4 16   0.166667
 4 17   0.166667     4 18   0.166667   4 19   0.166667   5 20   0.333333
```

```
 5 21   0.333333    5 22   0.333333    6  2   0.166667    6  3   0.166667
 6  4   0.166667    6  5  -0.166667    6  6  -0.166667    6  7  -0.166667
 7  8   0.166667    7  9   0.166667    7 10   0.166667    7 11  -0.166667
 7 12  -0.166667    7 13  -0.166667    8 14   0.166667    8 15   0.166667
 8 16   0.166667    8 17  -0.166667    8 18  -0.166667    8 19  -0.166667
 9  2   0.166667    9  3  -0.083333    9  4  -0.083333    9  5  -0.083333
 9  6  -0.083333    9  7   0.166667   10  3   0.25       10  4  -0.25
10  5  -0.25       10  6   0.25       11  8   0.166667   11  9  -0.083333
11 10  -0.083333   11 11  -0.083333   11 12  -0.083333   11 13   0.166667
12  9   0.25       12 10  -0.25       12 11  -0.25       12 12   0.25
13 14   0.166667   13 15  -0.083333   13 16  -0.083333   13 17  -0.083333
13 18  -0.083333   13 19   0.166667   14 15   0.25       14 16  -0.25
14 17  -0.25       14 18   0.25       15  2   0.166667   15  3  -0.083333
15  4  -0.083333   15  5   0.083333   15  6   0.083333   15  7  -0.166667
16  3   0.25       16  4  -0.25       16  5   0.25       16  6  -0.25
17  8   0.166667   17  9  -0.083333   17 10  -0.083333   17 11   0.083333
17 12   0.083333   17 13  -0.166667   18  9   0.25       18 10  -0.25
18 11   0.25       18 12  -0.25       19 14   0.166667   19 15  -0.083333
19 16  -0.083333   19 17   0.083333   19 18   0.083333   19 19  -0.166667
20 15   0.25       20 16  -0.25       20 17   0.25       20 18  -0.25
21 20   0.333333   21 21  -0.166667   21 22  -0.166667   22 21   0.5
22 22  -0.5        -3
  12.01     12.01     19.00     19.00     19.00     19.00
  19.00     19.00
000
```

HFC170

```
-09
   1  1  8  5 22 22  4 2211111
  4  1  1  0  3  1  6  0  8  2
CH3CH3  ethane
December 1992
 1  1   0.0        2  1   1.5324     3  1   0.0        1  2   0.0
 2  2   0.0        3  2   0.0        1  3   0.5167     2  3   1.9290
 3  3   0.8949     1  4   0.5167     2  4   1.9290     3  4  -0.8949
 1  5  -1.0333     2  5   1.9290     3  5   0.0        1  6   1.0333
 2  6  -0.3966     3  6   0.0        1  7  -0.5167     2  7  -0.3966
 3  7   0.8949     1  8  -0.5167     2  8  -0.3966     3  8  -0.8949
-1
 1  1  1  2
 2  1  1  3
 3  1  1  4
 4  1  1  5
 5  1  2  6
 6  1  2  7
 7  1  2  8
 8  2  2  1  3
 9  2  2  1  4
10  2  2  1  5
11  2  1  2  6
12  2  1  2  7
13  2  1  2  8
14  2  3  1  4
15  2  3  1  5
16  2  4  1  5
17  2  6  2  7
18  2  6  2  8
19  2  7  2  8
```

```
20  4  5  1  2  6
21  4  3  1  2  8
22  4  4  1  2  7
 1  1   1.000000    2  2   0.166667    2  3   0.166667    2  4   0.166667
 2  5   0.166667    2  6   0.166667    2  7   0.166667    3  8   0.166667
 3  9   0.166667    3 10   0.166667    3 11   0.166667    3 12   0.166667
 3 13   0.166667    4 14   0.166667    4 15   0.166667    4 16   0.166667
 4 17   0.166667    4 18   0.166667    4 19   0.166667    5 20   0.333333
 5 21   0.333333    5 22   0.333333    6  2   0.166667    6  3   0.166667
 6  4   0.166667    6  5  -0.166667    6  6  -0.166667    6  7  -0.166667
 7  8   0.166667    7  9   0.166667    7 10   0.166667    7 11  -0.166667
 7 12  -0.166667    7 13  -0.166667    8 14   0.166667    8 15   0.166667
 8 16   0.166667    8 17  -0.166667    8 18  -0.166667    8 19  -0.166667
 9  2   0.166667    9  3  -0.083333    9  4  -0.083333    9  5  -0.083333
 9  6  -0.083333    9  7   0.166667   10  3   0.25       10  4  -0.25
10  5  -0.25       10  6   0.25       11  8   0.166667   11  9  -0.083333
11 10  -0.083333   11 11  -0.083333   11 12  -0.083333   11 13   0.166667
12  9   0.25       12 10  -0.25       12 11  -0.25       12 12   0.25
13 14   0.166667   13 15  -0.083333   13 16  -0.083333   13 17  -0.083333
13 18  -0.083333   13 19   0.166667   14 15   0.25       14 16  -0.25
14 17  -0.25       14 18   0.25       15  2   0.166667   15  3  -0.083333
15  4  -0.083333   15  5   0.083333   15  6   0.083333   15  7  -0.166667
16  3   0.25       16  4  -0.25       16  5   0.25       16  6  -0.25
17  8   0.166667   17  9  -0.083333   17 10  -0.083333   17 11   0.083333
17 12   0.083333   17 13  -0.166667   18  9   0.25       18 10  -0.25
18 11   0.25       18 12  -0.25       19 14   0.166667   19 15  -0.083333
19 16  -0.083333   19 17   0.083333   19 18   0.083333   19 19  -0.166667
20 15  -0.25       20 16   0.25       20 17  -0.25       20 18   0.25
21 20   0.333333   21 21  -0.166667   21 22  -0.166667   22 21   0.5
22 22  -0.5       -3
  12.01       12.01       1.008       1.008       1.008       1.008
   1.008       1.008
000
```

HFC161

```
-09
   1  1  8  2 22 22  4 2211111
 14  3  8  1
CFH2CH3  1-fluoroethane
december 1992
 1  1   0.0        2  1   1.505      3  1   0.0        1  2   0.0
 2  2   0.0        3  2   0.0        1  3   0.5131     2  3   1.8724
 3  3   0.8887     4   0.5131        2  4   1.8724     3  4  -0.8887
 1  5  -1.0262     2  5   1.8724     3  5   0.0        1  6   1.3162
 2  6  -0.4713     3  6   0.0        1  7  -0.4741     2  7  -0.4261
 3  7   0.8904     1  8  -0.4741     2  8  -0.4261     3  8  -0.8904
-1
 1  1  1  2
 2  1  1  3
 3  1  1  4
 4  1  1  5
 5  1  2  6
 6  1  2  7
 7  1  2  8
 8  2  2  1  3
 9  2  2  1  4
10  2  2  1  5
11  2  1  2  6
```

```
12  2  1  2  7
13  2  1  2  8
14  2  3  1  4
15  2  3  1  5
16  2  4  1  5
17  2  6  2  7
18  2  6  2  8
19  2  7  2  8
20  4  5  1  2  6
21  4  3  1  2  8
22  4  4  1  2  7
 1  1    1.000000     2  2    0.5          2  3    0.5          3  4    1.0
 4  5    1.0          5  6    0.5          5  7    0.5          6  8    0.5
 6  9    0.5          7 10    1.0          8 11    1.0          9 12    0.5
 9 13    0.5         10 14    1.0         11 15    0.5         11 16    0.5
12 17    0.5         12 18    0.5         13 19    1.0         14 21    0.5
14 22   -0.5         15  2    0.5         15  3   -0.5         16  6    0.5
16  7   -0.5         17  8    0.5         17  9   -0.5         18 12    0.5
18 13   -0.5         19 15    0.5         19 16   -0.5         20 17    0.5
20 18   -0.5         21 20    1.0         22 21    0.5         22 22    0.5
-3
  12.01      12.01      1.008      1.008      1.008      19.00
   1.008      1.008
000
```

HFC152

```
-09
   1  1  8  4 22 22  4 2211111
 7  1  5  1  3  0  7  2
CFH2CFH2  1,2-difluoroethane
January 1992
 1  1   0.0          2  1   1.5033        3  1   0.0           1  2   0.0
 2  2   0.0          3  2   0.0           1  3   1.3029        2  3   1.9853
 3  3   0.0          1  4  -0.5091        2  4   1.8987        3  4  -0.8955
 1  5  -0.5091       2  5   1.8987        3  5   0.8955        1  6  -1.3029
 2  6  -0.4820       3  6   0.0           1  7   0.5091        2  7  -0.3954
 3  7   0.8955       1  8   0.5091        2  8  -0.3954        3  8  -0.8955
 -1
 1  1  1  2
 2  1  1  3
 3  1  1  4
 4  1  1  5
 5  1  2  6
 6  1  2  7
 7  1  2  8
 8  2  2  1  3
 9  2  2  1  4
10  2  2  1  5
11  2  1  2  6
12  2  1  2  7
13  2  1  2  8
14  2  3  1  4
15  2  3  1  5
16  2  4  1  5
17  2  6  2  7
18  2  6  2  8
19  2  7  2  8
20  4  3  1  2  6
```

```
21  4  4  1  2  7
22  4  5  1  2  8
 1  1    1.000000     2  2    0.5        2  5    0.5        3  3    0.25
 3  4    0.25         3  6    0.25       3  7    0.25       4  8    0.5
 4 11    0.5          5  9    0.25       5 10    0.25       5 12    0.25
 5 13    0.25         6 14    0.25       6 15    0.25       6 17    0.25
 6 18    0.25         7 16    0.5        7 19    0.5        8  3    0.25
 8  4   -0.25         8  6   -0.25       8  7    0.25       9  9    0.25
 9 10   -0.25         9 12   -0.25       9 13    0.25      10 14    0.25
10 15   -0.25        10 17   -0.25      10 18    0.25      11 20    1.0
12 21    0.5         12 22    0.5       13  3    0.25      13  4   -0.25
13  6    0.25        13  7   -0.25      14  9    0.25      14 10   -0.25
14 12    0.25        14 13   -0.25      15 14    0.25      15 15   -0.25
15 17    0.25        15 18   -0.25      16 21    0.5       16 22   -0.5
17  2    0.5         17  5   -0.5       18  3    0.25      18  4    0.25
18  6   -0.25        18  7   -0.25      19  8    0.5       19 11   -0.5
20  9    0.25        20 10    0.25      20 12   -0.25      20 13   -0.25
21 14    0.25        21 15    0.25      21 17   -0.25      21 18   -0.25
22 16    0.5         22 19   -0.5       -3
  12.01      12.01     19.00      1.008     1.008      19.00
   1.008      1.008
000
```

HFC152a

```
-09
   1  1  8  2 22 22  4 2211111
 14  3  8  1
Ch3Chf2  2,2-difluoroethane
december 1992
 1  1   0.0          2  1   1.54        3  1   0.0          1  2   0.0
 2  2   0.0          3  2   0.0         1  3   0.5209       2  3   1.8927
 3  3   0.9022       1  4   0.5209      2  4   1.8927       3  4  -0.9022
 1  5  -1.0417       2  5   1.8927      3  5   0.0          1  6   1.0350
 2  6  -0.3726       3  6   0.0         1  7  -0.6394       2  7  -0.4468
 3  7   1.0957       1  8  -0.6394      2  8  -0.4468       3  8  -1.0957
-1
 1  1  1  2
 2  1  1  3
 3  1  1  4
 4  1  1  5
 5  1  2  6
 6  1  2  7
 7  1  2  8
 8  2  2  1  3
 9  2  2  1  4
10  2  2  1  5
11  2  1  2  6
12  2  1  2  7
13  2  1  2  8
14  2  3  1  4
15  2  3  1  5
16  2  4  1  5
17  2  6  2  7
18  2  6  2  8
19  2  7  2  8
20  4  5  1  2  6
21  4  3  1  2  8
22  4  4  1  2  7
```

```
 1 1   1.000000    2 2   0.5         2 3   0.5         3 4   1.0
 4 5   1.0         5 6   0.5         5 7   0.5         6 8   0.5
 6 9   0.5         7 10   1.0        8 11   1.0        9 12   0.5
 9 13   0.5        10 14   1.0       11 15   0.5       11 16   0.5
 12 17   0.5       12 18   0.5       13 19   1.0       14 21   0.5
 14 22  -0.5       15 2   0.5        15 3  -0.5        16 6   0.5
 16 7  -0.5        17 8   0.5        17 9  -0.5        18 12   0.5
 18 13  -0.5       19 15   0.5       19 16  -0.5       20 17   0.5
 20 18  -0.5       21 20   1.0       22 21   0.5       22 22   0.5
-3
 12.01      12.01      1.008      1.008      1.008      1.008
 19.00      19.00
000
```

HFC143

```
-09
   1  1  8  1 22 22  4 2211111
 22  4
CFH2CF2H  1,2,2-trifluoroethane
December 1992
 1  1   0.0          2  1   1.50         3  1   0.0          1  2   0.0
 2  2   0.0          3  2   0.0          1  3   0.4046       2  3   1.8525
 3  3   0.9466       1  4   0.4046       2  4   1.8525       3  4  -0.9466
 1  5  -1.3114       2  5   1.9541       3  5   0.0          1  6   1.2789
 2  6  -0.4429       3  6   0.0          1  7  -0.5696       2  7  -0.4429
 3  7   1.1450       1  8  -0.5420       2  8  -0.3525       3  8  -0.8752
-1
 1  1  1  2
 2  1  1  3
 3  1  1  4
 4  1  1  5
 5  1  2  6
 6  1  2  7
 7  1  2  8
 8  2  2  1  3
 9  2  2  1  4
10  2  2  1  5
11  2  1  2  6
12  2  1  2  7
13  2  1  2  8
14  2  3  1  4
15  2  3  1  5
16  2  4  1  5
17  2  6  2  7
18  2  6  2  8
19  2  7  2  8
20  4  5  1  2  6
21  4  3  1  2  8
22  4  4  1  2  7
 1  1   1.000000     2  2   1.0          3  3   1.0          4  4   1.0
 5  5   1.0          6  6   1.0          7  7   1.0          8  8   1.0
 9  9   1.0          10 10   1.0         11 11   1.0         12 12   1.0
13 13   1.0          14 14   1.0         15 15   1.0         16 16   1.0
17 17   1.0          18 18   1.0         19 19   1.0         20 20   1.0
21 21   1.0          22 22   1.0         -3
 12.01      12.01     1.008      1.008     19.00      19.00
 19.00      1.008
000
```

HFC143a

```
-09
  1  1  8  3 22 22  2 2211111
 7  2 12  0  3  2
CF3CH3  1,1,1-trifluoroethane
June 1992
 1  1   0.0           2  1   1.530         3  1   0.0           1  2   0.0
 2  2   0.0           3  2   0.0           1  3   0.6232        2  3   2.0084
 3  3   1.0794        1  4   0.6232        2  4   2.0084        3  4  -1.0794
 1  5  -1.2463        2  5   2.0084        3  5   0.0           1  6   1.0301
 2  6  -0.3407        3  6   0.0           1  7  -0.5152        2  7  -0.3407
 3  7   0.8920        1  8  -0.5152        2  8  -0.3407        3  8  -0.8920
-1
 1  1  1  2
 2  1  1  3
 3  1  1  4
 4  1  1  5
 5  1  2  6
 6  1  2  7
 7  1  2  8
 8  2  3  1  2
 9  2  4  1  2
10  2  5  1  2
11  2  6  2  1
12  2  7  2  1
13  2  8  2  1
14  2  3  1  4
15  2  3  1  5
16  2  4  1  5
17  2  6  2  7
18  2  6  2  8
19  2  7  2  8
20  4  3  1  2  8
21  4  4  1  2  7
22  4  5  1  2  6
 1  1    1.000000     2  2    0.333333     2  3    0.333333     2  4    0.333333
 3  5    0.333333     3  6    0.333333     3  7    0.333333     4  8    0.333333
 4  9    0.333333     4 10    0.333333     5 11    0.333333     5 12    0.333333
 5 13    0.333333     6 14    0.333333     6 15    0.333333     6 16    0.333333
 7 17    0.333333     7 18    0.333333     7 19    0.333333     8  2    0.333333
 8  3   -0.166667     8  4   -0.166667     9  3    0.5          9  4   -0.5
10  5    0.333333    10  6   -0.166667    10  7   -0.166667    11  6    0.5
11  7   -0.5         12  8    0.333333    12  9   -0.166667    12 10   -0.166667
13  9    0.5         13 10   -0.5         14 11    0.333333    14 12   -0.166667
14 13   -0.166667    15 12    0.5         15 13   -0.5         16 14    0.333333
16 15   -0.166667    16 16   -0.166667    17 15    0.5         17 16   -0.5
18 17    0.333333    18 18   -0.166667    18 19   -0.166667    19 18    0.5
19 19   -0.5         20 20    0.333333    20 21    0.333333    20 22    0.333333
21 20    0.333333    21 21    0.333333    21 22    0.333333    22 20    0.333333
22 21    0.333333    22 22    0.333333   -3
  12.01      12.01    19.00      19.00    19.00       1.008
   1.008      1.008
000
```

HFC134

```
-09
  1  1  8  4 22 22  4 2211111
```

```
 7 1 5 1 3 0 7 2
CF2HCF2H  1,1,2,2-tetrafluoroethane
January 1992
 1 1   0.0             2 1   1.518          3 1   0.0            1 2   0.0
 2 2   0.0             3 2   0.0            1 3   1.0298         2 3   1.8989
 3 3   0.0             1 4  -0.6801         2 4   1.9397         3 4  -1.0873
 1 5  -0.6801          2 5   1.9397         3 5   1.0873         1 6  -1.0298
 2 6  -0.3809          3 6   0.0            1 7   0.6801         2 7  -0.4217
 3 7   1.0873          1 8   0.6801         2 8  -0.4217         3 8  -1.0873
-1
 1 1 1 2
 2 1 1 3
 3 1 1 4
 4 1 1 5
 5 1 2 6
 6 1 2 7
 7 1 2 8
 8 2 2 1 3
 9 2 2 1 4
10 2 2 1 5
11 2 1 2 6
12 2 1 2 7
13 2 1 2 8
14 2 3 1 4
15 2 3 1 5
16 2 4 1 5
17 2 6 2 7
18 2 6 2 8
19 2 7 2 8
20 4 3 1 2 6
21 4 4 1 2 7
22 4 5 1 2 8
 1 1   1.000000        2 2   0.5          2 5   0.5           3 3   0.25
 3 4   0.25            3 6   0.25         3 7   0.25          4 8   0.5
 4 11   0.5            5 9   0.25         5 10   0.25         5 12   0.25
 5 13   0.25           6 14   0.25        6 15   0.25         6 17   0.25
 6 18   0.25           7 16   0.5         7 19   0.5          8 3   0.25
 8 4  -0.25            8 6  -0.25         8 7   0.25          9 9   0.25
 9 10  -0.25           9 12  -0.25        9 13   0.25         10 14   0.25
10 15  -0.25           10 17  -0.25       10 18   0.25        11 20   1.0
12 21   0.5            12 22   0.5        13 3   0.25         13 4  -0.25
13 6   0.25            13 7  -0.25        14 9   0.25         14 10  -0.25
14 12   0.25           14 13  -0.25       15 14   0.25        15 15  -0.25
15 17   0.25           15 18  -0.25       16 21   0.5         16 22  -0.5
17 2   0.5             17 5  -0.5         18 3   0.25         18 4   0.25
18 6  -0.25            18 7  -0.25        19 8   0.5          19 11  -0.5
20 9   0.25            20 10   0.25       20 12  -0.25        20 13  -0.25
21 14   0.25           21 15   0.25       21 17  -0.25        21 18  -0.25
22 16   0.5            22 19  -0.5        -3
  12.01      12.01      1.008      19.00     19.00      1.008
  19.00      19.00
000
```

HFC134a

```
-09
   1  1  8  2 22 22  2 2211111
 14  3  8  1
CF3CFH2  1,1,1,2-tetrafluoroethane
```

```
May 1992
 1 1  0.0          2 1  1.525       3 1  0.0        1 2  0.0
 2 2  0.0          3 2  0.0         1 3  0.6237     2 3  2.0012
 3 3  1.0800       1 4  0.6237      2 4  2.0012     3 4 -1.0800
 1 5 -1.2472       2 5  2.0012      3 5  0.0        1 6  1.3086
 2 6 -0.4686       3 6  0.0         1 7 -0.5160     2 7 -0.3692
 3 7  0.8863       1 8 -0.5160      2 8 -0.3692     3 8 -0.8863
-1
 1 1 1 2
 2 1 1 3
 3 1 1 4
 4 1 1 5
 5 1 2 6
 6 1 2 7
 7 1 2 8
 8 2 2 1 3
 9 2 2 1 4
10 2 2 1 5
11 2 1 2 6
12 2 1 2 7
13 2 1 2 8
14 2 3 1 4
15 2 3 1 5
16 2 4 1 5
17 2 6 2 7
18 2 6 2 8
19 2 7 2 8
20 4 5 1 2 6
21 4 3 1 2 8
22 4 4 1 2 7
 1 1   1.0         2 2   0.5        2 3   0.5       3 4   1.0
 4 5   1.0         5 6   0.5        5 7   0.5       6 8   0.5
 6 9   0.5         7 10   1.0       8 11   1.0      9 12   0.5
 9 13   0.5        10 14   1.0      11 15   0.5     11 16   0.5
12 17   0.5        12 18   0.5      13 19   1.0     14 21   0.5
14 22  -0.5        15 2   0.5       15 3  -0.5      16 6   0.5
16 7  -0.5         17 8   0.5       17 9  -0.5      18 12   0.5
18 13  -0.5        19 15   0.5      19 16  -0.5     20 17   0.5
20 18  -0.5        21 20   1.0      22 21   0.5     22 22   0.5
-3
  12.01      12.01      19.00      19.00      19.00      19.00
   1.008      1.008
000
```

HFC125

```
-09
   1 1 8 2 22 22 4 2211111
 14 3 8 1
CF3CF2H pentafluoroethane
January 1992
 1 1  0.0          2 1  1.520       3 1  0.0        1 2  0.0
 2 2  0.0          3 2  0.0         1 3  0.6240     2 3  1.9941
 3 3  1.0807       1 4  0.6240      2 4  1.9941     3 4 -1.0807
 1 5 -1.2480       2 5  1.9941      3 5  0.0        1 6  1.0337
 2 6 -0.3762       3 6  0.0         1 7 -0.6365     2 7 -0.4512
 3 7  1.0957       1 8 -0.6365      2 8 -0.4512     3 8 -1.0957
-1
 1 1 1 2
```

```
 2  1  1  3
 3  1  1  4
 4  1  1  5
 5  1  2  6
 6  1  2  7
 7  1  2  8
 8  2  2  1  3
 9  2  2  1  4
10  2  2  1  5
11  2  1  2  6
12  2  1  2  7
13  2  1  2  8
14  2  3  1  4
15  2  3  1  5
16  2  4  1  5
17  2  6  2  7
18  2  6  2  8
19  2  7  2  8
20  4  5  1  2  6
21  4  3  1  2  8
22  4  4  1  2  7
 1  1   1.000000    2  2   0.5         2  3   0.5        3  4   1.0
 4  5   1.0         5  6   0.5         5  7   0.5        6  8   0.5
 6  9   0.5         7 10   1.0         8 11   1.0        9 12   0.5
 9 13   0.5        10 14   1.0        11 15   0.5       11 16   0.5
12 17   0.5        12 18   0.5        13 19   1.0       14 21   0.5
14 22  -0.5        15  2   0.5        15  3  -0.5       16  6   0.5
16  7  -0.5        17  8   0.5        17  9  -0.5       18 12   0.5
18 13  -0.5        19 15   0.5        19 16  -0.5       20 17   0.5
20 18  -0.5        21 20   1.0        22 21   0.5       22 22   0.5
-3
  12.01      12.01      19.00      19.00      19.00      1.008
  19.00      19.00
000
```

Data input for the program OVER.
(With initial force constants and frequencies.)

```
                                     CFC110
   1  1  9  4 18  2 1 1 1 0 0      1  0  0  0  1  0  1  0  0   0
hexachloroethane
november 1992
       3.5          1.8          0.1          0.1          0.01         0.64
      -0.64         0.6         -0.06
 1  2  6  8
ccl3ccl3
 1 22 18  9  5
 3  1  2  6  6
 1  2  3  4  5  6  7  8  9
978.0      432.0      169.0        0.0      679.0      375.0
858.0      858.0      341.0      341.0      224.0      224.0
780.0      780.0      278.0      278.0      115.0      115.0
 1  1  1 1.0          1  1  8 0.6300      1  1  9 0.3700      1  1  8 0.6300
 1  1  9 0.3700       1  1  8 0.6300      1  1  9 0.3700      1  1  8 0.6300
 1  1  9 0.3700       1  1  8 0.6300      1  1  9 0.3700      1  1  8 0.6300
 1  1  9 0.3700       1  2  8 0.6691      1  2  9-0.3271      1  3  8 0.6691
 1  3  9-0.3271       1  4  8 0.6691      1  4  9-0.3271      1  5  8 0.6691
```

```
 1  5  9-0.3271
 1  7  9-0.3271
 1  9  9 0.5800
 1 11  9 0.5800
 1 13  9 0.5800
 2  2  6 0.6617
 2  3  6 0.6617
 2  8  8 0.4534
 2 15  6 0.4728
 3  3  9 0.2892
 3  3  7 0.3379
 3  9  9 0.3774
 3 16  7 0.4728
 4  4  6 0.6617
 4 10  8 0.4534
 4 16  6 0.4728
 5  5  9 0.2792
 5  5  7 0.3379
 5  7  7-0.3379
 5 17  7 0.4728
 6  6  8 0.7108
 6  6  6 0.6617
 6 12  8 0.4534
 6 19  6 0.4728
 7  7  9 0.2892
 7  7  7 0.3379
 7 18  7 0.4728
 8  8  8 0.3700
 8  8  8 0.3700
 8  8  6 0.3379
 9  9  9-0.7568
 9  9  9-0.7568
 9  9  7-0.6617
10 10  8 0.3700
10 10  6 0.3379
11 11  3 1.0
11 11  9-0.7568
11 11  7-0.6617
12 12  8 0.3700
12 12  8 0.3700
12 12  6 0.3379
13 13  9-0.7568
13 13  9-0.7568
13 13  7-0.6617
14 14  6 0.3379
14 14  8 0.2892
15 15  4 1.0
15 15  7-0.6617
15 15  9-0.5916
16 16  6 0.3379
16 16  6 0.3379
16 16  8 0.2892
17 17  7-0.6617
17 17  7-0.6617
17 17  9-0.5916
18 18  6 0.3379
18 18  8 0.2892
19 19  4 1.0
 1  6  8 0.6691
 1  8  8 0.4828
 1 10  8 0.4828
 1 12  8 0.4828
 2  2  2 1.0
 2  2  7 0.3379
 2  3  7-0.3379
 2  8  9 0.3774
 2 15  7 0.4728
 3  3  6 0.6617
 3  4  6 0.6617
 3 14  6 0.4728
 4  4  2 1.0
 4  4  7 0.3379
 4 10  9 0.3774
 4 16  7 0.4728
 5  5  6 0.6617
 5  6  6 0.6617
 5 11  8 0.4534
 5 18  6 0.4728
 6  6  9 0.2892
 6  6  7 0.3379
 6 12  9 0.3774
 6 19  7 0.4728
 7  7  6 0.6617
 7 13  8 0.4534
 7 19  6 0.4728
 8  8  9-0.7568
 8  8  9-0.7568
 8  8  7-0.6617
 9  9  8 0.3700
 9  9  6 0.3379
10 10  3 1.0
10 10  9-0.7568
10 10  7-0.6617
11 11  8 0.3700
11 11  8 0.3700
11 11  6 0.3379
12 12  9-0.7568
12 12  9-0.7568
12 12  7-0.6617
13 13  8 0.3700
13 13  6 0.3379
14 14  4 1.0
14 14  7-0.6617
14 14  9-0.5916
15 15  6 0.3379
15 15  8 0.2892
15 15  6 0.3379
16 16  7-0.6617
16 16  7-0.6617
16 16  9-0.5916
17 17  6 0.3379
17 17  8 0.2892
18 18  4 1.0
18 18  7-0.6617
18 18  9-0.5916
19 19  6 0.3379
 1  6  9-0.3271
 1  8  9 0.5800
 1 10  9 0.5800
 1 12  9 0.5800
 2  2  8 0.7108
 2  2  6 0.6617
 2  4  6 0.6617
 2 14  6 0.4728
 3  3  2 1.0
 3  3  7 0.3379
 3  4  7-0.3379
 3 14  7 0.4728
 4  4  8 0.7108
 4  4  6 0.6617
 4 15  6 0.4728
 5  5  2 1.0
 5  5  7 0.3379
 5  6  7-0.3379
 5 11  9 0.3774
 5 18  7 0.4728
 6  6  6 0.6617
 6  7  6 0.6617
 6 17  6 0.4728
 7  7  2 1.0
 7  7  7 0.3379
 7 13  9 0.3774
 7 19  7 0.4728
 8  8  8 0.3700
 8  8  6 0.3379
 9  9  3 1.0
 9  9  9-0.7568
 9  9  7-0.6617
10 10  8 0.3700
10 10  8 0.3700
10 10  6 0.3379
11 11  9-0.7568
11 11  9-0.7568
11 11  7-0.6617
12 12  8 0.3700
12 12  6 0.3379
13 13  3 1.0
13 13  9-0.7568
13 13  7-0.6617
14 14  6 0.3379
14 14  8 0.2892
14 14  6 0.3379
15 15  7-0.6617
15 15  9-0.5916
15 15  7-0.6617
16 16  6 0.3379
16 16  8 0.2892
17 17  4 1.0
17 17  7-0.6617
17 17  9-0.5916
18 18  6 0.3379
18 18  6 0.3379
18 18  8 0.2892
19 19  7-0.6617
 1  7  8 0.6691
 1  9  8 0.4828
 1 11  8 0.4828
 1 13  8 0.4828
 2  2  9 0.2892
 2  2  7 0.3379
 2  4  7-0.3379
 2 14  7 0.4728
 3  3  8 0.7108
 3  3  6 0.6617
 3  9  8 0.4534
 3 16  6 0.4728
 4  4  9 0.2892
 4  4  7 0.3379
 4 15  7 0.4728
 5  5  8 0.7108
 5  5  6 0.6617
 5  7  6 0.6617
 5 17  6 0.4728
 6  6  2 1.0
 6  6  7 0.3379
 6  7  7-0.3379
 6 17  7 0.4728
 7  7  8 0.7108
 7  7  6 0.6617
 7 18  6 0.4728
 8  8  3 1.0
 8  8  9-0.7568
 8  8  7-0.6617
 9  9  8 0.3700
 9  9  8 0.3700
 9  9  6 0.3438
10 10  9-0.7568
10 10  9-0.7568
10 10  7-0.6617
11 11  8 0.3700
11 11  6 0.3379
12 12  3 1.0
12 12  9-0.7568
12 12  7-0.6617
13 13  8 0.3700
13 13  8 0.3700
13 13  6 0.3379
14 14  7-0.6617
14 14  9-0.5916
14 14  7-0.6617
15 15  6 0.3379
15 15  8 0.2892
16 16  4 1.0
16 16  7-0.6617
16 16  9-0.5916
17 17  6 0.3379
17 17  6 0.3379
17 17  8 0.2892
18 18  7-0.6617
18 18  7-0.6617
18 18  9-0.5916
19 19  6 0.3379
```

```
19 19  7-0.6617      19 19  8 0.2892      19 19  9-0.5916      19 19  8 0.2892
19 19  9-0.5916      19 19  6 0.3379      19 19  7-0.6617      20 20  5 1.0
21 21  5 1.0         22 22  5 1.0         -4
```

CFC111

```
  1  1 17  7 18  3 1 1 1 0 0        1  0  0  0  1  0  1  0  0  0
 pentachlorofluoroethane
september 1992
        3.5          1.8          4.4          0.1          0.3          0.1
        0.1          0.01         0.01         0.64         -0.064       0.6
        -0.06        0.5          -0.05        0.4          -0.04
 1  2  3 10 12 14 16
cfcl2ccl3
 1 22 18 17  2
 11  7
 1  2  3  4  5  6  7  8  9 10 11 12 13 14 15 16 17
1111.0      1009.0      847.0      725.0      508.0      407.0
 382.0       314.0      281.0      227.0      174.0      883.0
 796.0       395.0      314.0      266.0      174.0       77.0
 1  1  1 1.0          1  1 12 0.6199       1  1 13 0.3801       1  1 12 0.6199
 1  1 13 0.3801       1  1 12 0.6199       1  1 13 0.3801       1  1 12 0.6199
 1  1 13 0.3801       1  1 12 0.6199       1  1 13 0.3801       1  1 16 0.7052
 1  1 17 0.2948       1  2 12 0.6645       1  2 13-0.3307       1  3 12 0.6645
 1  3 13-0.3307       1  4 12 0.6645       1  4 13-0.3307       1  5 16 0.6652
 1  5 17-0.3314       1  6 12 0.6645       1  6 13-0.3307       1  7 12 0.6645
 1  7 13-0.3307       1  8 12 0.4854       1  8 13 0.5980       1  9 12 0.4854
 1  9 13 0.5980       1 10 12 0.4854       1 10 13 0.5980       1 11 16 0.4559
 1 11 17 0.3826       1 12 12 0.4854       1 12 13 0.5980       1 13 12 0.4854
 1 13 13 0.5980       2  2  2 1.0          2  2 12 0.7123       2  2 13 0.2877
 2  2 10 0.6669       2  2 11 0.3331       2  2 10 0.6669       2  2 11 0.3331
 2  3 10 0.6669       2  3 11-0.3331       2  4 10 0.6669       2  4 11-0.3331
 2  8 12 0.4527       2  8 13 0.3675       2 14 10 0.4713       2 14 11 0.4713
 2 15 10 0.4713       2 15 11 0.4713       3  3  2 1.0          3  3 12 0.7123
 3  3 13 0.2877       3  3 10 0.6669       3  3 11 0.3331       3  3 10 0.6669
 3  3 11 0.3331       3  4 10 0.6669       3  4 11-0.3331       3  9 12 0.4527
 3  9 13 0.3675       3 14 10 0.4713       3 14 11 0.4713       3 16 10 0.4713
 3 16 11 0.4713       4  4  2 1.0          4  4 12 0.7123       4  4 13 0.2877
 4  4 10 0.6669       4  4 11 0.3331       4  4 10 0.6669       4  4 11 0.3331
 4 10 12 0.4527       4 10 13 0.3675       4 15 10 0.4713       4 15 11 0.4713
 4 16 10 0.4713       4 16 11 0.4713       5  5  3 1.0          5  5 16 0.6275
 5  5 17 0.3725       5  5 14 0.5800       5  5 15 0.4200       5  5 14 0.5800
 5  5 15 0.4200       5  6 14 0.6589       5  6 15-0.3251       5  7 14 0.6589
 5  7 15-0.3251       5 11 16 0.4835       5 11 17 0.5761       5 17 14 0.4936
 5 17 15 0.7243       5 18 14 0.4936       5 18 15 0.7243       6  6  2 1.0
 6  6 12 0.7123       6  6 13 0.2877       6  6 14 0.7484       6  6 15 0.2516
 6  6 10 0.6669       6  6 11 0.3331       6  7 10 0.6669       6  7 11-0.3331
 6 12 12 0.4527       6 12 13 0.3675       6 17 14 0.4339       6 17 15 0.2957
 6 19 10 0.4713       6 19 11 0.4713       7  7  2 1.0          7  7 12 0.7123
 7  7 13 0.2877       7  7 14 0.7484       7  7 15 0.2516       7  7 10 0.6669
 7  7 11 0.3331       7 13 12 0.4527       7 13 13 0.3675       7 18 14 0.4339
 7 18 15 0.2957       7 19 10 0.4713       7 19 11 0.4713       8  8  4 1.0
 8  8 12 0.3801       8  8 13-0.7638       8  8 12 0.3801       8  8 13-0.7638
 8  8 12 0.3801       8  8 13-0.7638       8  8 10 0.3331       8  8 11-0.6669
 8  8 10 0.3331       8  8 11-0.6669       9  9  4 1.0          9  9 12 0.3801
 9  9 13-0.7638       9  9 12 0.3801       9  9 13-0.7638       9  9 12 0.3801
 9  9 13-0.7638       9  9 10 0.3331       9  9 11-0.6669       9  9 10 0.3331
 9  9 11-0.6669      10 10  4 1.0         10 10 12 0.3801      10 10 13-0.7638
10 10 12 0.3801      10 10 13-0.7638      10 10 12 0.3801      10 10 13-0.7638
```

```
10 10 10 0.3331     10 10 11-0.6669     10 10 10 0.3331     10 10 11-0.6669
11 11  5 1.0        11 11 16 0.2948     11 11 17-0.5917     11 11 12 0.3801
11 11 13-0.7638     11 11 12 0.3801     11 11 13-0.7638     11 11 14 0.4200
11 11 15-0.8512     11 11 14 0.4200     11 11 15-0.8512     12 12  4 1.0
12 12 12 0.3801     12 12 13-0.7638     12 12 12 0.3801     12 12 13-0.7638
12 12 16 0.2948     12 12 17-0.5917     12 12 14 0.2516     12 12 15-0.5100
12 12 10 0.3331     12 12 11-0.6669     13 13  4 1.0        13 13 12 0.3801
13 13 13-0.7638     13 13 12 0.3801     13 13 13-0.7638     13 13 16 0.2948
13 13 17-0.5917     13 13 14 0.2516     13 13 15-0.5100     13 13 10 0.3331
13 13 11-0.6669     14 14  6 1.0        14 14 10 0.3331     14 14 11-0.6669
14 14 10 0.3331     14 14 11-0.6669     14 14 12 0.2877     14 14 13-0.5782
14 14 12 0.2877     14 14 13-0.5782     14 14 10 0.3331     14 14 11-0.6669
15 15  6 1.0        15 15 10 0.3331     15 15 11-0.6669     15 15 10 0.3331
15 15 11-0.6669     15 15 10 0.3331     15 15 11-0.6669     15 15 12 0.2877
15 15 13-0.5782     15 15 12 0.2877     15 15 13-0.5782     16 16  6 1.0
16 16 10 0.3331     16 16 11-0.6669     16 16 10 0.3331     16 16 11-0.6669
16 16 10 0.3331     16 16 11-0.6669     16 16 12 0.2877     16 16 13-0.5782
16 16 12 0.2877     16 16 13-0.5782     17 17  7 1.0        17 17 14 0.4200
17 17 15-0.8512     17 17 14 0.4200     17 17 15-0.8512     17 17 10 0.3331
17 17 11-0.6669     17 17 12 0.2877     17 17 13-0.5782     17 17 16 0.3725
17 17 17-0.7477     18 18  7 1.0        18 18 14 0.4200     18 18 15-0.8512
18 18 14 0.4200     18 18 15-0.8512     18 18 10 0.3331     18 18 11-0.6669
18 18 12 0.2877     18 18 13-0.5782     18 18 16 0.3725     18 18 17-0.7477
19 19  6 1.0        19 19 10 0.3331     19 19 11-0.6669     19 19 14 0.2516
19 19 15-0.5100     19 19 14 0.2516     19 19 15-0.5100     19 19 12 0.2877
19 19 13-0.5782     19 19 12 0.2877     19 19 13-0.5782     20 20  8 1.0
21 21  9 1.0        22 22  9 1.0        -4
```

CFC112

```
 1 1 17 5 18 5 1 1 1 0 0          1 0 0 0 1 0 1 0 0 0
 1,1,2,2-tetrachlorodifluoroethane
october 1992
      3.5         4.4        1.8        0.3        0.1        0.1
      0.1         0.01       0.01       0.4        -0.04      0.6
      -0.06       0.5        -0.05      0.64       -0.064
 1 2 3 4 5
CFC112
 1 22 18 17  4
 6 4 3 5
 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
  0.0     0.0     0.0     0.0     0.0     0.0
  0.0     0.0     0.0     0.0     0.0     0.0
  0.0     0.0     0.0     0.0     0.0     0.0
1  1  1 1.0        1  1 10 0.7052     1  1 11 0.2948     1  1 12 0.6199
1  1 13 0.3801     1  1 12 0.6199     1  1 13 0.3801     1  1 10 0.7052
1  1 11 0.2948     1  1 12 0.6199     1  1 13 0.3801     1  1 12 0.6199
1  1 13 0.3801     1  2 10 0.6652     1  2 11-0.3314     1  3 12 0.6645
1  3 13-0.3307     1  4 12 0.6645     1  4 13-0.3307     1  5 10 0.6652
1  5 11-0.3314     1  6 12 0.6645     1  6 13-0.3307     1  7 12 0.6645
1  7 13-0.3307     1  8 10 0.4559     1  8 11 0.3826     1  9 12 0.4854
1  9 13 0.5980     1 10 12 0.4854     1 10 13 0.5980     1 11 10 0.4559
1 11 11 0.3826     1 12 12 0.4854     1 12 13 0.5980     1 13 12 0.4854
1 13 13 0.5980     2  2  2 1.0        2  2 10 0.6275     2  2 11 0.3725
2  2 14 0.5806     2  2 15 0.4204     2  2 14 0.5806     2  2 15 0.4204
2  3 14 0.6595     2  3 15-0.3254     2  4 14 0.6595     2  4 15-0.3254
2  8 10 0.4835     2  8 11 0.5761     2 14 14 0.4941     2 14 15 0.7251
2 15 14 0.4941     2 15 15 0.7251     3  3  3 1.0        3  3 12 0.7123
3  3 13 0.2877     3  3 14 0.7492     3  3 15 0.2519     3  3 16 0.6669
```

```
3  3 17 0.3331     3  4 16 0.6669     3  4 17-0.3331     3  9 12 0.4527
3  9 13 0.3675     3 14 14 0.4344     3 14 15 0.2960     3 16 16 0.4713
3 16 17 0.4713     4  4  3 1.0        4  4 12 0.7123     4  4 13 0.2877
4  4 14 0.7492     4  4 15 0.2519     4  4 16 0.6669     4  4 17 0.3331
4 10 12 0.4527     4 10 13 0.3675     4 15 14 0.4344     4 15 15 0.2960
4 16 16 0.4713     4 16 17 0.4713     5  5  2 1.0        5  5 10 0.6275
5  5 11 0.3725     5  5 14 0.5806     5  5 15 0.4204     5  5 14 0.5806
5  5 15 0.4204     5  6 14 0.6595     5  6 15-0.3254     5  7 14 0.6595
5  7 15-0.3254     5 11 10 0.4835     5 11 11 0.5761     5 17 14 0.4941
5 17 15 0.7251     5 18 14 0.4941     5 18 15 0.7251     6  6  3 1.0
6  6 12 0.7123     6  6 13 0.2877     6  7 16 0.6669     6  7 17-0.3331
6  6 14 0.7492     6  6 15 0.2519     6  6 16 0.6669     6  6 17 0.3331
6 12 12 0.4527     6 12 13 0.3675     6 17 14 0.4344     6 17 15 0.2960
6 19 16 0.4713     6 19 17 0.4713     7  7  3 1.0        7  7 12 0.7123
7  7 13 0.2877     7  7 14 0.7492     7  7 15 0.2519     7  7 16 0.6669
7  7 17 0.3331     7 13 12 0.4527     7 13 13 0.3675     7 18 14 0.4344
7 18 15 0.2960     7 19 16 0.4713     7 19 17 0.4713     8  8  4 1.0
8  8 10 0.2948     8  8 11-0.5917     8  8 12 0.3801     8  8 13-0.7638
8  8 12 0.3801     8  8 13-0.7638     8  8 14 0.4204     8  8 15-0.8521
8  8 14 0.4204     8  8 15-0.8521     9  9  5 1.0        9  9 12 0.3801
9  9 13-0.7638     9  9 12 0.3801     9  9 13-0.7638     9  9 10 0.2948
9  9 11-0.5917     9  9 16 0.3331     9  9 17-0.6669     9  9 14 0.2519
9  9 15-0.5105     10 10  5 1.0       10 10 12 0.3801    10 10 13-0.7638
10 10 12 0.3801    10 10 13-0.7638    10 10 10 0.2948    10 10 11-0.5917
10 10 16 0.3331    10 10 17-0.6669    10 10 14 0.2519    10 10 15-0.5105
11 11  4 1.0       11 11 10 0.2948    11 11 11-0.5917    11 11 12 0.3801
11 11 13-0.7638    11 11 12 0.3801    11 11 13-0.7638    11 11 14 0.4204
11 11 15-0.8521    11 11 14 0.4204    11 11 15-0.8521    12 12  5 1.0
12 12 12 0.3801    12 12 13-0.7638    12 12 12 0.3801    12 12 13-0.7638
12 12 10 0.2948    12 12 11-0.5917    12 12 16 0.3331    12 12 17-0.6669
12 12 14 0.2519    12 12 15-0.5105    13 13  5 1.0       13 13 12 0.3801
13 13 13-0.7638    13 13 12 0.3801    13 13 13-0.7638    13 13 10 0.2948
13 13 11-0.5917    13 13 16 0.3331    13 13 17-0.6669    13 13 14 0.2519
13 13 15-0.5105    14 14  6 1.0       14 14 14 0.4204    14 14 15-0.8521
14 14 14 0.4204    14 14 15-0.8521    14 14 10 0.3725    14 14 11-0.7477
14 14 12 0.2877    14 14 13-0.5782    14 14 16 0.3331    14 14 17-0.6669
15 15  6 1.0       15 15 14 0.4204    15 15 15-0.8521    15 15 14 0.4204
15 15 15-0.8521    15 15 10 0.3725    15 15 11-0.7477    15 15 12 0.2877
15 15 13-0.5782    15 15 16 0.3331    15 15 17-0.6669    16 16  7 1.0
16 16 16 0.3331    16 16 17-0.6669    16 16 14 0.2519    16 16 15-0.5105
16 16 14 0.2519    16 16 15-0.5105    16 16 12 0.2877    16 16 13-0.5782
16 16 12 0.2877    16 16 13-0.5782    17 17  6 1.0       17 17 14 0.4204
17 17 15-0.8521    17 17 14 0.4204    17 17 15-0.8521    17 17 10 0.3725
17 17 11-0.7477    17 17 12 0.2877    17 17 13-0.5782    17 17 16 0.3331
17 17 17-0.6669    18 18  6 1.0       18 18 14 0.4204    18 18 15-0.8521
18 18 14 0.4204    18 18 15-0.8521    18 18 10 0.3725    18 18 11-0.7477
18 18 12 0.2877    18 18 13-0.5782    18 18 16 0.3331    18 18 17-0.6669
19 19  7 1.0       19 19 16 0.3331    19 19 17-0.6669    19 19 14 0.2519
19 19 15-0.5105    19 19 14 0.2519    19 19 15-0.5105    19 19 12 0.2877
19 19 13-0.5782    19 19 12 0.2877    19 19 13-0.5782    20 20  8 1.0
21 21  9 1.0       22 22  9 1.0       -4
```

CFC112a

```
 1 1 20 8 18 3 1 1 1 0 0      1 0 0 0 1 0 1 0 0 0
1,1,1,2-tetrachlorodifluoroethane
november 1992
    3.5         1.8         4.4         0.1         0.3         0.1
    0.1         0.1         0.01        0.01        0.6        -0.06
```

```
        0.4            -0.04          0.64           -0.064          0.5            -0.05
        1.1            -0.11
  1 2 3 4 5 6 7 8
 CFC112a
  1 22 18 20  2
 11  7
  1  2  3  4  5  6  7  8  9 10 11 12 13 14 15 16 17 18 19 20
 1111.0     1027.0      847.0     775.0     627.0      525.0
  446.0      420.0      331.0     231.0     165.0     1165.0
  844.0      456.0      331.0     268.0     183.0       81.0
  1  1  1 1.0         1  1 11 0.6351     1  1 12 0.3649     1  1 13 0.7170
  1  1 14 0.2830      1  1 13 0.7170     1  1 14 0.2830     1  1 11 0.6351
  1  1 12 0.3649      1  1 11 0.6351     1  1 12 0.3649     1  1 11 0.6351
  1  1 12 0.3649      1  2 11 0.6748     1  2 12-0.3213     1  3 11 0.6748
  1  3 12-0.3213      1  4 11 0.6748     1  4 12-0.3213     1  5 11 0.6741
  1  5 12-0.3224      1  6 13 0.6514     1  6 14-0.3424     1  7 13 0.6514
  1  7 14-0.3424      1  8 11 0.4814     1  8 12 0.5808     1  9 11 0.4814
  1  9 12 0.5808      1 10 11 0.4814     1 10 12 0.5808     1 11 11 0.4804
  1 11 12 0.5700      1 12 13 0.4555     1 12 14 0.3605     1 13 13 0.4555
  1 13 14 0.3605      2  2  2 1.0        2  2 11 0.7170     2  2 12 0.2830
  2  2 15 0.6561      2  2 16 0.3438     2  2 15 0.6561     2  2 16 0.3438
  2  3 15 0.6561      2  3 16-0.3438     2  4 15 0.6561     2  4 16-0.3438
  2  8 11 0.4504      2  8 12 0.3734     2 14 15 0.4749     2 14 16 0.4749
  2 15 15 0.4749      2 15 16 0.4749     3  3  2 1.0        3  3 11 0.7170
  3  3 12 0.2830      3  3 15 0.6561     3  3 16 0.3438     3  3 15 0.6561
  3  3 16 0.3438      3  4 15 0.6561     3  4 16-0.3438     3  9 11 0.4504
  3  9 12 0.3734      3 14 15 0.4749     3 14 16 0.4749     3 16 15 0.4749
  3 16 16 0.4749      4  4  2 1.0        4  4 11 0.7170     4  4 12 0.2830
  4  4 15 0.6561      4  4 16 0.3438     4  4 15 0.6561     4  4 16 0.3438
  4 10 11 0.4504      4 10 12 0.3734     4 15 15 0.4749     4 15 16 0.4749
  4 16 15 0.4749      4 16 16 0.4749     5  5  2 1.0        5  5 11 0.7125
  5  5 12 0.2872      5  5 17 0.7534     5  5 18 0.2403     5  5 17 0.7534
  5  5 18 0.2403      5  6 17 0.6624     5  6 18-0.3144     5  7 17 0.6624
  5  7 18-0.3144      5 11 11 0.4523     5 11 12 0.3812     5 17 17 0.4255
  5 17 18 0.2859      5 18 17 0.4255     5 18 18 0.2859     6  6  3 1.0
  6  6 13 0.6009      6  6 14 0.3990     6  6 17 0.5824     6  6 18 0.4113
  6  6 19 0.6545      6  6 20 0.3455     6  7 19 0.6545     6  7 20-0.3455
  6 12 13 0.4897      6 12 14 0.6186     6 17 17 0.4894     6 17 18 0.7283
  6 19 19 0.4755      6 19 20 0.4755     7  7  3 1.0        7  7 13 0.6009
  7  7 14 0.3990      7  7 17 0.5824     7  7 18 0.4113     7  7 19 0.6545
  7  7 20 0.3455      7 13 13 0.4897     7 13 14 0.6186     7 18 17 0.4894
  7 18 18 0.7283      7 19 19 0.4755     7 19 20 0.4755     8  8  4 1.0
  8  8 11 0.3649      8  8 12-0.7662     8  8 11 0.3649     8  8 12-0.7662
  8  8 11 0.3649      8  8 12-0.7662     8  8 15 0.3438     8  8 16-0.6561
  8  8 15 0.3438      8  8 16-0.6561     9  9  4 1.0        9  9 11 0.3649
  9  9 12-0.7662      9  9 11 0.3649     9  9 12-0.7662     9  9 11 0.3649
  9  9 12-0.7662      9  9 15 0.3438     9  9 16-0.6561     9  9 15 0.3438
  9  9 16-0.6561     10 10  4 1.0       10 10 11 0.3649    10 10 12-0.7662
 10 10 11 0.3649     10 10 12-0.7662    10 10 11 0.3649    10 10 12-0.7662
 10 10 15 0.3438     10 10 16-0.6561    10 10 15 0.3438    10 10 16-0.6561
 11 11  4 1.0        11 11 11 0.3619    11 11 12-0.7567    11 11 13 0.2938
 11 11 14-0.5590     11 11 13 0.2938    11 11 14-0.5590    11 11 17 0.2403
 11 11 18-0.5063     11 11 17 0.2403    11 11 18-0.5063    12 12  5 1.0
 12 12 13 0.2938     12 12 14-0.5590    12 12 13 0.2938    12 12 14-0.5590
 12 12 11 0.3619     12 12 12-0.7567    12 12 17 0.4113    12 12 18-0.8666
 12 12 19 0.3455     12 12 20-0.6545    13 13  5 1.0       13 13 13 0.2938
 13 13 14-0.5590     13 13 13 0.2938    13 13 14-0.5590    13 13 11 0.3619
 13 13 12-0.7567     13 13 17 0.4113    13 13 18-0.8666    13 13 19 0.3455
```

```
13 13 20-0.6545      14 14  6 1.0         14 14 15 0.3438      14 14 16-0.6561
14 14 15 0.3438      14 14 16-0.6561      14 14 11 0.2830      14 14 12-0.5943
14 14 11 0.2830      14 14 12-0.5943      14 14 15 0.3438      14 14 16-0.6561
15 15  6 1.0         15 15 15 0.3438      15 15 16-0.6561      15 15 15 0.3438
15 15 16-0.6561      15 15 11 0.2830      15 15 12-0.5943      15 15 11 0.2830
15 15 12-0.5943      15 15 15 0.3438      15 15 16-0.6561      16 16  6 1.0
16 16 15 0.3438      16 16 16-0.6561      16 16 15 0.3438      16 16 16-0.6561
16 16 15 0.3438      16 16 16-0.6561      16 16 11 0.2830      16 16 12-0.5943
16 16 11 0.2830      16 16 12-0.5943      17 17  7 1.0         17 17 17 0.2403
17 17 18-0.5063      17 17 17 0.2403      17 17 18-0.5063      17 17 19 0.3455
17 17 20-0.6545      17 17 13 0.3990      17 17 14-0.7592      17 17 11 0.2872
17 17 12-0.6005      18 18  7 1.0         18 18 17 0.2403      18 18 18-0.5063
18 18 17 0.2403      18 18 18-0.5063      18 18 19 0.3455      18 18 20-0.6545
18 18 13 0.3990      18 18 14-0.7592      18 18 11 0.2872      18 18 12-0.6005
19 19  8 1.0         19 19 19 0.3455      19 19 20-0.6545      19 19 17 0.4113
19 19 18-0.8666      19 19 17 0.4113      19 19 18-0.8666      19 19 13 0.3990
19 19 14-0.7592      19 19 13 0.3990      19 19 14-0.7592      20 20  9 1.0
21 21 10 1.0         22 22 10 1.0         -4

                                   CFC113
  1  1 21  2 18  3 1 1 1 0 0       1  0  0  0  1  0  1  0  0  0
 1,1,2-trichlorotrifluoroethane
november 1992
       3.5          1.8          4.4          0.1          0.3          0.1
       0.1          0.1          0.01         0.01         0.01         0.6
       -0.06        0.4          -0.04        0.64         -0.064       0.5
       -0.05        1.1          -0.11
 12 14
CFC113
 1 22 18 21  1
 18
 1  2  3  4  5  6  7  8  9 10 11 12 13 14 15 16 17 18 19 20 21
1212.0      1119.0      1047.0        0.0       909.0      816.0
 632.0       532.0       460.0      442.0       391.0      350.0
 309.0       288.0       240.0      203.0       168.0       80.0
 1  1  1 1.0          1  1 14 0.7099       1  1 15 0.2901       1  1 14 0.7099
 1  1 15 0.2901       1  1 12 0.6257       1  1 13 0.3743       1  1 12 0.6238
 1  1 13 0.3762       1  1 12 0.6238       1  1 13 0.3762       1  1 14 0.7059
 1  1 15 0.2941       1  2 12 0.6649       1  2 13-0.3311       1  3 12 0.6649
 1  3 13-0.3311       1  4 14 0.6651       1  4 15-0.3313       1  5 14 0.6648
 1  5 15-0.3310       1  6 14 0.6648       1  6 15-0.3310       1  7 12 0.6650
 1  7 13-0.3312       1  8 12 0.4844       1  8 13 0.5867       1  9 12 0.4844
 1  9 13 0.5867       1 10 14 0.4556       1 10 15 0.3811       1 11 14 0.4538
 1 11 15 0.3725       1 12 14 0.4538       1 12 15 0.3725       1 13 12 0.4839
 1 13 13 0.5811       2  2  2 1.0          2  2 12 0.7087       2  2 13 0.2913
 2  2 16 0.6674       2  2 17 0.3333       2  2 18 0.7461       2  2 19 0.2545
 2  3 16 0.6674       2  3 17-0.3333       2  4 18 0.6599       2  4 19-0.3258
 2  8 12 0.4544       2  8 13 0.3751       2 14 16 0.4717       2 14 17 0.4717
 2 15 18 0.4358       2 15 19 0.3010       3  3  2 1.0          3  3 12 0.7087
 3  3 13 0.2913       3  3 16 0.6674       3  3 17 0.3333       3  3 18 0.7461
 3  3 19 0.2545       3  4 18 0.6599       3  4 19-0.3258       3  9 12 0.4544
 3  9 13 0.3751       3 14 16 0.4717       3 14 17 0.4717       3 16 18 0.4358
 3 16 19 0.3010       4  4  3 1.0          4  4 14 0.6267       4  4 15 0.3733
 4  4 18 0.5835       4  4 19 0.4171       4  4 18 0.5835       4  4 19 0.4171
 4 10 14 0.4837       4 10 15 0.5783       4 15 18 0.4934       4 15 19 0.7142
 4 16 18 0.4934       4 16 19 0.7142       5  5  3 1.0          5  5 14 0.6225
 5  5 15 0.3775       5  5 20 0.6673       5  5 21 0.3333       5  5 18 0.5812
 5  5 19 0.4194       5  6 20 0.6673       5  6 21-0.3333       5  7 18 0.6594
```

```
5  7 19-0.3254     5 11 14 0.4848     5 11 15 0.5906     5 17 20 0.4716
5 17 21 0.4716     5 18 18 0.4937     5 18 19 0.7220     6  6  3 1.0
6  6 14 0.6225     6  6 15 0.3775     6  6 20 0.6673     6  6 21 0.3333
6  6 18 0.5812     6  6 19 0.4194     6  7 18 0.6594     6  7 19-0.3254
6 12 14 0.4848     6 12 15 0.5906     6 17 20 0.4716     6 17 21 0.4716
6 19 18 0.4937     6 19 19 0.7220     7  7  2 1.0        7  7 12 0.7068
7  7 13 0.2932     7  7 18 0.7482     7  7 19 0.2525     7  7 18 0.7482
7  7 19 0.2525     7 13 12 0.4552     7 13 13 0.3791     7 18 18 0.4346
7 18 19 0.2972     7 19 18 0.4346     7 19 19 0.2972     8  8  4 1.0
8  8 12 0.3762     8  8 13-0.7555     8  8 14 0.2941     8  8 15-0.5904
8  8 12 0.3762     8  8 13-0.7555     8  8 16 0.3333     8  8 17-0.6674
8  8 18 0.2545     8  8 19-0.5154     9  9  4 1.0        9  9 12 0.3762
9  9 13-0.7555     9  9 14 0.2941     9  9 15-0.5904     9  9 12 0.3762
9  9 13-0.7555     9  9 18 0.2545     9  9 19-0.5154     9  9 16 0.3333
9  9 17-0.6674    10 10  5 1.0       10 10 14 0.2941    10 10 15-0.5904
10 10 12 0.3762   10 10 13-0.7555    10 10 12 0.3762    10 10 13-0.7555
10 10 18 0.4171   10 10 19-0.8447    10 10 18 0.4171    10 10 19-0.8447
11 11  5 1.0      11 11 14 0.2901    11 11 15-0.5828    11 11 14 0.2901
11 11 15-0.5828   11 11 12 0.3743    11 11 13-0.7514    11 11 20 0.3333
11 11 21-0.6673   11 11 18 0.4194    11 11 19-0.8500    12 12  5 1.0
12 12 14 0.2901   12 12 15-0.5828    12 12 12 0.3743    12 12 13-0.7514
12 12 14 0.2901   12 12 15-0.5828    12 12 20 0.3333    12 12 21-0.6673
12 12 18 0.2525   12 12 19-0.5116    13 13  4 1.0       13 13 12 0.3743
13 13 13-0.7514   13 13 14 0.2901    13 13 15-0.5828    13 13 14 0.2901
13 13 15-0.5828   13 13 18 0.2525    13 13 19-0.5116    13 13 18 0.2525
13 13 19-0.5116   14 14  6 1.0       14 14 16 0.3333    14 14 17-0.6674
14 14 18 0.2545   14 14 19-0.5154    14 14 12 0.2913    14 14 13-0.5851
14 14 12 0.2913   14 14 13-0.5851    14 14 18 0.2545    14 14 19-0.5154
15 15  7 1.0      15 15 18 0.2545    15 15 19-0.5154    15 15 16 0.3333
15 15 17-0.6674   15 15 18 0.4171    15 15 19-0.8447    15 15 12 0.2913
15 15 13-0.5851   15 15 14 0.3733    15 15 15-0.7493    16 16  7 1.0
16 16 18 0.2545   16 16 19-0.5154    16 16 16 0.3333    16 16 17-0.6674
16 16 18 0.4171   16 16 19-0.8447    16 16 12 0.2913    16 16 13-0.5851
16 16 14 0.3733   16 16 15-0.7493    17 17  8 1.0       17 17 20 0.3333
17 17 21-0.6673   17 17 18 0.4194    17 17 19-0.8500    17 17 18 0.4194
17 17 19-0.8500   17 17 14 0.3775    17 17 15-0.7583    17 17 14 0.3775
17 17 15-0.7583   18 18  7 1.0       18 18 18 0.4194    18 18 19-0.8500
18 18 20 0.3333   18 18 21-0.6673    18 18 18 0.2525    18 18 19-0.5116
18 18 12 0.2932   18 18 13-0.5886    18 18 14 0.3775    18 18 15-0.7583
19 19  7 1.0      19 19 18 0.4194    19 19 19-0.8500    19 19 20 0.3333
19 19 21-0.6673   19 19 18 0.2525    19 19 19-0.5116    19 19 14 0.3775
19 19 15-0.7583   19 19 12 0.2932    19 19 13-0.5886    20 20  9 1.0
21 21 10 1.0      22 22 11 1.0       -4
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CFC113a

```
 1  1 16  2 18  3 1 1 1 0 0      1 0 0 0 1 0 1 0 0 0
 1,1,1-trichlorotrifluoroethane
december 1992
      3.5         4.4        1.8        0.3        0.1        0.1
      0.1         0.01       0.4       -0.04       0.6       -0.06
      1.1        -0.11       0.64      -0.064
13 15
cf3ccl3
 1 22 18 16  3
 5 12  1
 1  2  3  4  5  6  7  8  9 10 11 12 13 14 15 16
1255.0    909.0    714.0    430.0    260.0    1225.0
1225.0    859.0    857.0    563.0    563.0     366.0
```

```
366.0      265.0
1  1  1 1.0
1  1 12 0.3680
1  1 10 0.2885
1  1 10 0.2885
1  3 10-0.3352
1  5 12-0.3210
1  7 12-0.3210
1  9 10 0.3613
1 11 12 0.5900
1 13 12 0.5900
2  2 13 0.6707
2  3 13 0.6707
2  8  9 0.4876
2 15 13 0.4696
3  3 10 0.3894
3  3 14 0.3289
3  9 10 0.6114
3 16 14 0.4696
4  4 13 0.6707
4 10  9 0.4876
4 16 13 0.4696
5  5 12 0.2801
5  5 16 0.3438
5  7 16-0.3438
5 17 16 0.4749
6  6 11 0.7199
6  6 15 0.6561
6 12 11 0.4490
6 19 15 0.4749
7  7 12 0.2801
7  7 16 0.3438
7 18 16 0.4749
8  8  9 0.2885
8  8  9 0.2885
8  8 13 0.3289
9  9 10-0.5674
9  9 10-0.5674
9  9 14-0.6707
10 10  9 0.2885
10 10 13 0.3289
11 11  5 1.0
11 11 12-0.7732
11 11 16-0.6561
12 12 11 0.3680
12 12 11 0.3680
12 12 15 0.3438
13 13 12-0.7732
13 13 12-0.7732
13 13 16-0.6561
14 14 13 0.3289
14 14  9 0.3894
15 15  6 1.0
15 15 14-0.6707
15 15 10-0.7656
16 16 13 0.3289
16 16 13 0.3289
16 16  9 0.3894
```

```
265.0      182.0
1  1 11 0.6320
1  1 11 0.6320
1  1  9 0.7114
1  2  9 0.6591
1  4  9 0.6591
1  6 11 0.6745
1  8  9 0.4531
1 10  9 0.4531
1 12 11 0.4823
2  2  2 1.0
2  2 14 0.3289
2  3 14-0.3289
2  8 10 0.6114
2 15 14 0.4696
3  3 13 0.6707
3  4 13 0.6707
3 14 13 0.4696
4  4  2 1.0
4  4 14 0.3289
4 10 10 0.6114
4 16 14 0.4696
5  5 15 0.6561
5  6 15 0.6561
5 11 11 0.4490
5 18 15 0.4749
6  6 12 0.2801
6  6 16 0.3438
6 12 12 0.3670
6 19 16 0.4749
7  7 15 0.6561
7 13 11 0.4490
7 19 15 0.4749
8  8 10-0.5674
8  8 10-0.5674
8  8 14-0.6707
9  9  9 0.2885
9  9 13 0.3289
10 10  4 1.0
10 10 10-0.5674
10 10 14-0.6707
11 11 11 0.3680
11 11 11 0.3680
11 11 15 0.3438
12 12 12-0.7732
12 12 12-0.7732
12 12 16-0.6561
13 13 11 0.3680
13 13 15 0.3438
14 14  6 1.0
14 14 14-0.6707
14 14 10-0.7656
15 15 13 0.3289
15 15 13 0.3289
15 15  9 0.3894
16 16 14-0.6707
16 16 14-0.6707
16 16 10-0.7656
```

```
182.0          0.0
1  1 12 0.3680
1  1 12 0.3680
1  1 10 0.2885
1  2 10-0.3352
1  4 10-0.3352
1  6 12-0.3210
1  8 10 0.3613
1 10 10 0.3613
1 12 12 0.5900
2  2  9 0.6106
2  2 13 0.6707
2  4 13 0.6707
2 14 13 0.4696
3  3  2 1.0
3  3 14 0.3289
3  4 14-0.3289
3 14 14 0.4696
4  4  9 0.6106
4  4 13 0.6707
4 15 13 0.4696
5  5  3 1.0
5  5 16 0.3438
5  6 16-0.3438
5 11 12 0.3670
5 18 16 0.4749
6  6 15 0.6561
6  7 15 0.6561
6 17 15 0.4749
7  7  3 1.0
7  7 16 0.3438
7 13 12 0.3670
7 19 16 0.4749
8  8  9 0.2885
8  8 13 0.3289
9  9  4 1.0
9  9 10-0.5674
9  9 14-0.6707
10 10  9 0.2885
10 10  9 0.2885
10 10 13 0.3289
11 11 12-0.7732
11 11 12-0.7732
11 11 16-0.6561
12 12 11 0.3680
12 12 15 0.3438
13 13  5 1.0
13 13 12-0.7732
13 13 16-0.6561
14 14 13 0.3289
14 14  9 0.3894
14 14 13 0.3289
15 15 14-0.6707
15 15 14-0.6707
15 15 10-0.7656
16 16 13 0.3289
16 16  9 0.3894
17 17  7 1.0
```

```
1  1 11 0.6320
1  1  9 0.7114
1  1  9 0.7114
1  3  9 0.6591
1  5 11 0.6745
1  7 11 0.6745
1  9  9 0.4531
1 11 11 0.4823
1 13 11 0.4823
2  2 10 0.3894
2  2 14 0.3289
2  4 14-0.3289
2 14 14 0.4696
3  3  9 0.6106
3  3 13 0.6707
3  9  9 0.4876
3 16 13 0.4696
4  4 10 0.3894
4  4 14 0.3289
4 15 14 0.4696
5  5 11 0.7199
5  5 15 0.6561
5  7 15 0.6561
5 17 15 0.4749
6  6  3 1.0
6  6 16 0.3438
6  7 16-0.3438
6 17 16 0.4749
7  7 11 0.7199
7  7 15 0.6561
7 18 15 0.4749
8  8  4 1.0
8  8 10-0.5674
8  8 14-0.6707
9  9  9 0.2885
9  9  9 0.2885
9  9 13 0.3289
10 10 10-0.5674
10 10 10-0.5674
10 10 14-0.6707
11 11 11 0.3680
11 11 15 0.3438
12 12  5 1.0
12 12 12-0.7732
12 12 16-0.6561
13 13 11 0.3680
13 13 11 0.3680
13 13 15 0.3438
14 14 14-0.6707
14 14 10-0.7656
14 14 14-0.6707
15 15 13 0.3289
15 15  9 0.3894
16 16  6 1.0
16 16 14-0.6707
16 16 10-0.7656
17 17 15 0.3438
```

```
17 17 16-0.6561      17 17 15 0.3438      17 17 16-0.6561      17 17 15 0.3438
17 17 16-0.6561      17 17 11 0.2801      17 17 12-0.5884      17 17 11 0.2801
17 17 12-0.5884      18 18  7 1.0         18 18 15 0.3438      18 18 16-0.6561
18 18 15 0.3438      18 18 16-0.6561      18 18 15 0.3438      18 18 16-0.6561
18 18 11 0.2801      18 18 12-0.5884      18 18 11 0.2801      18 18 12-0.5884
19 19  7 1.0         19 19 15 0.3438      19 19 16-0.6561      19 19 15 0.3438
19 19 16-0.6561      19 19 15 0.3438      19 19 16-0.6561      19 19 11 0.2801
19 19 12-0.5884      19 19 11 0.2801      19 19 12-0.5884      20 20  8 1.0
21 21  8 1.0         22 22  8 1.0         -4
```

CFC114

```
  1  1 17  5 18  5 1 1 1 0 0          1  0  0  0  1  0  1  0  0  0
 1,2-dichlorotetrafluoroethane
december 1992
        3.5          1.8          4.4          0.1          0.3          0.1
        0.1          0.01         0.01         0.6          -0.06        0.4
        -0.04        0.5          -0.05        1.1          -0.11
 1  2  3  4  5
CFC114
 1 22 18 17  4
 6  4  3  5
 1  2  3  4  5  6  7  8  9 10 11 12 13 14 15 16 17
  0.0       0.0       0.0       0.0       0.0       0.0
  0.0       0.0       0.0       0.0       0.0       0.0
  0.0       0.0       0.0       0.0       0.0       0.0
 1  1  1 1.0         1  1 10 0.6381      1  1 11 0.3621      1  1 12 0.7062
 1  1 13 0.2938      1  1 12 0.7062      1  1 13 0.2938      1  1 10 0.6381
 1  1 11 0.3621      1  1 12 0.7062      1  1 13 0.2938      1  1 12 0.7062
 1  1 13 0.2938      1  2 10 0.6744      1  2 11-0.3225      1  3 12 0.6514
 1  3 13-0.3424      1  4 12 0.6514      1  4 13-0.3424      1  5 10 0.6744
 1  5 11-0.3225      1  6 12 0.6514      1  6 13-0.3424      1  7 12 0.6514
 1  7 13-0.3424      1  8 10 0.4807      1  8 11 0.5703      1  9 12 0.4555
 1  9 13 0.3605      1 10 12 0.4555      1 10 13 0.3605      1 11 10 0.4807
 1 11 11 0.5703      1 12 12 0.4555      1 12 13 0.3605      1 13 12 0.4555
 1 13 13 0.3605      2  2  2 1.0         2  2 10 0.7128      2  2 11 0.2873
 2  2 12 0.7534      2  2 13 0.2403      2  2 12 0.7534      2  2 13 0.2403
 2  3 12 0.6624      2  3 13-0.3144      2  4 12 0.6624      2  4 13-0.3144
 2  8 10 0.4526      2  8 11 0.3814      2 14 12 0.4255      2 14 13 0.2860
 2 15 12 0.4255      2 15 13 0.2860      3  3  3 1.0         3  3 12 0.6009
 3  3 13 0.3990      3  3 12 0.5824      3  3 13 0.4113      3  3 16 0.6545
 3  3 17 0.3455      3  4 16 0.6545      3  4 17-0.3455      3  9 12 0.4897
 3  9 13 0.6186      3 14 12 0.4895      3 14 13 0.7283      3 16 16 0.4755
 3 16 17 0.4755      4  4  3 1.0         4  4 12 0.6009      4  4 13 0.3990
 4  4 12 0.5724      4  4 13 0.4113      4  4 16 0.6545      4  4 17 0.3455
 4 10 12 0.4897      4 10 13 0.6186      4 15 12 0.4895      4 15 13 0.7283
 4 16 16 0.4755      4 16 17 0.4755      5  5  2 1.0         5  5 10 0.7128
 5  5 11 0.2873      5  5 14 0.7534      5  5 15 0.2403      5  5 14 0.7534
 5  5 15 0.2403      5  6 14 0.6624      5  6 15-0.3144      5  7 14 0.6624
 5  7 15-0.3144      5 11 10 0.4526      5 11 11 0.3814      5 17 14 0.4255
 5 17 15 0.2860      5 18 14 0.4255      5 18 15 0.2860      6  6  3 1.0
 6  6 12 0.6009      6  6 13 0.3990      6  6 14 0.5824      6  6 15 0.4113
 6  6 16 0.6545      6  6 17 0.3455      6  7 16 0.6545      6  7 17-0.3455
 6 12 12 0.4897      6 12 13 0.6186      6 17 14 0.4895      6 17 15 0.7283
 6 19 16 0.4755      6 19 17 0.4755      7  7  3 1.0         7  7 12 0.6009
 7  7 13 0.3990      7  7 14 0.5824      7  7 15 0.4113      7  7 16 0.6545
 7  7 17 0.3455      7 13 12 0.4897      7 13 13 0.6186      7 18 14 0.4895
 7 18 15 0.7283      7 19 16 0.4755      7 19 17 0.4755      8  8  4 1.0
 8  8 10 0.3621      8  8 11-0.7571      8  8 12 0.2938      8  8 13-0.5590
```

```
 8  8 12 0.2938     8  8 13-0.5590     8  8 12 0.2403     8  8 13-0.5063
 8  8 12 0.2403     8  8 13-0.5063     9  9  5 1.0        9  9 12 0.2938
 9  9 13-0.5590     9  9 12 0.2938     9  9 13-0.5590     9  9 10 0.3621
 9  9 11-0.7571     9  9 16 0.3455     9  9 17-0.6545     9  9 12 0.4113
 9  9 13-0.8666    10 10  5 1.0       10 10 12 0.2938    10 10 13-0.5590
10 10 12 0.2938    10 10 13-0.5590    10 10 10 0.3621    10 10 11-0.7571
10 10 16 0.3455    10 10 17-0.6545    10 10 12 0.4113    10 10 13-0.8666
11 11  4 1.0       11 11 10 0.3621    11 11 11-0.7571    11 11 12 0.2938
11 11 13-0.5590    11 11 12 0.2938    11 11 13-0.5590    11 11 14 0.2403
11 11 15-0.5063    11 11 14 0.2403    11 11 15-0.5063    12 12  5 1.0
12 12 12 0.2938    12 12 13-0.5590    12 12 12 0.2938    12 12 13-0.5590
12 12 10 0.3621    12 12 11-0.7571    12 12 14 0.4113    12 12 15-0.8666
12 12 16 0.3455    12 12 17-0.6545    13 13  5 1.0       13 13 12 0.2938
13 13 13-0.5590    13 13 12 0.2938    13 13 13-0.5590    13 13 10 0.3621
13 13 11-0.7571    13 13 14 0.4113    13 13 15-0.8666    13 13 16 0.3455
13 13 17-0.6545    14 14  6 1.0       14 14 12 0.2403    14 14 13-0.5063
14 14 12 0.2403    14 14 13-0.5063    14 14 10 0.2873    14 14 11-0.6008
14 14 12 0.3990    14 14 13-0.7592    14 14 16 0.3455    14 14 17-0.6545
15 15  6 1.0       15 15 12 0.2403    15 15 13-0.5063    15 15 12 0.2403
15 15 13-0.5063    15 15 16 0.3455    15 15 17-0.6545    15 15 10 0.2873
15 15 11-0.6008    15 15 12 0.3990    15 15 13-0.7592    16 16  7 1.0
16 16 16 0.3455    16 16 17-0.6545    16 16 12 0.4113    16 16 13-0.8666
16 16 12 0.4113    16 16 13-0.8666    16 16 12 0.3990    16 16 13-0.7592
16 16 12 0.3990    16 16 13-0.7592    17 17  6 1.0       17 17 14 0.2403
17 17 15-0.5063    17 17 14 0.2403    17 17 15-0.5063    17 17 16 0.3455
17 17 17-0.6545    17 17 12 0.3990    17 17 13-0.7592    17 17 10 0.2873
17 17 11-0.6008    18 18  6 1.0       18 18 14 0.2403    18 18 15-0.5063
18 18 14 0.2403    18 18 15-0.5063    18 18 16 0.3455    18 18 17-0.6545
18 18 12 0.3990    18 18 13-0.7592    18 18 10 0.2873    18 18 11-0.6008
19 19  7 1.0       19 19 16 0.3455    19 19 17-0.6545    19 19 14 0.4113
19 19 15-0.8666    19 19 14 0.4113    19 19 15-0.8666    19 19 12 0.3990
19 19 13-0.7592    19 19 12 0.3990    19 19 13-0.7592    20 20  8 1.0
21 21  9 1.0       22 22  9 1.0       -4

                              CFC114a
  1  1 20  5 18  3 1 1 1 0 0     1 0 0 0 1 0 1 0 0 0
 1,1-dichlorotetrafluoroethane
december 1992
      3.5          4.4          1.8          0.3          0.1          0.1
      0.1          0.1          0.01         0.01         0.4         -0.04
      0.6         -0.06         1.1         -0.11         0.5         -0.05
      0.64        -0.064
 11 13 15 17 19
CFC114a
 1 22 18 20  2
 11  7
 1  2  3  4  5  6  7  8  9 10 11 12 13 14 15 16 17 18 19 20
1295.0     1232.0     1110.0     943.0     735.0      590.0
 507.0      399.0      311.0     265.0     200.0     1232.0
 897.0      560.0      399.0     330.0     181.0        0.0
 1  1  1 1.0       1  1 11 0.7024     1  1 12 0.2976     1  1 13 0.6224
 1  1 14 0.3776    1  1 13 0.6224     1  1 14 0.3776     1  1 11 0.7187
 1  1 12 0.2813    1  1 11 0.7187     1  1 12 0.2813     1  1 11 0.7187
 1  1 12 0.2813    1  2 11 0.6638     1  2 12-0.3299     1  3 11 0.6638
 1  3 12-0.3299    1  4 11 0.6638     1  4 12-0.3299     1  5 11 0.6655
 1  5 12-0.3316    1  6 13 0.6647     1  6 14-0.3309     1  7 13 0.6647
 1  7 14-0.3309    1  8 11 0.4496     1  8 12 0.3540     1  9 11 0.4496
 1  9 12 0.3540    1 10 11 0.4496     1 10 12 0.3540     1 11 11 0.4572
```

```
 1 11 12 0.3888
 1 13 14 0.5908
 2  2 15 0.6674
 2  3 15 0.6674
 2  8 11 0.4871
 2 15 15 0.4717
 3  3 12 0.3870
 3  3 16 0.3333
 3  9 12 0.6186
 3 16 16 0.4717
 4  4 15 0.6674
 4 10 11 0.4871
 4 16 15 0.4717
 5  5 12 0.3695
 5  5 18 0.4148
 5  7 18-0.3262
 5 17 18 0.7063
 6  6 13 0.7099
 6  6 19 0.6674
 6 12 13 0.4538
 6 19 19 0.4717
 7  7 14 0.2900
 7  7 20 0.3333
 7 18 18 0.3050
 8  8 11 0.2813
 8  8 11 0.2813
 8  8 15 0.3333
 9  9 12-0.5659
 9  9 12-0.5659
 9  9 16-0.6674
10 10 11 0.2813
10 10 15 0.3333
11 11  4 1.0
11 11 14-0.7585
11 11 18-0.8395
12 12 13 0.3776
12 12 11 0.2976
12 12 19 0.3333
13 13 14-0.7585
13 13 12-0.5972
13 13 20-0.6674
14 14 15 0.3333
14 14 11 0.3870
15 15  6 1.0
15 15 16-0.6674
15 15 12-0.7785
16 16 15 0.3333
16 16 15 0.3333
16 16 11 0.3870
17 17 18-0.8395
17 17 20-0.6674
17 17 12-0.7415
18 18 17 0.4148
18 18 13 0.2900
19 19  8 1.0
19 19 18-0.5193
19 19 14-0.5826
21 21 10 1.0
 1 12 13 0.4848
 2  2  2 1.0
 2  2 16 0.3333
 2  3 16-0.3333
 2  8 12 0.6186
 2 15 16 0.4717
 3  3 15 0.6674
 3  4 15 0.6674
 3 14 15 0.4717
 4  4  2 1.0
 4  4 16 0.3333
 4 10 12 0.6186
 4 16 16 0.4717
 5  5 17 0.5859
 5  6 17 0.6603
 5 11 11 0.4827
 5 18 17 0.4930
 6  6 14 0.2900
 6  6 20 0.3333
 6 12 14 0.3723
 6 19 20 0.4717
 7  7 17 0.7441
 7 13 13 0.4538
 7 19 19 0.4717
 8  8 12-0.5659
 8  8 12-0.5659
 8  8 16-0.6674
 9  9 11 0.2813
 9  9 15 0.3333
10 10  4 1.0
10 10 12-0.5659
10 10 16-0.6674
11 11 11 0.2976
11 11 13 0.3776
11 11 17 0.4148
12 12 14-0.7585
12 12 12-0.5972
12 12 20-0.6674
13 13 13 0.3776
13 13 17 0.2566
14 14  6 1.0
14 14 16-0.6674
14 14 12-0.7785
15 15 15 0.3333
15 15 11 0.3870
15 15 15 0.3333
16 16 16-0.6674
16 16 16-0.6674
16 16 12-0.7785
17 17 17 0.4148
17 17 13 0.2900
18 18  7 1.0
18 18 18-0.8395
18 18 14-0.5826
19 19 19 0.3333
19 19 17 0.2566
19 19 13 0.2900
22 22 10 1.0
 1 12 14 0.5908
 2  2 11 0.6130
 2  2 15 0.6674
 2  4 15 0.6674
 2 14 15 0.4717
 3  3  2 1.0
 3  3 16 0.3333
 3  4 16-0.3333
 3 14 16 0.4717
 4  4 11 0.6130
 4  4 15 0.6674
 4 15 15 0.4717
 5  5  2 1.0
 5  5 18 0.4148
 5  6 18-0.3262
 5 11 12 0.5677
 5 18 18 0.7063
 6  6 17 0.7441
 6  7 19 0.6674
 6 17 17 0.4369
 7  7  3 1.0
 7  7 18 0.2566
 7 13 14 0.3723
 7 19 20 0.4717
 8  8 11 0.2813
 8  8 15 0.3333
 9  9  4 1.0
 9  9 12-0.5659
 9  9 16-0.6674
10 10 11 0.2813
10 10 11 0.2813
10 10 15 0.3333
11 11 12-0.5972
11 11 14-0.7585
11 11 18-0.8395
12 12 13 0.3776
12 12 17 0.2566
13 13  5 1.0
13 13 14-0.7585
13 13 18-0.5193
14 14 15 0.3333
14 14 11 0.3870
14 14 15 0.3333
15 15 16-0.6674
15 15 12-0.7785
15 15 16-0.6674
16 16 15 0.3333
16 16 11 0.3870
17 17  7 1.0
17 17 18-0.8395
17 17 14-0.5826
18 18 17 0.4148
18 18 19 0.3333
18 18 11 0.3695
19 19 20-0.6674
19 19 18-0.5193
19 19 14-0.5826
-4
 1 13 13 0.4848
 2  2 12 0.3870
 2  2 16 0.3333
 2  4 16-0.3333
 2 14 16 0.4717
 3  3 11 0.6130
 3  3 15 0.6674
 3  9 11 0.4871
 3 16 15 0.4717
 4  4 12 0.3870
 4  4 16 0.3333
 4 15 16 0.4717
 5  5 11 0.6305
 5  5 17 0.5859
 5  7 17 0.6603
 5 17 17 0.4930
 6  6  3 1.0
 6  6 18 0.2566
 6  7 20-0.3333
 6 17 18 0.3050
 7  7 13 0.7099
 7  7 19 0.6674
 7 18 17 0.4369
 8  8  4 1.0
 8  8 12-0.5659
 8  8 16-0.6674
 9  9 11 0.2813
 9  9 11 0.2813
 9  9 15 0.3333
10 10 12-0.5659
10 10 12-0.5659
10 10 16-0.6674
11 11 13 0.3776
11 11 17 0.4148
12 12  5 1.0
12 12 14-0.7585
12 12 18-0.5193
13 13 13 0.3776
13 13 11 0.2976
13 13 19 0.3333
14 14 16-0.6674
14 14 12-0.7785
14 14 16-0.6674
15 15 15 0.3333
15 15 11 0.3870
16 16  6 1.0
16 16 16-0.6674
16 16 12-0.7785
17 17 17 0.4148
17 17 19 0.3333
17 17 11 0.3695
18 18 18-0.8395
18 18 20-0.6674
18 18 12-0.7415
19 19 17 0.2566
19 19 13 0.2900
20 20  9 1.0
```

CFC115

```
 1  1 17  4 18  3 1 1 1 0 0          1  0  0  0  1  0  1  0  0  0
 chloropentafluoroethane
december 1992
        3.5            4.4            1.8            0.3            0.1            0.1
        0.1            0.01           0.01           0.4            -0.04          0.6
        -0.06          1.1            -0.11          0.5            -0.05
 1  2  3  4
cf2clcf3
 1 22 18 17  2
11  7
 1  2  3  4  5  6  7  8  9 10 11 12 13 14 15 16 17
1351.0    1224.0    1133.0    982.0     762.0     648.0
 560.0     441.0     362.0    314.0     186.0    1241.0
1185.0     596.0     454.0    331.0     186.0       0.0
 1  1  1 1.0            1  1 12 0.6391         1  1 13 0.3609         1  1 10 0.7127
 1  1 11 0.2950         1  1 10 0.7127         1  1 11 0.2950         1  1 10 0.7274
 1  1 11 0.2726         1  1 10 0.7274         1  1 11 0.2726         1  1 10 0.7274
 1  1 11 0.2726         1  2 10 0.6755         1  2 11-0.3188         1  3 10 0.6755
 1  3 11-0.3188         1  4 10 0.6755         1  4 11-0.3188         1  5 12 0.6744
 1  5 13-0.3226         1  6 10 0.6564         1  6 11-0.3450         1  7 10 0.6564
 1  7 11-0.3450         1  8 10 0.4453         1  8 11 0.3537         1  9 10 0.4453
 1  9 11 0.3537         1 10 10 0.4453         1 10 11 0.3537         1 11 12 0.4803
 1 11 13 0.5672         1 12 10 0.4586         1 12 11 0.3612         1 13 10 0.4586
 1 13 11 0.3612         2  2  2 1.0            2  2 10 0.6273         2  2 11 0.3727
 2  2 14 0.6545         2  2 15 0.3455         2  2 14 0.6545         2  2 15 0.3455
 2  3 14 0.6545         2  3 15-0.3455         2  4 14 0.6545         2  4 15-0.3455
 2  8 10 0.4835         2  8 11 0.6087         2 14 14 0.4755         2 14 15 0.4755
 2 15 14 0.4755         2 15 15 0.4755         3  3  2 1.0            3  3 10 0.6273
 3  3 11 0.3727         3  3 14 0.6545         3  3 15 0.3455         3  3 14 0.6545
 3  3 15 0.3455         3  4 14 0.6545         3  4 15-0.3455         3  9 10 0.4835
 3  9 11 0.6087         3 14 14 0.4755         3 14 15 0.4755         3 16 14 0.4755
 3 16 15 0.4755         4  4  2 1.0            4  4 10 0.6273         4  4 11 0.3727
 4  4 14 0.6545         4  4 15 0.3455         4  4 14 0.6545         4  4 15 0.3455
 4 10 10 0.4835         4 10 11 0.6087         4 15 14 0.4755         4 15 15 0.4755
 4 16 14 0.4755         4 16 15 0.4755         5  5  3 1.0            5  5 12 0.7117
 5  5 13 0.2883         5  5 16 0.7709         5  5 17 0.2459         5  5 16 0.7709
 5  5 17 0.2459         5  6 16 0.6778         5  6 17-0.3217         5  7 16 0.6778
 5  7 17-0.3217         5 11 12 0.4530         5 11 13 0.3836         5 17 16 0.4354
 5 17 17 0.2926         5 18 16 0.4354         5 18 17 0.2926         6  6  2 1.0
 6  6 10 0.6045         6  6 11 0.4033         6  6 14 0.6545         6  6 15 0.3455
 6  6 16 0.5959         6  6 17 0.4209         6  7 14 0.6545         6  7 15-0.3455
 6 12 10 0.4938         6 12 11 0.6269         6 17 16 0.5008         6 17 17 0.7452
 6 19 14 0.4755         6 19 15 0.4755         7  7  2 1.0            7  7 10 0.6045
 7  7 11 0.4033         7  7 16 0.5959         7  7 17 0.4209         7  7 14 0.6545
 7  7 15 0.3455         7 13 10 0.4938         7 13 11 0.6269         7 18 16 0.5008
 7 18 17 0.7452         7 19 14 0.4755         7 19 15 0.4755         8  8  4 1.0
 8  8 10 0.2726         8  8 11-0.5778         8  8 10 0.2726         8  8 11-0.5778
 8  8 10 0.2726         8  8 11-0.5778         8  8 14 0.3455         8  8 15-0.6545
 8  8 14 0.3455         8  8 15-0.6545         9  9  4 1.0            9  9 10 0.2726
 9  9 11-0.5778         9  9 10 0.2726         9  9 11-0.5778         9  9 10 0.2726
 9  9 11-0.5778         9  9 14 0.3455         9  9 15-0.6545         9  9 14 0.3455
 9  9 15-0.6545        10 10  4 1.0           10 10 10 0.2726        10 10 11-0.5778
10 10 10 0.2726        10 10 11-0.5778        10 10 10 0.2726        10 10 11-0.5778
10 10 14 0.3455        10 10 15-0.6545        10 10 14 0.3455        10 10 15-0.6545
11 11  5 1.0           11 11 12 0.3609        11 11 13-0.7547        11 11 10 0.2950
11 11 11-0.5614        11 11 10 0.2950        11 11 11-0.5614        11 11 16 0.2459
```

```
11 11 17-0.5181
12 12 10 0.2950
12 12 12 0.3609
12 12 14 0.3455
13 13 11-0.5614
13 13 13-0.7547
13 13 15-0.6545
14 14 14 0.3455
14 14 10 0.3727
15 15  6 1.0
15 15 15-0.6545
15 15 11-0.7898
16 16 14 0.3455
16 16 14 0.3455
16 16 10 0.3727
17 17 17-0.5181
17 17 15-0.6545
17 17 13-0.6027
18 18 14 0.3455
18 18 12 0.2883
19 19  6 1.0
19 19 17-0.8868
19 19 11-0.7674
21 21  9 1.0
11 11 16 0.2459
12 12 11-0.5614
12 12 13-0.7547
12 12 15-0.6545
13 13 10 0.2950
13 13 16 0.4209
14 14  6 1.0
14 14 15-0.6545
14 14 11-0.7898
15 15 14 0.3455
15 15 14 0.3455
15 15 10 0.3727
16 16 15-0.6545
16 16 15-0.6545
16 16 11-0.7898
17 17 16 0.2459
17 17 10 0.4033
18 18  7 1.0
18 18 15-0.6545
18 18 13-0.6027
19 19 14 0.3455
19 19 16 0.4209
19 19 10 0.4033
22 22  9 1.0
11 11 17-0.5181
12 12 10 0.2950
12 12 16 0.4209
13 13  4 1.0
13 13 11-0.5614
13 13 17-0.8868
14 14 14 0.3455
14 14 14 0.3455
14 14 10 0.3727
15 15 15-0.6545
15 15 15-0.6545
15 15 11-0.7898
16 16 14 0.3455
16 16 10 0.3727
17 17  7 1.0
17 17 17-0.5181
17 17 11-0.7674
18 18 16 0.2459
18 18 10 0.4033
18 18 16 0.2459
19 19 15-0.6545
19 19 17-0.8868
19 19 11-0.7674
-4
12 12  4 1.0
12 12 11-0.5614
12 12 17-0.8868
13 13 10 0.2950
13 13 12 0.3609
13 13 14 0.3455
14 14 15-0.6545
14 14 15-0.6545
14 14 11-0.7898
15 15 14 0.3455
15 15 10 0.3727
16 16  6 1.0
16 16 15-0.6545
16 16 11-0.7898
17 17 16 0.2459
17 17 14 0.3455
17 17 12 0.2883
18 18 17-0.5181
18 18 11-0.7674
18 18 17-0.5181
19 19 16 0.4209
19 19 10 0.4033
20 20  8 1.0
```

FC116

```
   1 1 9 1 18 2 1 1 1 0 0          1 0 0 0 1 0 1 0 0 0
hexafluoroethane
december 1992
        3.5          4.4          0.3          0.1          0.01          0.4
       -0.04         1.1         -0.11
 4
cf3cf3
 1 22 18  9  5
 3  1  2  6  6
 1  2  3  4  5  6  7  8  9
1417.0      808.0     348.0       0.0    1117.0     714.0
1250.0     1250.0     619.0     619.0     372.0     372.0
1251.0     1251.0     523.0     523.0     216.0     216.0
 1  1  1 1.0
 1  1  7 0.2813
 1  1  7 0.2813
 1  1  7 0.2813
 1  3  7-0.3278
 1  5  7-0.3278
 1  7  7-0.3278
 1  9  7 0.3579
 1 11  7 0.3579
 1 13  7 0.3579
 2  2  8 0.6633
 2  3  8 0.6633
 2  8  6 0.4858
 2 15  8 0.4722
 3  3  7 0.3819
 3  3  9 0.3362
 3  9  7 0.6104
 3 16  9 0.4722
 4  4  8 0.6633
 1  1  6 0.7187
 1  1  6 0.7187
 1  1  6 0.7187
 1  2  6 0.6665
 1  4  6 0.6665
 1  6  6 0.6665
 1  8  6 0.4496
 1 10  6 0.4496
 1 12  6 0.4496
 2  2  2 1.0
 2  2  9 0.3362
 2  3  9-0.3362
 2  8  7 0.6104
 2 15  9 0.4722
 3  3  8 0.6633
 3  4  8 0.6633
 3 14  8 0.4722
 4  4  2 1.0
 4  4  9 0.3362
 1  1  7 0.2813
 1  1  7 0.2813
 1  1  7 0.2813
 1  2  7-0.3278
 1  4  7-0.3278
 1  6  7-0.3278
 1  8  7 0.3579
 1 10  7 0.3579
 1 12  7 0.3579
 2  2  6 0.6181
 2  2  8 0.6633
 2  4  8 0.6633
 2 14  8 0.4722
 3  3  2 1.0
 3  3  9 0.3362
 3  4  9-0.3362
 3 14  9 0.4722
 4  4  6 0.6181
 4  4  8 0.6633
 1  1  6 0.7187
 1  1  6 0.7187
 1  1  6 0.7187
 1  3  6 0.6665
 1  5  6 0.6665
 1  7  6 0.6665
 1  9  6 0.4496
 1 11  6 0.4496
 1 13  6 0.4496
 2  2  7 0.3819
 2  2  9 0.3362
 2  4  9-0.3362
 2 14  9 0.4722
 3  3  6 0.6181
 3  3  8 0.6633
 3  9  6 0.4858
 3 16  8 0.4722
 4  4  7 0.3819
 4  4  9 0.3362
```

```
4 10  6 0.4858
4 16  8 0.4722
5  5  7 0.3819
5  5  9 0.3362
5  7  9-0.3362
5 17  9 0.4722
6  6  6 0.6181
6  6  8 0.6633
6 12  6 0.4858
6 19  8 0.4722
7  7  7 0.3819
7  7  9 0.3362
7 18  9 0.4722
8  8  6 0.2813
8  8  6 0.2813
8  8  8 0.3362
9  9  7-0.5720
9  9  7-0.5720
9  9  9-0.6633
10 10  6 0.2813
10 10  8 0.3362
11 11  3 1.0
11 11  7-0.5720
11 11  9-0.6633
12 12  6 0.2813
12 12  6 0.2813
12 12  8 0.3362
13 13  7-0.5720
13 13  7-0.5720
13 13  9-0.6633
14 14  8 0.3362
14 14  6 0.3819
15 15  4 1.0
15 15  9-0.6633
15 15  7-0.7766
16 16  8 0.3362
16 16  8 0.3362
16 16  6 0.3819
17 17  9-0.6633
17 17  9-0.6633
17 17  7-0.7766
18 18  8 0.3362
18 18  6 0.3819
19 19  4 1.0
19 19  9-0.6633
19 19  7-0.7766
21 21  5 1.0
4 10  7 0.6104
4 16  9 0.4722
5  5  8 0.6633
5  6  8 0.6633
5 11  6 0.4858
5 18  8 0.4722
6  6  7 0.3819
6  6  9 0.3362
6 12  7 0.6104
6 19  9 0.4722
7  7  8 0.6633
7 13  6 0.4858
7 19  8 0.4722
8  8  7-0.5720
8  8  7-0.5720
8  8  9-0.6633
9  9  6 0.2813
9  9  8 0.3362
10 10  3 1.0
10 10  7-0.5720
10 10  9-0.6633
11 11  6 0.2813
11 11  6 0.2813
11 11  8 0.3362
12 12  7-0.5720
12 12  7-0.5720
12 12  9-0.6633
13 13  6 0.2813
13 13  8 0.3362
14 14  4 1.0
14 14  9-0.6633
14 14  7-0.7766
15 15  8 0.3362
15 15  6 0.3819
15 15  8 0.3362
16 16  9-0.6633
16 16  9-0.6633
16 16  7-0.7766
17 17  8 0.3362
17 17  6 0.3819
18 18  4 1.0
18 18  9-0.6633
18 18  7-0.7766
19 19  8 0.3362
19 19  6 0.3819
19 19  8 0.3362
22 22  5 1.0
4 15  8 0.4722
5  5  2 1.0
5  5  9 0.3362
5  6  9-0.3362
5 11  7 0.6104
5 18  9 0.4722
6  6  8 0.6633
6  7  8 0.6633
6 17  8 0.4722
7  7  2 1.0
7  7  9 0.3362
7 13  7 0.6104
7 19  9 0.4722
8  8  6 0.2813
8  8  8 0.3362
9  9  3 1.0
9  9  7-0.5720
9  9  9-0.6633
10 10  6 0.2813
10 10  6 0.2813
10 10  8 0.3362
11 11  7-0.5720
11 11  7-0.5720
11 11  9-0.6633
12 12  6 0.2813
12 12  8 0.3362
13 13  3 1.0
13 13  7-0.5720
13 13  9-0.6633
14 14  8 0.3362
14 14  6 0.3819
14 14  8 0.3362
15 15  9-0.6633
15 15  7-0.7766
15 15  9-0.6633
16 16  8 0.3362
16 16  6 0.3819
17 17  4 1.0
17 17  9-0.6633
17 17  7-0.7766
18 18  8 0.3362
18 18  8 0.3362
18 18  6 0.3819
19 19  9-0.6633
19 19  7-0.7766
19 19  9-0.6633
-4
4 15  9 0.4722
5  5  6 0.6181
5  5  8 0.6633
5  7  8 0.6633
5 17  8 0.4722
6  6  2 1.0
6  6  9 0.3362
6  7  9-0.3362
6 17  9 0.4722
7  7  6 0.6181
7  7  8 0.6633
7 18  8 0.4722
8  8  3 1.0
8  8  7-0.5720
8  8  9-0.6633
9  9  6 0.2813
9  9  6 0.2813
9  9  8 0.3362
10 10  7-0.5720
10 10  7-0.5720
10 10  9-0.6633
11 11  6 0.2813
11 11  8 0.3362
12 12  3 1.0
12 12  7-0.5720
12 12  9-0.6633
13 13  6 0.2813
13 13  6 0.2813
13 13  8 0.3362
14 14  9-0.6633
14 14  7-0.7766
14 14  9-0.6633
15 15  8 0.3362
15 15  6 0.3819
16 16  4 1.0
16 16  9-0.6633
16 16  7-0.7766
17 17  8 0.3362
17 17  8 0.3362
17 17  6 0.3819
18 18  9-0.6633
18 18  9-0.6633
18 18  7-0.7766
19 19  8 0.3362
19 19  6 0.3819
20 20  5 1.0
```

HFC170

```
  1  1  9  2 18  3 1 1 1 0 0        1 0 0 0 1 0 1 0 0 0
ethane
february 1993
      3.5          4.6          0.4          0.43          0.01          0.09
      -0.009       0.4          -0.04
 2  3
ch3ch3
 1 22 18  9  5
 3  1  2  6  6
```

```
 1 2 3 4 5 6 7 8 9
2954.0    1388.0      995.0     289.0     2954.0    1379.0
2969.0    2969.0     1460.0    1460.0     1190.0    1190.0
2996.0    2996.0     1486.0    1486.0      820.0     820.0
 1  1  1 1.0        1  1  8 0.7770     1  1  9 0.2229     1  1  8 0.7770
 1  1  9 0.2229     1  1  8 0.7770     1  1  9 0.2229     1  1  8 0.7770
 1  1  9 0.2229     1  1  8 0.7770     1  1  9 0.2229     1  1  8 0.7770
 1  1  9 0.2229     1  2  8 0.6670     1  2  9-0.3087     1  3  8 0.6670
 1  3  9-0.3087     1  4  8 0.6670     1  4  9-0.3087     1  5  8 0.6670
 1  5  9-0.3087     1  6  8 0.6670     1  6  9-0.3087     1  7  8 0.6670
 1  7  9-0.3087     1  8  8 0.4162     1  8  9 0.2581     1  9  8 0.4162
 1  9  9 0.2581     1 10  8 0.4162     1 10  9 0.2581     1 11  8 0.4162
 1 11  9 0.2581     1 12  8 0.4162     1 12  9 0.2581     1 13  8 0.4162
 1 13  9 0.2581     2  2  2 1.0        2  2  8 0.5726     2  2  9 0.4274
 2  2  6 0.6537     2  2  7 0.3463     2  2  6 0.6537     2  2  7 0.3463
 2  3  6 0.6537     2  3  7-0.3463     2  4  6 0.6537     2  4  7-0.3463
 2  8  8 0.4947     2  8  9 0.7978     2 14  6 0.4758     2 14  7 0.4758
 2 15  6 0.4758     2 15  7 0.4758     3  3  2 1.0        3  3  8 0.5726
 3  3  9 0.4274     3  3  6 0.6537     3  3  7 0.3463     3  3  6 0.6537
 3  3  7 0.3463     3  4  6 0.6537     3  4  7-0.3463     3  9  8 0.4947
 3  9  9 0.7978     3 14  6 0.4758     3 14  7 0.4758     3 16  6 0.4758
 3 16  7 0.4758     4  4  2 1.0        4  4  8 0.5726     4  4  9 0.4274
 4  4  6 0.6537     4  4  7 0.3463     4  4  6 0.6537     4  4  7 0.3463
 4 10  8 0.4947     4 10  9 0.7978     4 15  6 0.4758     4 15  7 0.4758
 4 16  6 0.4758     4 16  7 0.4758     5  5  2 1.0        5  5  8 0.5726
 5  5  9 0.4274     5  5  6 0.6537     5  5  7 0.3463     5  5  6 0.6537
 5  5  7 0.3463     5  6  6 0.6537     5  6  7-0.3463     5  7  6 0.6537
 5  7  7-0.3463     5 11  8 0.4947     5 11  9 0.7978     5 17  6 0.4758
 5 17  7 0.4758     5 18  6 0.4758     5 18  7 0.4758     6  6  2 1.0
 6  6  8 0.5726     6  6  9 0.4274     6  6  6 0.6537     6  6  7 0.3463
 6  6  6 0.6537     6  6  7 0.3463     6  7  6 0.6537     6  7  7-0.3463
 6 12  8 0.4947     6 12  9 0.7978     6 17  6 0.4758     6 17  7 0.4758
 6 19  6 0.4758     6 19  7 0.4758     7  7  2 1.0        7  7  8 0.5726
 7  7  9 0.4274     7  7  6 0.6537     7  7  7 0.3463     7  7  6 0.6537
 7  7  7 0.3463     7 13  8 0.4947     7 13  9 0.7978     7 18  6 0.4758
 7 18  7 0.4758     7 19  6 0.4758     7 19  7 0.4758     8  8  3 1.0
 8  8  8 0.2229     8  8  9-0.4818     8  8  8 0.2229     8  8  9-0.4818
 8  8  8 0.2229     8  8  9-0.4818     8  8  6 0.3463     8  8  7-0.6537
 8  8  6 0.3463     8  8  7-0.6537     9  9  3 1.0        9  9  8 0.2229
 9  9  9-0.4818     9  9  8 0.2229     9  9  9-0.4818     9  9  8 0.2229
 9  9  9-0.4818     9  9  6 0.3463     9  9  7-0.6537     9  9  6 0.3463
 9  9  7-0.6537    10 10  3 1.0       10 10  8 0.2229    10 10  9-0.4818
10 10  8 0.2229    10 10  9-0.4818    10 10  8 0.2229    10 10  9-0.4818
10 10  6 0.3463    10 10  7-0.6537    10 10  6 0.3463    10 10  7-0.6537
11 11  3 1.0       11 11  8 0.2229    11 11  9-0.4818    11 11  8 0.2229
11 11  9-0.4818    11 11  8 0.2229    11 11  9-0.4818    11 11  6 0.3463
11 11  7-0.6537    11 11  6 0.3463    11 11  7-0.6537    12 12  3 1.0
12 12  8 0.2229    12 12  9-0.4818    12 12  8 0.2229    12 12  9-0.4818
12 12  8 0.2229    12 12  9-0.4818    12 12  6 0.3463    12 12  7-0.6537
12 12  6 0.3463    12 12  7-0.6537    13 13  3 1.0       13 13  8 0.2229
13 13  9-0.4818    13 13  8 0.2229    13 13  9-0.4818    13 13  8 0.2229
13 13  9-0.4818    13 13  6 0.3463    13 13  7-0.6537    13 13  6 0.3463
13 13  7-0.6537    14 14  4 1.0       14 14  6 0.3463    14 14  7-0.6537
14 14  6 0.3463    14 14  7-0.6537    14 14  8 0.4274    14 14  9-0.9235
14 14  8 0.4274    14 14  9-0.9235    14 14  6 0.3463    14 14  7-0.6537
15 15  4 1.0       15 15  6 0.3463    15 15  7-0.6537    15 15  6 0.3463
15 15  7-0.6537    15 15  8 0.4274    15 15  9-0.9235    15 15  8 0.4274
15 15  9-0.9235    15 15  6 0.3463    15 15  7-0.6537    16 16  4 1.0
```

```
16 16  6 0.3463      16 16  7-0.6537      16 16  6 0.3463      16 16  7-0.6537
16 16  6 0.3463      16 16  7-0.6537      16 16  8 0.4274      16 16  9-0.9235
16 16  8 0.4274      16 16  9-0.9235      17 17  4 1.0         17 17  6 0.3463
17 17  7-0.6537      17 17  6 0.3463      17 17  7-0.6537      17 17  6 0.3463
17 17  7-0.6537      17 17  8 0.4274      17 17  9-0.9235      17 17  8 0.4274
17 17  9-0.9235      18 18  4 1.0         18 18  6 0.3463      18 18  7-0.6537
18 18  6 0.3463      18 18  7-0.6537      18 18  6 0.3463      18 18  7-0.6537
18 18  8 0.4274      18 18  9-0.9235      18 18  8 0.4274      18 18  9-0.9235
19 19  4 1.0         19 19  6 0.3463      19 19  7-0.6537      19 19  6 0.3463
19 19  7-0.6537      19 19  8 0.4274      19 19  9-0.9235      19 19  8 0.4274
19 19  9-0.9235      19 19  6 0.3463      19 19  7-0.6537      20 20  5 1.0
21 21  5 1.0         22 22  5 1.0         -4
```

HFC161

```
  1  1 17  3 18  2 1 1 1 0 0          1  0  0  0  1  0  1  0  0  0
 fluoroethane
february 1993
        3.5          4.6          4.4          0.14         0.3          0.43
        0.1          0.01         0.01         0.09         -0.009       0.4
        -0.04        0.06         -0.006       0.4          -0.04
 5 14 16
ch3cfh2
 1 22 18 17  2
11  7
 1  2  3  4  5  6  7  8  9 10 11 12 13 14 15 16 17
3003.0    2941.0    2915.0    1479.0    1449.0    1395.0
1365.0    1108.0    1048.0     880.0     415.0    3003.0
3003.0    1449.0    1277.0    1048.0     810.0     243.0
 1  1  1 1.0          1  1 12 0.7690       1  1 13 0.2310       1  1 12 0.7690
 1  1 13 0.2310       1  1 12 0.7690       1  1 13 0.2310       1  1 12 0.7856
 1  1 13 0.2144       1  1 12 0.7856       1  1 13 0.2144       1  1 16 0.6928
 1  1 17 0.3073       1  2 12 0.6560       1  2 13-0.3189       1  3 12 0.6560
 1  3 13-0.3189       1  4 12 0.6560       1  4 13-0.3189       1  5 16 0.6679
 1  5 17-0.3308       1  6 12 0.6837       1  6 13-0.2946       1  7 12 0.6837
 1  7 13-0.2946       1  8 12 0.4215       1  8 13 0.2604       1  9 12 0.4215
 1  9 13 0.2604       1 10 12 0.4215       1 10 13 0.2604       1 11 16 0.4614
 1 11 17 0.4132       1 12 12 0.4104       1 12 13 0.2598       1 13 12 0.4104
 1 13 13 0.2598       2  2  2 1.0          2  2 12 0.5596       2  2 13 0.4404
 2  2 10 0.6575       2  2 11 0.3370       2  2 10 0.6575       2  2 11 0.3370
 2  3 10 0.6575       2  3 11-0.3370       2  4 10 0.6575       2  4 11-0.3370
 2  8 12 0.4964       2  8 13 0.8035       2 14 10 0.4708       2 14 11 0.4708
 2 15 10 0.4708       2 15 11 0.4708       3  3  2 1.0          3  3 12 0.5596
 3  3 13 0.4404       3  3 10 0.6575       3  3 11 0.3370       3  3 10 0.6575
 3  3 11 0.3370       3  4 10 0.6575       3  4 11-0.3370       3  9 12 0.4964
 3  9 13 0.8035       3 14 10 0.4708       3 14 11 0.4708       3 16 10 0.4708
 3 16 11 0.4708       4  4  2 1.0          4  4 12 0.5596       4  4 13 0.4404
 4  4 10 0.6575       4  4 11 0.3370       4  4 10 0.6575       4  4 11 0.3370
 4 10 12 0.4964       4 10 13 0.8035       4 15 10 0.4708       4 15 11 0.4708
 4 16 10 0.4708       4 16 11 0.4708       5  5  3 1.0          5  5 16 0.6439
 5  5 17 0.3561       5  5 14 0.7239       5  5 15 0.2767       5  5 14 0.7239
 5  5 15 0.2767       5  6 14 0.6308       5  6 15-0.3533       5  7 14 0.6308
 5  7 15-0.3533       5 11 16 0.4789       5 11 17 0.5347       5 17 14 0.4476
 5 17 15 0.3054       5 18 14 0.4476       5 18 15 0.3054       6  6  2 1.0
 6  6 12 0.5950       6  6 13 0.4049       6  6 14 0.5496       6  6 15 0.4510
 6  6 10 0.6611       6  6 11 0.3388       6  7 10 0.6611       6  7 11-0.3388
 6 12 12 0.4909       6 12 13 0.7752       6 17 14 0.4979       6 17 15 0.7295
 6 19 10 0.4733       6 19 11 0.4733       7  7  2 1.0          7  7 12 0.5950
 7  7 13 0.4049       7  7 14 0.5496       7  7 15 0.4510       7  7 10 0.6611
```

```
 7  7 11 0.3388     7 13 12 0.4909     7 13 13 0.7752     7 18 14 0.4979
 7 18 15 0.7295     7 19 10 0.4733     7 19 11 0.4733     8  8  4 1.0
 8  8 12 0.2310     8  8 13-0.4751     8  8 12 0.2310     8  8 13-0.4751
 8  8 12 0.2310     8  8 13-0.4751     8  8 10 0.3370     8  8 11-0.6575
 8  8 10 0.3370     8  8 11-0.6575     9  9  4 1.0        9  9 12 0.2310
 9  9 13-0.4751     9  9 12 0.2310     9  9 13-0.4751     9  9 12 0.2310
 9  9 13-0.4751     9  9 10 0.3370     9  9 11-0.6575     9  9 10 0.3370
 9  9 11-0.6575    10 10  4 1.0       10 10 12 0.2310    10 10 13-0.4751
10 10 12 0.2310    10 10 13-0.4751    10 10 12 0.2310    10 10 13-0.4751
10 10 10 0.3370    10 10 11-0.6575    10 10 10 0.3370    10 10 11-0.6575
11 11  5 1.0       11 11 16 0.3073    11 11 17-0.6204    11 11 12 0.2144
11 11 13-0.4975    11 11 12 0.2144    11 11 13-0.4975    11 11 14 0.2767
11 11 15-0.4940    11 11 14 0.2767    11 11 15-0.4940    12 12  4 1.0
12 12 12 0.2144    12 12 13-0.4975    12 12 12 0.2144    12 12 13-0.4975
12 12 16 0.3073    12 12 17-0.6204    12 12 14 0.4510    12 12 15-0.8053
12 12 10 0.3388    12 12 11-0.6611    13 13  4 1.0       13 13 12 0.2144
13 13 13-0.4975    13 13 12 0.2144    13 13 13-0.4975    13 13 16 0.3073
13 13 17-0.6204    13 13 14 0.4510    13 13 15-0.8053    13 13 10 0.3388
13 13 11-0.6611    14 14  6 1.0       14 14 10 0.3370    14 14 11-0.6575
14 14 10 0.3370    14 14 11-0.6575    14 14 12 0.4404    14 14 13-0.9058
14 14 12 0.4404    14 14 13-0.9058    14 14 10 0.3370    14 14 11-0.6575
15 15  6 1.0       15 15 10 0.3370    15 15 11-0.6575    15 15 10 0.3370
15 15 11-0.6575    15 15 10 0.3370    15 15 11-0.6575    15 15 12 0.4404
15 15 13-0.9058    15 15 12 0.4404    15 15 13-0.9058    16 16  6 1.0
16 16 10 0.3370    16 16 11-0.6575    16 16 10 0.3370    16 16 11-0.6575
16 16 10 0.3370    16 16 11-0.6575    16 16 12 0.4404    16 16 13-0.9058
16 16 12 0.4404    16 16 13-0.9058    17 17  7 1.0       17 17 14 0.2767
17 17 15-0.4940    17 17 14 0.2767    17 17 15-0.4940    17 17 10 0.3388
17 17 11-0.6611    17 17 12 0.4049    17 17 13-0.9397    17 17 16 0.3561
17 17 17-0.7190    18 18  7 1.0       18 18 14 0.2767    18 18 15-0.4940
18 18 14 0.2767    18 18 15-0.4940    18 18 10 0.3388    18 18 11-0.6611
18 18 12 0.4049    18 18 13-0.9397    18 18 16 0.3561    18 18 17-0.7190
19 19  6 1.0       19 19 10 0.3388    19 19 11-0.6611    19 19 14 0.4510
19 19 15-0.8053    19 19 14 0.4510    19 19 15-0.8053    19 19 12 0.4049
19 19 13-0.9397    19 19 12 0.4049    19 19 13-0.9397    20 20  8 1.0
21 21  9 1.0       22 22  9 1.0       -4
```

HFC152

```
 1 1 17 2 18 2 1 1 1 0 0          1 0 0 0 1 0 1 0 0 0
1,2-difluoroethane
february 1993
      3.5         4.4         4.6         0.3         0.14        0.1
      0.43        0.01        0.01        0.4         -0.04       0.4
      -0.04       0.06        -0.006      0.09        -0.009
10 12
CFH2CFH2
 1 22 18 17  4
 6  4  3  5
 1  2  3  4  5  6  7  8  9 10 11 12 13 14 15 16 17
2962.0    1416.0    1079.0    1049.0     858.0     804.0
2994.0    1415.0     320.0       0.0    2990.0    1285.0
 450.0    2951.0    1376.0    1065.0     897.0     652.0
 1  1  1 1.0        1  1 10 0.6990     1  1 11 0.3011     1  1 12 0.7726
 1  1 13 0.2274     1  1 12 0.7726     1  1 13 0.2274     1  1 10 0.6990
 1  1 11 0.3011     1  1 12 0.7726     1  1 13 0.2274     1  1 12 0.7726
 1  1 13 0.2274     1  2 10 0.6727     1  2 11-0.3258     1  3 12 0.6682
 1  3 13-0.3098     1  4 12 0.6682     1  4 13-0.3098     1  5 10 0.6727
 1  5 11-0.3258     1  6 12 0.6682     1  6 13-0.3098     1  7 12 0.6682
```

```
 1  7 13-0.3098
 1  9 13 0.2661
 1 11 11 0.4080
 1 13 13 0.2661
 2  2 14 0.7298
 2  3 14 0.6462
 2  8 10 0.4778
 2 15 14 0.4434
 3  3 13 0.4221
 3  3 17 0.3413
 3  9 13 0.7781
 3 16 17 0.4742
 4  4 14 0.5722
 4 10 12 0.4939
 4 16 16 0.4742
 5  5 11 0.3525
 5  5 15 0.2694
 5  7 15-0.3391
 5 17 15 0.3118
 6  6 12 0.5779
 6  6 14 0.5722
 6 12 12 0.4939
 6 19 16 0.4742
 7  7 13 0.4221
 7  7 17 0.3413
 7 18 15 0.7028
 8  8 10 0.3011
 8  8 12 0.2274
 8  8 14 0.2694
 9  9 13-0.4905
 9  9 11-0.6217
 9  9 15-0.8136
10 10 12 0.2274
10 10 16 0.3413
11 11  4 1.0
11 11 13-0.4905
11 11 15-0.5133
12 12 12 0.2274
12 12 10 0.3011
12 12 14 0.4270
13 13 13-0.4905
13 13 11-0.6217
13 13 15-0.8136
14 14 14 0.2694
14 14 12 0.4221
15 15  6 1.0
15 15 15-0.5133
15 15 13-0.9104
16 16 16 0.3413
16 16 14 0.4270
16 16 12 0.4221
17 17 15-0.5133
17 17 11-0.7280
17 17 17-0.6586
18 18 14 0.2694
18 18 12 0.4221
19 19  7 1.0
19 19 15-0.8136
```

```
 1  8 10 0.4587
 1 10 12 0.4192
 1 12 12 0.4192
 2  2  2 1.0
 2  2 15 0.2694
 2  3 15-0.3391
 2  8 11 0.5372
 2 15 15 0.3118
 3  3 14 0.5722
 3  4 16 0.6586
 3 14 14 0.4943
 4  4  3 1.0
 4  4 15 0.4270
 4 10 13 0.7781
 4 16 17 0.4742
 5  5 14 0.7298
 5  6 14 0.6462
 5 11 10 0.4778
 5 18 14 0.4434
 6  6 13 0.4221
 6  6 15 0.4270
 6 12 13 0.7781
 6 19 17 0.4742
 7  7 14 0.5722
 7 13 12 0.4939
 7 19 16 0.4742
 8  8 11-0.6217
 8  8 13-0.4905
 8  8 15-0.5133
 9  9 12 0.2274
 9  9 16 0.3413
10 10  5 1.0
10 10 13-0.4905
10 10 17-0.6586
11 11 10 0.3011
11 11 12 0.2274
11 11 14 0.2694
12 12 13-0.4905
12 12 11-0.6217
12 12 15-0.8136
13 13 12 0.2274
13 13 16 0.3413
14 14  6 1.0
14 14 15-0.5133
14 14 13-0.9104
15 15 14 0.2694
15 15 10 0.3525
15 15 16 0.3413
16 16 17-0.6586
16 16 15-0.8136
16 16 13-0.9104
17 17 14 0.2694
17 17 12 0.4221
18 18  6 1.0
18 18 15-0.5133
18 18 13-0.9104
19 19 16 0.3413
19 19 14 0.4270
```

```
 1  8 11 0.4080
 1 10 13 0.2661
 1 12 13 0.2661
 2  2 10 0.6475
 2  2 14 0.7298
 2  4 14 0.6462
 2 14 14 0.4434
 3  3  3 1.0
 3  3 15 0.4270
 3  4 17-0.3413
 3 14 15 0.7028
 4  4 12 0.5779
 4  4 16 0.6586
 4 15 14 0.4943
 5  5  2 1.0
 5  5 15 0.2694
 5  6 15-0.3391
 5 11 11 0.5372
 5 18 15 0.3118
 6  7 16 0.6586
 6  6 16 0.6586
 6 17 14 0.4943
 7  7  3 1.0
 7  7 15 0.4270
 7 13 13 0.7781
 7 19 17 0.4742
 8  8 12 0.2274
 8  8 14 0.2694
 9  9  5 1.0
 9  9 13-0.4905
 9  9 17-0.6586
10 10 12 0.2274
10 10 10 0.3011
10 10 14 0.4270
11 11 11-0.6217
11 11 13-0.4905
11 11 15-0.5133
12 12 12 0.2274
12 12 16 0.3413
13 13  5 1.0
13 13 13-0.4905
13 13 17-0.6586
14 14 14 0.2694
14 14 10 0.3525
14 14 16 0.3413
15 15 15-0.5133
15 15 11-0.7280
15 15 17-0.6586
16 16 14 0.4270
16 16 12 0.4221
17 17  6 1.0
17 17 15-0.5133
17 17 13-0.9104
18 18 14 0.2694
18 18 10 0.3525
18 18 16 0.3413
19 19 17-0.6586
19 19 15-0.8136
```

```
 1  9 12 0.4192
 1 11 10 0.4587
 1 13 12 0.4192
 2  2 11 0.3525
 2  2 15 0.2694
 2  4 15-0.3391
 2 14 15 0.3118
 3  3 12 0.5779
 3  3 16 0.6586
 3  9 12 0.4939
 3 16 16 0.4742
 4  4 13 0.4221
 4  4 17 0.3413
 4 15 15 0.7028
 5  5 10 0.6475
 5  5 14 0.7298
 5  7 14 0.6462
 5 17 14 0.4434
 6  6  3 1.0
 6  7 17-0.3413
 6  6 17 0.3413
 6 17 15 0.7028
 7  7 12 0.5779
 7  7 16 0.6586
 7 18 14 0.4943
 8  8  4 1.0
 8  8 13-0.4905
 8  8 15-0.5133
 9  9 12 0.2274
 9  9 10 0.3011
 9  9 14 0.4270
10 10 13-0.4905
10 10 11-0.6217
10 10 15-0.8136
11 11 12 0.2274
11 11 14 0.2694
12 12  5 1.0
12 12 13-0.4905
12 12 17-0.6586
13 13 12 0.2274
13 13 10 0.3011
13 13 14 0.4270
14 14 15-0.5133
14 14 11-0.7280
14 14 17-0.6586
15 15 14 0.2694
15 15 12 0.4221
16 16  7 1.0
16 16 15-0.8136
16 16 13-0.9104
17 17 14 0.2694
17 17 10 0.3525
17 17 16 0.3413
18 18 15-0.5133
18 18 11-0.7280
18 18 17-0.6586
19 19 14 0.4270
19 19 12 0.4221
```

```
19 19 13-0.9104      19 19 12 0.4221      19 19 13-0.9104      20 20  8 1.0
21 21  9 1.0         22 22  9 1.0         -4
```

HFC152a

```
 1  1 20  1 18  2 1 1 1 0 0        1  0  0  0  1  0  1  0  0   0
 2,2-difluoroethane
february 1993
      3.5          4.6          4.4          0.14         0.3          0.43
      0.1          0.1          0.01         0.01         0.4          -0.04
      0.4          -0.04        0.09         -0.009       0.06         -0.006
      1.1          -0.11
19
CH3CHF2
 1 22 18 20  2
11  7
 1  2  3  4  5  6  7  8  9 10 11 12 13 14 15 16 17 18 19 20
3018.0     2978.0     2960.0     1460.0     1414.0     1372.0
1143.0     1129.0      868.0      571.0      470.0     3001.0
1460.0     1360.0     1171.0      930.0      383.0      222.0
 1  1  1 1.0         1  1 11 0.7735       1  1 12 0.2265       1  1 13 0.7103
 1  1 14 0.2896      1  1 13 0.7103       1  1 14 0.2896       1  1 11 0.7674
 1  1 12 0.2326      1  1 11 0.7674       1  1 12 0.2326       1  1 11 0.7674
 1  1 12 0.2326      1  2 11 0.6462       1  2 12-0.3256       1  3 11 0.6462
 1  3 12-0.3256      1  4 11 0.6462       1  4 12-0.3256       1  5 11 0.6558
 1  5 12-0.3171      1  6 13 0.6638       1  6 14-0.3316       1  7 13 0.6638
 1  7 14-0.3316      1  8 11 0.4225       1  8 12 0.2541       1  9 11 0.4225
 1  9 12 0.2541      1 10 11 0.4225       1 10 12 0.2541       1 11 11 0.4186
 1 11 12 0.2535      1 12 13 0.4536       1 12 14 0.3702       1 13 13 0.4536
 1 13 14 0.3702      2  2  2 1.0          2  2 11 0.5442       2  2 12 0.4559
 2  2 15 0.6727      2  2 16 0.3274       2  2 15 0.6727       2  2 16 0.3274
 2  3 15 0.6727      2  3 16-0.3274       2  4 15 0.6727       2  4 16-0.3274
 2  8 11 0.4981      2  8 12 0.8281       2 14 15 0.4693       2 14 16 0.4693
 2 15 15 0.4693      2 15 16 0.4693       3  3  2 1.0          3  3 11 0.5442
 3  3 12 0.4559      3  3 15 0.6727       3  3 16 0.3274       3  3 15 0.6727
 3  3 16 0.3274      3  4 15 0.6727       3  4 16-0.3274       3  9 11 0.4981
 3  9 12 0.8281      3 14 15 0.4693       3 14 16 0.4693       3 16 15 0.4693
 3 16 16 0.4693      4  4  2 1.0          4  4 11 0.5442       4  4 12 0.4559
 4  4 15 0.6727      4  4 16 0.3274       4  4 15 0.6727       4  4 16 0.3274
 4 10 11 0.4981      4 10 12 0.8281       4 15 15 0.4693       4 15 16 0.4693
 4 16 15 0.4693      4 16 16 0.4693       5  5  2 1.0          5  5 11 0.5561
 5  5 12 0.4439      5  5 17 0.5975       5  5 18 0.4020       5  5 17 0.5975
 5  5 18 0.4020      5  6 17 0.6607       5  6 18-0.3287       5  7 17 0.6607
 5  7 18-0.3287      5 11 11 0.4968       5 11 12 0.8204       5 17 17 0.4901
 5 17 18 0.6626      5 18 17 0.4901       5 18 18 0.6626       6  6  3 1.0
 6  6 13 0.6203      6  6 14 0.3797       6  6 17 0.7306       6  6 18 0.2689
 6  6 19 0.6636      6  6 20 0.3364       6  7 19 0.6636       6  7 20-0.3364
 6 12 13 0.4853      6 12 14 0.5946       6 17 17 0.4432       6 17 18 0.3278
 6 19 19 0.4725      6 19 20 0.4725       7  7  3 1.0          7  7 13 0.6203
 7  7 14 0.3797      7  7 17 0.7306       7  7 18 0.2689       7  7 19 0.6636
 7  7 20 0.3364      7 13 13 0.4853       7 13 14 0.5946       7 18 17 0.4432
 7 18 18 0.3278      7 19 19 0.4725       7 19 20 0.4725       8  8  4 1.0
 8  8 11 0.2326      8  8 12-0.4616       8  8 11 0.2326       8  8 12-0.4616
 8  8 11 0.2326      8  8 12-0.4616       8  8 15 0.3274       8  8 16-0.6727
 8  8 15 0.3274      8  8 16-0.6727       9  9  4 1.0          9  9 11 0.2326
 9  9 12-0.4616      9  9 11 0.2326       9  9 12-0.4616       9  9 11 0.2326
 9  9 12-0.4616      9  9 15 0.3274       9  9 16-0.6727       9  9 15 0.3274
 9  9 16-0.6727     10 10  4 1.0         10 10 11 0.2326      10 10 12-0.4616
10 10 11 0.2326     10 10 12-0.4616      10 10 11 0.2326      10 10 12-0.4616
```

```
10 10 15 0.3274    10 10 16-0.6727    10 10 15 0.3274    10 10 16-0.6727
11 11  4 1.0       11 11 11 0.2265    11 11 12-0.4684    11 11 13 0.2896
11 11 14-0.5797    11 11 13 0.2896    11 11 14-0.5797    11 11 17 0.4020
11 11 18-0.8079    11 11 17 0.4020    11 11 18-0.8079    12 12  5 1.0
12 12 13 0.2896    12 12 14-0.5797    12 12 13 0.2896    12 12 14-0.5797
12 12 11 0.2265    12 12 12-0.4684    12 12 17 0.2689    12 12 18-0.5404
12 12 19 0.3364    12 12 20-0.6636    13 13  5 1.0       13 13 13 0.2896
13 13 14-0.5797    13 13 13 0.2896    13 13 14-0.5797    13 13 11 0.2265
13 13 12-0.4684    13 13 17 0.2689    13 13 18-0.5404    13 13 19 0.3364
13 13 20-0.6636    14 14  6 1.0       14 14 15 0.3274    14 14 16-0.6727
14 14 15 0.3274    14 14 16-0.6727    14 14 11 0.4559    14 14 12-0.9047
14 14 11 0.4559    14 14 12-0.9047    14 14 15 0.3274    14 14 16-0.6727
15 15  6 1.0       15 15 15 0.3274    15 15 16-0.6727    15 15 15 0.3274
15 15 16-0.6727    15 15 11 0.4559    15 15 12-0.9047    15 15 11 0.4559
15 15 12-0.9047    15 15 15 0.3274    15 15 16-0.6727    16 16  6 1.0
16 16 15 0.3274    16 16 16-0.6727    16 16 15 0.3274    16 16 16-0.6727
16 16 15 0.3274    16 16 16-0.6727    16 16 11 0.4559    16 16 12-0.9047
16 16 11 0.4559    16 16 12-0.9047    17 17  7 1.0       17 17 17 0.4020
17 17 18-0.8079    17 17 17 0.4020    17 17 18-0.8079    17 17 19 0.3364
17 17 20-0.6636    17 17 13 0.3797    17 17 14-0.7600    17 17 11 0.4439
17 17 12-0.9182    18 18  7 1.0       18 18 17 0.4020    18 18 18-0.8079
18 18 17 0.4020    18 18 18-0.8079    18 18 19 0.3364    18 18 20-0.6636
18 18 13 0.3797    18 18 14-0.7600    18 18 11 0.4439    18 18 12-0.9182
19 19  8 1.0       19 19 19 0.3364    19 19 20-0.6636    19 19 17 0.2689
19 19 18-0.5404    19 19 17 0.2689    19 19 18-0.5404    19 19 13 0.3797
19 19 14-0.7600    19 19 13 0.3797    19 19 14-0.7600    20 20  9 1.0
21 21 10 1.0       22 22 10 1.0       -4
```

HFC143

```
 1  1 21  3 18  2 1 1 1 0 0        1 0 0 0 1 0 1 0 0 0
 1,1,2-trifluoroethane
february 1993
        3.5          4.6          4.4          0.14         0.3          0.43
        0.1          0.1          0.01         0.01         0.01         0.4
        -0.04        0.4          -0.04        0.09         -0.009       0.06
        -0.006       1.1          -0.11
 6  7  8
CFH2CF2H
 1 22 18 21  1
18
 1  2  3  4  5  6  7  8  9 10 11 12 13 14 15 16 17 18 19 20 21
3005.0    2986.0    2978.0    1465.0    1433.0    1379.0
1319.0    1249.0    1152.0    1125.0    1076.0       0.0
 905.0     577.0     476.0     426.0     247.0     117.0
 1  1  1 1.0       1  1 14 0.6977     1  1 15 0.3023     1  1 14 0.6977
 1  1 15 0.3023    1  1 12 0.7640     1  1 13 0.2359     1  1 12 0.7640
 1  1 13 0.2359    1  1 12 0.7640     1  1 13 0.2359     1  1 14 0.6815
 1  1 15 0.2953    1  2 12 0.6492     1  2 13-0.3253     1  3 12 0.6492
 1  3 13-0.3253    1  4 14 0.6469     1  4 15-0.3273     1  5 14 0.6623
 1  5 15-0.3351    1  6 14 0.6623     1  6 15-0.3351     1  7 12 0.6492
 1  7 13-0.3253    1  8 12 0.4246     1  8 13 0.2617     1  9 12 0.4246
 1  9 13 0.2617    1 10 14 0.4486     1 10 15 0.3842     1 11 14 0.4593
 1 11 15 0.3933    1 12 14 0.4593     1 12 15 0.3933     1 13 12 0.4246
 1 13 13 0.2617    2  2  2 1.0        2  2 12 0.5516     2  2 13 0.4484
 2  2 16 0.7567    2  2 17 0.2432     2  2 18 0.5237     2  2 19 0.4470
 2  3 16 0.7567    2  3 17-0.2432     2  4 18 0.5975     2  4 19-0.3594
 2  8 12 0.4973    2  8 13 0.8069     2 14 16 0.4290     2 14 17 0.4290
 2 15 18 0.4838    2 15 19 0.6866     3  3  2 1.0        3  3 12 0.5516
```

```
 3  3 13 0.4484    3  3 16 0.7567    3  3 17 0.2432    3  3 18 0.5237
 3  3 19 0.4470    3  4 18 0.5975    3  4 19-0.3594    3  9 12 0.4973
 3  9 13 0.8069    3 14 16 0.4290    3 14 17 0.4290    3 16 18 0.4838
 3 16 19 0.6866    4  4  3 1.0       4  4 14 0.6141    4  4 15 0.3628
 4  4 18 0.6818    4  4 19 0.2889    4  4 18 0.6818    4  4 19 0.2889
 4 10 14 0.4720    4 10 15 0.5511    4 15 18 0.4438    4 15 19 0.3127
 4 16 18 0.4438    4 16 19 0.3127    5  5  3 1.0       5  5 14 0.6287
 5  5 15 0.3713    5  5 20 0.6454    5  5 21 0.3547    5  5 18 0.7462
 5  5 19 0.2516    5  6 20 0.6454    5  6 21-0.3547    5  7 18 0.6454
 5  7 19-0.3547    5 11 14 0.4832    5 11 15 0.5641    5 17 20 0.4784
 5 17 21 0.4784    5 18 18 0.4333    5 18 19 0.3146    6  6  3 1.0
 6  6 14 0.6287    6  6 15 0.3713    6  6 20 0.6454    6  6 21 0.3547
 6  6 18 0.7462    6  6 19 0.2516    6  7 18 0.6738    6  7 19-0.3130
 6 12 14 0.4832    6 12 15 0.5641    6 17 20 0.4784    6 17 21 0.4784
 6 19 18 0.4333    6 19 19 0.3146    7  7  2 1.0       7  7 12 0.5516
 7  7 13 0.4484    7  7 18 0.6085    7  7 19 0.3893    7  7 18 0.6085
 7  7 19 0.3893    7 13 12 0.4973    7 13 13 0.8069    7 18 18 0.4867
 7 18 19 0.6704    7 19 18 0.4867    7 19 19 0.6704    8  8  4 1.0
 8  8 12 0.2359    8  8 13-0.4709    8  8 14 0.2953    8  8 15-0.5837
 8  8 12 0.2359    8  8 13-0.4709    8  8 16 0.2492    8  8 17-0.7567
 8  8 18 0.4470    8  8 19-0.7432    9  9  4 1.0       9  9 12 0.2359
 9  9 13-0.4709    9  9 14 0.2953    9  9 15-0.5837    9  9 12 0.2359
 9  9 13-0.4709    9  9 18 0.4470    9  9 19-0.7432    9  9 16 0.2432
 9  9 17-0.7567   10 10  5 1.0      10 10 14 0.2953   10 10 15-0.5837
10 10 12 0.2359   10 10 13-0.4709   10 10 12 0.2359   10 10 13-0.4709
10 10 18 0.2889   10 10 19-0.4804   10 10 18 0.2889   10 10 19-0.4804
11 11  5 1.0      11 11 14 0.3023   11 11 15-0.5975   11 11 14 0.3023
11 11 15-0.5975   11 11 12 0.2359   11 11 13-0.4709   11 11 20 0.3547
11 11 21-0.6454   11 11 18 0.2516   11 11 19-0.5417   12 12  5 1.0
12 12 14 0.3023   12 12 15-0.5975   12 12 12 0.2359   12 12 13-0.4709
12 12 14 0.3023   12 12 15-0.5975   12 12 20 0.3547   12 12 21-0.6454
12 12 18 0.3893   12 12 19-0.8381   13 13  4 1.0      13 13 12 0.2359
13 13 13-0.4709   13 13 14 0.3023   13 13 15-0.5975   13 13 14 0.3093
13 13 15-0.5975   13 13 18 0.3893   13 13 19-0.8381   13 13 18 0.3893
13 13 19-0.8381   14 14  6 1.0      14 14 16 0.3547   14 14 17-0.6454
14 14 18 0.4470   14 14 19-0.7432   14 14 12 0.4484   14 14 13-0.8949
14 14 12 0.4484   14 14 13-0.8949   14 14 18 0.4470   14 14 19-0.7432
15 15  7 1.0      15 15 18 0.4470   15 15 19-0.7432   15 15 16 0.2432
15 15 17-0.7567   15 15 18 0.2889   15 15 19-0.4804   15 15 12 0.4484
15 15 13-0.8949   15 15 14 0.3628   15 15 15-0.7170   16 16  7 1.0
16 16 18 0.4470   16 16 19-0.7432   16 16 16 0.2432   16 16 17-0.7567
16 16 18 0.2889   16 16 19-0.4804   16 16 12 0.4484   16 16 13-0.8949
16 16 14 0.3628   16 16 15-0.7170   17 17  8 1.0      17 17 20 0.3547
17 17 21-0.6454   17 17 18 0.2516   17 17 19-0.5417   17 17 18 0.2516
17 17 19-0.5417   17 17 14 0.3713   17 17 15-0.7340   17 17 14 0.3713
17 17 15-0.7340   18 18  7 1.0      18 18 18 0.2516   18 18 19-0.5417
18 18 20 0.3547   18 18 21-0.6454   18 18 18 0.3893   18 18 19-0.8381
18 18 12 0.4484   18 18 13-0.8949   18 18 14 0.3713   18 18 15-0.7340
19 19  7 1.0      19 19 18 0.2516   19 19 19-0.5417   19 19 20 0.3547
19 19 21-0.6454   19 19 18 0.3893   19 19 19-0.8381   19 19 14 0.3713
19 19 15-0.7340   19 19 12 0.4484   19 19 13-0.8949   20 20  9 1.0
21 21 10 1.0      22 22 11 1.0      -4
```

<u>HFC143a</u>

```
  1  1 16  2 18  2 1 1 1 0 0      1 0 0 0 1 0 1 0 0 0
 1,1,1-trifluoroethane
february 1993
    3.5         4.4         4.6         0.3         0.14         0.1
```

```
        0.43           0.01          0.4           -0.04          0.4          -0.04
        1.1           -0.11          0.09          -0.009
 4  6
cf3ch3
 1 22 18 16  3
 5 12  1
 1  2  3  4  5  6  7  8  9 10 11 12 13 14 15 16
 2975.0    1408.0    1280.0     830.0     602.0    3035.0
 3035.0    1443.0    1443.0    1233.0    1233.0     970.0
  970.0     541.0     541.0     365.0     365.0     220.0
 1  1  1 1.0        1  1 11 0.7673     1  1 12 0.2327     1  1 11 0.7673
 1  1 12 0.2327     1  1 11 0.7673     1  1 12 0.2327     1  1  9 0.7226
 1  1 10 0.2783     1  1  9 0.7226     1  1 10 0.2783     1  1  9 0.7226
 1  1 10 0.2783     1  2  9 0.6776     1  2 10-0.3189     1  3  9 0.6776
 1  3 10-0.3189     1  4  9 0.6776     1  4 10-0.3189     1  5 11 0.6421
 1  5 12-0.3281     1  6 11 0.6421     1  6 12-0.3281     1  7 11 0.6421
 1  7 12-0.3281     1  8  9 0.4484     1  8 10 0.3669     1  9  9 0.4484
 1  9 10 0.3669     1 10  9 0.4484     1 10 10 0.3669     1 11 11 0.4225
 1 11 12 0.2507     1 12 11 0.4225     1 12 12 0.2507     1 13 11 0.4225
 1 13 12 0.2507     2  2  2 1.0        2  2  9 0.6354     2  2 10 0.3655
 2  2 13 0.6537     2  2 14 0.3463     2  2 13 0.6537     2  2 14 0.3463
 2  3 13 0.6537     2  3 14-0.3463     2  4 13 0.6537     2  4 14-0.3463
 2  8  9 0.4819     2  8 10 0.5890     2 14 13 0.4758     2 14 14 0.4758
 2 15 13 0.4758     2 15 14 0.4758     3  3  2 1.0        3  3  9 0.6354
 3  3 10 0.3655     3  3 13 0.6537     3  3 14 0.3463     3  3 13 0.6537
 3  3 14 0.3463     3  4 13 0.6537     3  4 14-0.3463     3  9  9 0.4819
 3  9 10 0.5890     3 14 13 0.4758     3 14 14 0.4758     3 16 13 0.4758
 3 16 14 0.4758     4  4  2 1.0        4  4  9 0.6354     4  4 10 0.3655
 4  4 13 0.6537     4  4 14 0.3463     4  4 13 0.6537     4  4 14 0.3463
 4 10  9 0.4819     4 10 10 0.5890     4 15 13 0.4758     4 15 14 0.4758
 4 16 13 0.4758     4 16 14 0.4758     5  5  3 1.0        5  5 11 0.5373
 5  5 12 0.4627     5  5 15 0.6759     5  5 16 0.3241     5  5 15 0.6759
 5  5 16 0.3241     5  6 15 0.6759     5  6 16-0.3241     5  7 15 0.6759
 5  7 16-0.3241     5 11 11 0.4986     5 11 12 0.8402     5 17 15 0.4680
 5 17 16 0.4680     5 18 15 0.4680     5 18 16 0.4680     6  6  3 1.0
 6  6 11 0.5373     6  6 12 0.4627     6  6 15 0.6759     6  6 16 0.3241
 6  6 15 0.6759     6  6 16 0.3241     6  7 15 0.6759     6  7 16-0.3241
 6 12 11 0.4986     6 12 12 0.8402     6 17 15 0.4680     6 17 16 0.4680
 6 19 15 0.4680     6 19 16 0.4680     7  7  3 1.0        7  7 11 0.5373
 7  7 12 0.4627     7  7 15 0.6759     7  7 16 0.3241     7  7 15 0.6759
 7  7 16 0.3241     7 13 11 0.4986     7 13 12 0.8402     7 18 15 0.4680
 7 18 16 0.4680     7 19 15 0.4680     7 19 16 0.4680     8  8  4 1.0
 8  8  9 0.2783     8  8 10-0.5912     8  8  9 0.2783     8  8 10-0.5912
 8  8  9 0.2783     8  8 10-0.5912     8  8 13 0.3463     8  8 14-0.6537
 8  8 13 0.3463     8  8 14-0.6537     9  9  4 1.0        9  9  9 0.2783
 9  9 10-0.5912     9  9  9 0.2783     9  9 10-0.5912     9  9  9 0.2783
 9  9 10-0.5912     9  9 13 0.3463     9  9 14-0.6537     9  9 13 0.3463
 9  9 14-0.6537    10 10  4 1.0       10 10  9 0.2783    10 10 10-0.5912
10 10  9 0.2783    10 10 10-0.5912    10 10  9 0.2783    10 10 10-0.5912
10 10 13 0.3463    10 10 14-0.6537    10 10 13 0.3463    10 10 14-0.6537
11 11  5 1.0       11 11 11 0.2327    11 11 12-0.4553    11 11 11 0.2327
11 11 12-0.4553    11 11 11 0.2327    11 11 12-0.4553    11 11 15 0.3241
11 11 16-0.6759    11 11 15 0.3241    11 11 16-0.6759    12 12  5 1.0
12 12 11 0.2327    12 12 12-0.4553    12 12 11 0.2327    12 12 12-0.4553
12 12 11 0.2327    12 12 12-0.4553    12 12 15 0.3241    12 12 16-0.6759
12 12 15 0.3241    12 12 16-0.6759    13 13  5 1.0       13 13 11 0.2327
13 13 12-0.4553    13 13 11 0.2327    13 13 12-0.4553    13 13 11 0.2327
13 13 12-0.4553    13 13 15 0.3241    13 13 16-0.6759    13 13 15 0.3241
```

```
13 13 16-0.6759     14 14  6 1.0        14 14 13 0.3463     14 14 14-0.6537
14 14 13 0.3463     14 14 14-0.6537     14 14  9 0.3655     14 14 10-0.7765
14 14  9 0.3655     14 14 10-0.7765     14 14 13 0.3463     14 14 14-0.6537
15 15  6 1.0        15 15 13 0.3463     15 15 14-0.6537     15 15 13 0.3463
15 15 14-0.6537     15 15 13 0.3463     15 15 14-0.6537     15 15  9 0.3655
15 15 10-0.7765     15 15  9 0.3655     15 15 10-0.7765     16 16  6 1.0
16 16 13 0.3463     16 16 14-0.6537     16 16 13 0.3463     16 16 14-0.6537
16 16 13 0.3463     16 16 14-0.6537     16 16  9 0.3655     16 16 10-0.7765
16 16  9 0.3655     16 16 10-0.7765     17 17  7 1.0        17 17 15 0.3241
17 17 16-0.6759     17 17 15 0.3241     17 17 16-0.6759     17 17 15 0.3241
17 17 16-0.6759     17 17 11 0.4627     17 17 12-0.9054     17 17 11 0.4627
17 17 12-0.9054     18 18  7 1.0        18 18 15 0.3241     18 18 16-0.6759
18 18 15 0.3241     18 18 16-0.6759     18 18 15 0.3241     18 18 16-0.6759
18 18 11 0.4627     18 18 12-0.9054     18 18 11 0.4627     18 18 12-0.9054
19 19  7 1.0        19 19 15 0.3241     19 19 16-0.6759     19 19 15 0.3241
19 19 16-0.6759     19 19 15 0.3241     19 19 16-0.6759     19 19 11 0.4627
19 19 12-0.9054     19 19 11 0.4627     19 19 12-0.9054     20 20  8 1.0
21 21  8 1.0        22 22  8 1.0        -4
```

HFC134

```
  1  1 17  2 18  2 1 1 1 0 0         1  0  0  0  1  0  1  0  0  0
1,1,2,2-tetrafluoroethane
february 1993
        3.5         4.6         4.4         0.14        0.3         0.1
        0.1         0.01        0.01        0.4         -0.04       0.4
        -0.04       0.06        -0.006      1.1         -0.11
 3 16
CF2HCF2H
 1 22 18 17  4
 6  4  3  5
 1  2  3  4  5  6  7  8  9 10 11 12 13 14 15 16 17
2995.0     1442.0     1149.0     1106.0     625.0     362.0
1330.0     1136.0      212.0       82.0    1365.0    1081.0
 480.0     2995.0     1320.0     1125.0     541.0     414.0
 1  1  1 1.0        1  1 10 0.7727      1  1 11 0.2273      1  1 12 0.6958
 1  1 13 0.3042     1  1 12 0.6958      1  1 13 0.3042      1  1 10 0.7727
 1  1 11 0.2273     1  1 12 0.6958      1  1 13 0.3042      1  1 12 0.6958
 1  1 13 0.3042     1  2 10 0.6611      1  2 11-0.3142      1  3 12 0.6544
 1  3 13-0.3420     1  4 12 0.6544      1  4 13-0.3420      1  5 10 0.6611
 1  5 11-0.3142     1  6 12 0.6544      1  6 13-0.3420      1  7 12 0.6544
 1  7 13-0.3420     1  8 10 0.4191      1  8 11 0.2593      1  9 12 0.4601
 1  9 13 0.3848     1 10 12 0.4601      1 10 13 0.3848      1 11 10 0.4191
 1 11 11 0.2593     1 12 12 0.4601      1 12 13 0.3848      1 13 12 0.4601
 1 13 13 0.3848     2  2  2 1.0         2  2 10 0.5656      2  2 11 0.4344
 2  2 14 0.6142     2  2 15 0.3852      2  2 14 0.6142      2  2 15 0.3852
 2  3 14 0.6763     2  3 15-0.3133      2  4 14 0.6763      2  4 15-0.3133
 2  8 10 0.4957     2  8 11 0.8010      2 14 14 0.4864      2 14 15 0.6584
 2 15 14 0.4864     2 15 15 0.6584      3  3  3 1.0         3  3 12 0.6154
 3  3 13 0.3846     3  3 14 0.7446      3  3 15 0.2548      3  3 16 0.6487
 3  3 17 0.3513     3  4 16 0.6487      3  4 17-0.3513      3  9 12 0.4865
 3  9 13 0.5817     3 14 14 0.4356      3 14 15 0.3218      3 16 16 0.4774
 3 16 17 0.4774     4  4  3 1.0         4  4 12 0.6154      4  4 13 0.3846
 4  4 14 0.7446     4  4 15 0.2548      4  4 16 0.6487      4  4 17 0.3513
 4 10 12 0.4865     4 10 13 0.5817      4 15 14 0.4356      4 15 15 0.3218
 4 16 16 0.4774     4 16 17 0.4774      5  5  2 1.0         5  5 10 0.5656
 5  5 11 0.4344     5  5 14 0.6142      5  5 15 0.3852      5  5 14 0.6142
 5  5 15 0.3852     5  6 14 0.6763      5  6 15-0.3133      5  7 14 0.6763
 5  7 15-0.3133     5 11 10 0.4957      5 11 11 0.8010      5 17 14 0.4864
```

```
5 17 15 0.6584
6 6 12 0.6154
6 6 16 0.6487
6 12 12 0.4865
6 19 16 0.4774
7 7 13 0.3846
7 7 17 0.3513
7 18 15 0.3218
8 8 10 0.2273
8 8 12 0.3042
8 8 14 0.3852
9 9 13-0.5819
9 9 11-0.4782
9 9 15-0.5500
10 10 12 0.3042
10 10 16 0.3513
11 11 4 1.0
11 11 13-0.5819
11 11 15-0.8315
12 12 12 0.3042
12 12 10 0.2273
12 12 16 0.3513
13 13 13-0.5819
13 13 11-0.4782
13 13 17-0.6487
14 14 14 0.3852
14 14 12 0.3846
15 15 6 1.0
15 15 15-0.8315
15 15 11-0.9140
16 16 16 0.3513
16 16 14 0.2548
16 16 12 0.3846
17 17 15-0.8315
17 17 17-0.6487
17 17 11-0.9140
18 18 14 0.3852
18 18 12 0.3846
19 19 7 1.0
19 19 15-0.5500
19 19 13-0.7358
21 21 9 1.0
5 18 14 0.4864
6 6 13 0.3846
6 6 17 0.3513
6 12 13 0.5817
6 19 17 0.4774
7 7 14 0.7446
7 13 12 0.4865
7 19 16 0.4774
8 8 11-0.4782
8 8 13-0.5819
8 8 15-0.8315
9 9 12 0.3042
9 9 16 0.3513
10 10 5 1.0
10 10 13-0.5819
10 10 17-0.6487
11 11 10 0.2273
11 11 12 0.3042
11 11 14 0.3852
12 12 13-0.5819
12 12 11-0.4782
12 12 17-0.6487
13 13 12 0.3042
13 13 14 0.2548
14 14 6 1.0
14 14 15-0.8315
14 14 13-0.7358
15 15 14 0.3852
15 15 16 0.3513
15 15 12 0.3846
16 16 17-0.6487
16 16 15-0.5500
16 16 13-0.7358
17 17 14 0.3852
17 17 12 0.3846
18 18 6 1.0
18 18 15-0.8315
18 18 13-0.7358
19 19 16 0.3513
19 19 14 0.2548
19 19 12 0.3846
22 22 9 1.0
5 18 15 0.6584
6 6 14 0.7446
6 7 16 0.6487
6 17 14 0.4356
7 7 3 1.0
7 7 15 0.2548
7 13 13 0.5817
7 19 17 0.4774
8 8 12 0.3042
8 8 14 0.3852
9 9 5 1.0
9 9 13-0.5819
9 9 17-0.6487
10 10 12 0.3042
10 10 10 0.2273
10 10 14 0.2548
11 11 11-0.4782
11 11 13-0.5819
11 11 15-0.8315
12 12 12 0.3042
12 12 14 0.2548
13 13 5 1.0
13 13 13-0.5819
13 13 15-0.5500
14 14 14 0.3852
14 14 10 0.4344
14 14 16 0.3513
15 15 15-0.8315
15 15 17-0.6487
15 15 13-0.7358
16 16 14 0.2548
16 16 12 0.3846
17 17 6 1.0
17 17 15-0.8315
17 17 13-0.7358
18 18 14 0.3852
18 18 16 0.3513
18 18 10 0.4344
19 19 17-0.6487
19 19 15-0.5500
19 19 13-0.7358
-4
6 6 3 1.0
6 6 15 0.2548
6 7 17-0.3513
6 17 15 0.3218
7 7 12 0.6154
7 7 16 0.6487
7 18 14 0.4356
8 8 4 1.0
8 8 13-0.5819
8 8 15-0.8315
9 9 12 0.3042
9 9 10 0.2273
9 9 14 0.2548
10 10 13-0.5819
10 10 11-0.4782
10 10 13-0.5500
11 11 12 0.3042
11 11 14 0.3852
12 12 5 1.0
12 12 13-0.5819
12 12 15-0.5500
13 13 12 0.3042
13 13 10 0.2273
13 13 16 0.3513
14 14 15-0.8315
14 14 11-0.9140
14 14 17-0.6487
15 15 14 0.3852
15 15 10 0.4344
16 16 7 1.0
16 16 15-0.5500
16 16 13-0.7358
17 17 14 0.3852
17 17 16 0.3513
17 17 10 0.4344
18 18 15-0.8315
18 18 17-0.6487
18 18 11-0.9140
19 19 14 0.2548
19 19 12 0.3846
20 20 8 1.0
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HFC134a

```
 1 1 20 3 18 2 1 1 1 0 0      1 0 0 0 1 0 1 0 0 0
 1,1,1,2-tetrafluoroethane
february 1993
      3.5        4.4        4.6        0.3        0.14       0.1
      0.1        0.43       0.01       0.01       0.4        -0.04
      0.4        -0.04      1.1        -0.11      0.06       -0.006
      0.09       -0.009
 3 5 7
CF3CFH2
 1 22 18 20 2
 11 7
 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20
2984.0    1464.0    1427.0    1298.0    1103.0    972.0
 842.0     665.0     549.0     408.0     225.0    3013.0
```

```
1374.0 1182.0 885.0 539.0 352.0 120.0
1 1 1 1.0
1 1 14 0.2267
1 1 12 0.2797
1 1 12 0.2797
1 3 12-0.3196
1 5 12-0.3304
1 7 14-0.3172
1 9 12 0.3690
1 11 12 0.3994
1 13 14 0.2538
2 2 15 0.6545
2 3 15 0.6545
2 8 11 0.4815
2 15 15 0.4755
3 3 12 0.3650
3 3 16 0.3455
3 9 12 0.5858
3 16 16 0.4755
4 4 15 0.6545
4 10 11 0.4815
4 16 15 0.4755
5 5 12 0.3625
5 5 18 0.2563
5 7 18-0.3268
5 17 18 0.3033
6 6 13 0.5563
6 6 19 0.6611
6 12 13 0.4968
6 19 19 0.4733
7 7 14 0.4437
7 7 20 0.3389
7 18 18 0.7102
8 8 11 0.2797
8 8 11 0.2797
8 8 15 0.3455
9 9 12-0.5920
9 9 12-0.5920
9 9 16-0.6545
10 10 11 0.2797
10 10 15 0.3455
11 11 4 1.0
11 11 14-0.4688
11 11 18-0.5169
12 12 13 0.2267
12 12 11 0.3011
12 12 19 0.3389
13 13 14-0.4688
13 13 12-0.6084
13 13 20-0.6611
14 14 15 0.3455
14 14 11 0.3650
15 15 6 1.0
15 15 16-0.6545
15 15 12-0.7726
16 16 15 0.3455
16 16 15 0.3455
16 16 11 0.3650
1 1 11 0.6989
1 1 13 0.7733
1 1 11 0.7203
1 2 11 0.6763
1 4 11 0.6763
1 6 13 0.6559
1 8 11 0.4489
1 10 11 0.4489
1 12 13 0.4187
2 2 2 1.0
2 2 16 0.3455
2 3 16-0.3455
2 8 12 0.5858
2 15 16 0.4755
3 3 15 0.6545
3 4 15 0.6545
3 14 15 0.4755
4 4 2 1.0
4 4 16 0.3455
4 10 12 0.5858
4 16 16 0.4755
5 5 17 0.7442
5 6 17 0.6591
5 11 11 0.4807
5 18 17 0.4367
6 6 14 0.4437
6 6 20 0.3389
6 12 14 0.8196
6 19 20 0.4733
7 7 17 0.5838
7 13 13 0.4968
7 19 19 0.4733
8 8 12-0.5920
8 8 12-0.5920
8 8 16-0.6545
9 9 11 0.2797
9 9 15 0.3455
10 10 4 1.0
10 10 12-0.5920
10 10 16-0.6545
11 11 11 0.3011
11 11 13 0.2267
11 11 17 0.2563
12 12 14-0.4688
12 12 12-0.6084
12 12 20-0.6611
13 13 13 0.2267
13 13 17 0.4168
14 14 6 1.0
14 14 16-0.6545
14 14 12-0.7726
15 15 15 0.3455
15 15 11 0.3650
15 15 15 0.3455
16 16 16-0.6545
16 16 16-0.6545
16 16 12-0.7726
1 1 12 0.3011
1 1 14 0.2267
1 1 12 0.2797
1 2 12-0.3196
1 4 12-0.3196
1 6 14-0.3172
1 8 12 0.3690
1 10 12 0.3690
1 12 14 0.2538
2 2 11 0.6350
2 2 15 0.6545
2 4 15 0.6545
2 14 15 0.4755
3 3 2 1.0
3 3 16 0.3455
3 4 16-0.3455
3 14 16 0.4755
4 4 11 0.6350
4 4 15 0.6545
4 15 15 0.4755
5 5 2 1.0
5 5 18 0.2563
5 6 18-0.3268
5 11 12 0.5522
5 18 18 0.3033
6 6 17 0.5838
6 7 19 0.6611
6 17 17 0.4932
7 7 3 1.0
7 7 18 0.4168
7 13 14 0.8196
7 19 20 0.4733
8 8 11 0.2797
8 8 15 0.3455
9 9 4 1.0
9 9 12-0.5920
9 9 16-0.6545
10 10 11 0.2797
10 10 11 0.2797
10 10 15 0.3455
11 11 12-0.6084
11 11 14-0.4688
11 11 18-0.5169
12 12 13 0.2267
12 12 17 0.4168
13 13 5 1.0
13 13 14-0.4688
13 13 18-0.8406
14 14 15 0.3455
14 14 11 0.3650
14 14 15 0.3455
15 15 16-0.6545
15 15 12-0.7726
15 15 16-0.6545
16 16 15 0.3455
16 16 11 0.3650
17 17 7 1.0
1 1 13 0.7733
1 1 11 0.7203
1 1 11 0.7203
1 3 11 0.6763
1 5 11 0.6675
1 7 13 0.6559
1 9 11 0.4489
1 11 11 0.4588
1 13 13 0.4187
2 2 12 0.3650
2 2 16 0.3455
2 4 16-0.3455
2 14 16 0.4755
3 3 11 0.6350
3 3 15 0.6545
3 9 11 0.4815
3 16 15 0.4755
4 4 12 0.3650
4 4 16 0.3455
4 15 16 0.4755
5 5 11 0.6375
5 5 17 0.7442
5 7 17 0.6591
5 17 17 0.4367
6 6 3 1.0
6 6 18 0.4168
6 7 20-0.3389
6 17 18 0.7102
7 7 13 0.5563
7 7 19 0.6611
7 18 17 0.4932
8 8 4 1.0
8 8 12-0.5920
8 8 16-0.6545
9 9 11 0.2797
9 9 11 0.2797
9 9 15 0.3455
10 10 12-0.5920
10 10 12-0.5920
10 10 16-0.6545
11 11 13 0.2267
11 11 17 0.2563
12 12 5 1.0
12 12 14-0.4688
12 12 18-0.8406
13 13 13 0.2267
13 13 11 0.3011
13 13 19 0.3389
14 14 16-0.6545
14 14 12-0.7726
14 14 16-0.6545
15 15 15 0.3455
15 15 11 0.3650
16 16 6 1.0
16 16 16-0.6545
16 16 12-0.7726
17 17 17 0.2563
```

```
17 17 18-0.5169     17 17 17 0.2563     17 17 18-0.5169     17 17 19 0.3389
17 17 20-0.6611     17 17 13 0.4737     17 17 14-0.9177     17 17 11 0.3625
17 17 12-0.7323     18 18  7 1.0        18 18 17 0.2563     18 18 18-0.5169
18 18 17 0.2563     18 18 18-0.5169     18 18 19 0.3389     18 18 20-0.6611
18 18 13 0.4437     18 18 14-0.9177     18 18 11 0.3625     18 18 12-0.7323
19 19  8 1.0        19 19 19 0.3389     19 19 20-0.6611     19 19 17 0.4168
19 19 18-0.8406     19 19 17 0.4168     19 19 18-0.8406     19 19 13 0.4437
19 19 14-0.9177     19 19 13 0.4437     19 19 14-0.9177     20 20  9 1.0
21 21 10 1.0        22 22 10 1.0        -4
```

HFC125

```
  1  1 17  1 18  2 1 1 1 0 0        1  0  0  0  1  0  1  0  0  0
 pentafluoroethane
february 1993
        3.5          4.4          4.6          0.3          0.14         0.1
        0.1          0.01         0.01         0.4          -0.04        0.4
        -0.04        1.1          -0.11        0.06         -0.006
 1
cf2hcf3
 1 22 18 17  2
 11  7
 1  2  3  4  5  6  7  8  9 10 11 12 13 14 15 16 17
3008.0     1393.0     1309.0     1218.0     1111.0      867.0
 725.0      577.0      523.0      361.0      246.0     1359.0
1198.0     1145.0      508.0      413.0      216.0       82.0
 1  1  1 1.0        1  1 12 0.7709      1  1 13 0.2291      1  1 10 0.7076
 1  1 11 0.2924     1  1 10 0.7076      1  1 11 0.2924      1  1 10 0.7186
 1  1 11 0.2815     1  1 10 0.7186      1  1 11 0.2815      1  1 10 0.7186
 1  1 11 0.2815     1  2 10 0.6756      1  2 11-0.3205      1  3 10 0.6756
 1  3 11-0.3205     1  4 10 0.6756      1  4 11-0.3205      1  5 12 0.6585
 1  5 13-0.3165     1  6 10 0.6659      1  6 11-0.3304      1  7 10 0.6659
 1  7 11-0.3304     1  8 10 0.4497      1  8 11 0.3713      1  9 10 0.4497
 1  9 11 0.3713     1 10 10 0.4497      1 10 11 0.3713      1 11 12 0.4202
 1 11 13 0.2598     1 12 10 0.4549      1 12 11 0.3787      1 13 10 0.4549
 1 13 11 0.3787     2  2  2 1.0         2  2 10 0.6351      2  2 11 0.3649
 2  2 14 0.6554     2  2 15 0.3447      2  2 14 0.6554      2  2 15 0.3447
 2  3 14 0.6554     2  3 15-0.3447      2  4 14 0.6554      2  4 15-0.3447
 2  8 10 0.4814     2  8 11 0.5830      2 14 14 0.4753      2 14 15 0.4753
 2 15 14 0.4753     2 15 15 0.4753      3  3  2 1.0         3  3 10 0.6351
 3  3 11 0.3649     3  3 14 0.6554      3  3 15 0.3447      3  3 14 0.6554
 3  3 15 0.3447     3  4 14 0.6554      3  4 15-0.3447      3  9 10 0.4814
 3  9 11 0.5830     3 14 14 0.4753      3 14 15 0.4753      3 16 14 0.4753
 3 16 15 0.4753     4  4  2 1.0         4  4 10 0.6351      4  4 11 0.3649
 4  4 14 0.6554     4  4 15 0.3447      4  4 14 0.6554      4  4 15 0.3447
 4 10 10 0.4814     4 10 11 0.5830      4 15 14 0.4753      4 15 15 0.4753
 4 16 14 0.4753     4 16 15 0.4753      5  5  3 1.0         5  5 12 0.5626
 5  5 13 0.4374     5  5 16 0.5971      5  5 17 0.4033      5  5 16 0.5917
 5  5 17 0.4033     5  6 16 0.6605      5  6 17-0.3298      5  7 16 0.6605
 5  7 17-0.3298     5 11 12 0.4960      5 11 13 0.8024      5 17 16 0.4907
 5 17 17 0.6637     5 18 16 0.4907      5 18 17 0.6637      6  6  2 1.0
 6  6 10 0.6266     6  6 11 0.3734      6  6 14 0.6636      6  6 15 0.3364
 6  6 16 0.7306     6  6 17 0.2698      6  7 14 0.6636      6  7 15-0.3364
 6 12 10 0.4837     6 12 11 0.5809      6 17 16 0.4439      6 17 17 0.3282
 6 19 14 0.4724     6 19 15 0.4724      7  7  2 1.0         7  7 10 0.6266
 7  7 11 0.3734     7  7 16 0.7306      7  7 17 0.2698      7  7 14 0.6636
 7  7 15 0.3364     7 13 10 0.4837      7 13 11 0.5809      7 18 16 0.4439
 7 18 17 0.3282     7 19 14 0.4724      7 19 15 0.4724      8  8  4 1.0
 8  8 10 0.2815     8  8 11-0.5933      8  8 10 0.2815      8  8 11-0.5933
```

```
 8  8 10 0.2815
 8  8 14 0.3447
 9  9 11-0.5933
 9  9 11-0.5933
 9  9 15-0.6554
10 10 10 0.2815
10 10 14 0.3447
11 11  5 1.0
11 11 11-0.5892
11 11 17-0.8076
12 12 10 0.2924
12 12 12 0.2291
12 12 14 0.3364
13 13 11-0.5892
13 13 13-0.4766
13 13 15-0.6636
14 14 14 0.3447
14 14 10 0.3649
15 15  6 1.0
15 15 15-0.6554
15 15 11-0.7692
16 16 14 0.3447
16 16 14 0.3447
16 16 10 0.3649
17 17 17-0.8076
17 17 15-0.6636
17 17 13-0.9100
18 18 14 0.3364
18 18 12 0.4374
19 19  6 1.0
19 19 17-0.5402
19 19 11-0.7525
21 21  9 1.0
 8  8 11-0.5933
 8  8 15-0.6554
 9  9 10 0.2815
 9  9 14 0.3447
10 10  4 1.0
10 10 11-0.5933
10 10 15-0.6554
11 11 12 0.2291
11 11 10 0.2924
11 11 16 0.4033
12 12 11-0.5892
12 12 13-0.4766
12 12 15-0.6636
13 13 10 0.2924
13 13 16 0.2698
14 14  6 1.0
14 14 15-0.6554
14 14 11-0.7692
15 15 14 0.3447
15 15 14 0.3447
15 15 10 0.3649
16 16 15-0.6554
16 16 15-0.6554
16 16 11-0.7692
17 17 16 0.4033
17 17 10 0.3734
18 18  7 1.0
18 18 15-0.6636
18 18 13-0.9100
19 19 14 0.3364
19 19 16 0.2698
19 19 10 0.3734
22 22  9 1.0
 8  8 14 0.3447
 9  9  4 1.0
 9  9 11-0.5933
 9  9 15-0.6554
10 10 10 0.2815
10 10 10 0.2815
10 10 14 0.3447
11 11 13-0.4766
11 11 11-0.5892
11 11 17-0.8076
12 12 10 0.2924
12 12 16 0.2698
13 13  4 1.0
13 13 11-0.5892
13 13 17-0.5402
14 14 14 0.3447
14 14 14 0.3447
14 14 10 0.3649
15 15 15-0.6554
15 15 15-0.6554
15 15 11-0.7692
16 16 14 0.3447
16 16 10 0.3649
17 17  7 1.0
17 17 17-0.8076
17 17 11-0.7525
18 18 16 0.4033
18 18 10 0.3734
18 18 16 0.4033
19 19 15-0.6636
19 19 17-0.5402
19 19 11-0.7525
-4
 8  8 15-0.6554
 9  9 10 0.2815
 9  9 10 0.2815
 9  9 14 0.3447
10 10 11-0.5933
10 10 11-0.5933
10 10 15-0.6554
11 11 10 0.2924
11 11 16 0.4033
12 12  4 1.0
12 12 11-0.5892
12 12 17-0.5402
13 13 10 0.2924
13 13 12 0.2291
13 13 14 0.3364
14 14 15-0.6554
14 14 15-0.6554
14 14 11-0.7692
15 15 14 0.3447
15 15 10 0.3649
16 16  6 1.0
16 16 15-0.6554
16 16 11-0.7692
17 17 16 0.4033
17 17 14 0.3364
17 17 12 0.4374
18 18 17-0.8076
18 18 11-0.7525
18 18 17-0.8076
19 19 16 0.2698
19 19 10 0.3734
20 20  8 1.0
```

Appendix C

Data input for the *ab initio* calculations.

CFC110

```
%chk=cfc110
# rhf/6-31G*  Opt test

cfc110 optimisation

0 1
C
C2  C   cc
Cl  C   clc  C2   clcc
Cl2 C   clc  C2   clcc Cl   120.0
Cl3 C   clc  C2   clcc Cl   -120.0
Cl4 C2  clc  C    clcc Cl   60.0
Cl5 C2  clc  C    clcc Cl   -60.0
Cl6 C2  clc  C    clcc Cl   180.0

cc=1.499
clc=1.763
clcc=110.7

--Link1--
%chk=cfc110
# rhf/6-31G* freq geom=checkpoint test

cfc110 hf/6-31G* freq vib110

0 1
```

CFC111

```
%chk=cfc111
# rhf/6-31G*  Opt test

cfc111 optimisation

0 1
C
C2  C   cc
Cl  C   clc   C2  clcc
Cl2 C   clc   C2  clcc    Cl          dcl
Cl3 C   clc   C2  clcc    Cl          -dcl
F   C2  fc    C   fcc     Cl          df1
Cl4 C2  clc2  C   clcc2   F  -dcl1
Cl5 C2  clc2  C   clcc2   F  dcl1

cc=1.54
clc=1.77
clc2=1.70
fc=1.37
clcc=109.40
fcc=109.45
```

```
clcc2=109.50
dcl1=120.5

dcl=120.0
df1=60.0

--Link1--
%chk=cfc111
# rhf/6-31G* freq geom=checkpoint test

cfc111 hf/6-31G* freq vib111

0 1
```

CFC112

```
%chk=cfc112
# rhf/6-31G*  Opt test

cfc112 optimisation

0 1
C
C2  C   cc
F   C   fc    C2  fcc
Cl  C   clc   C2  clcc   F  df
Cl2 C   clc   C2  clcc   F  -df
F2  C2  fc    C   fcc    F  df1
Cl3 C2  clc   C   clcc   F  -dcl
Cl4 C2  clc   C   clcc   F  dcl

cc=1.54
clc=1.77
fc=1.37
clcc=109.40
fcc=109.50

df=120.0
df1=180.0
dcl=60.0

--Link1--
%chk=cfc112
# rhf/6-31G* freq geom=checkpoint test

cfc112 hf/6-31G* freq vib112

0 1
```

CFC112a

```
%chk=cfc112a
# rhf/6-31G*  Opt test

cfc112a optimisation

0 1
C
```

```
C2  C   cc
Cl  C   clc   C2  clcc
Cl2 C   clc   C2  clcc   Cl   dcl
Cl3 C   clc   C2  clcc   Cl   -dcl
Cl4 C2  clc2  C   clcc2  Cl   dcl1
F   C2  fc    C   fcc    Cl4  -df
F2  C2  fc    C   fcc    Cl4  df

cc=1.55
clc=1.76
clc2=1.74
fc=1.33
clcc=110.7
clcc2=110.6
fcc=108.0
df=121.7

dcl=120.0
dcl1=60.0

--Link1--
%chk=cfc112a
# rhf/6-31G* freq geom=checkpoint test

cfc112a hf/6-31G* freq vib112a

0 1
```

CFC113

```
%chk=cfc113
# rhf/6-31G*  Opt test

cfc113 optimisation

0 1
C
C2  C   cc
Cl  C   clc   C2  clcc
Cl2 C   clc   C2  clcc   Cl   dcl
F   C   fc    C2  fcc    Cl   df
F2  C2  fc2   C   fcc2   F    df1
F3  C2  fc2   C   fcc2   F    df2
Cl3 C2  clc2  C   clcc2  F    dcl1

cc=1.54
clc=1.75
clc2=1.74
fc=1.37
fc2=1.35
clcc=109.4
clcc2=109.55
fcc=109.45
fcc2=109.5
df=-120.04
df2=59.98
dcl=120.02
dcl1=-60.03
```

```
df1=180.0

--Link1--
%chk=cfc113
# rhf/6-31G* freq geom=checkpoint test

cfc113 hf/6-31G* freq vib113

0 1
```

CFC113a

```
%chk=cfc113a
# rhf/6-31G*  Opt test

cfc113a optimisation

0 1
C
C2  C   cc
F   C   fc    C2  fcc
F2  C   fc    C2  fcc    F     120.0
F3  C   fc    C2  fcc    F     -120.0
Cl  C2  clc   C   clcc   F     60.0
Cl2 C2  clc   C   clcc   F     -60.0
Cl3 C2  clc   C   clcc   F     180.0

cc=1.545
clc=1.771
fc=1.33
clcc=110.7
fcc=108.9

--Link1--
%chk=cfc113a
# rhf/6-31G* freq geom=checkpoint test

cfc113a hf/6-31G* freq vib113a

0 1
```

CFC114

```
%chk=cfc114
# rhf/6-31G*  Opt test

cfc114 optimisation

0 1
C
C2  C   cc
Cl  C   clc   C2  clcc
F   C   fc    C2  fcc    Cl    df
F2  C   fc    C2  fcc    Cl    -df
F3  C2  fc    C   fcc    Cl    -df1
F4  C2  fc    C   fcc    Cl    df1
Cl2 C2  clc   C   clcc   Cl    dcl
```

```
cc=1.55
clc=1.74
fc=1.33
clcc=110.6
fcc=108.0

df=-121.7
df1=58.3
dcl=180.0

--Link1--
%chk=cfc114
# rhf/6-31G* freq geom=checkpoint test

cfc114 hf/6-31G* freq vib114

0 1
```

CFC114a

```
%chk=cfc114a
# rhf/6-31G*  Opt test

cfc114a optimisation

0 1
C
C2  C   cc
F   C   fc    C2  fcc
F2  C   fc    C2  fcc    F    df
F3  C   fc    C2  fcc    F    -df
F4  C2  fc2   C   fcc2   F    df1
Cl  C2  clc   C   clcc   F4   -df2
Cl2 C2  clc   C   clcc   F4   df2

cc=1.56
clc=1.78
fc=1.33
fc2=1.40
clcc=109.4
fcc=109.45
fcc2=109.5
df2=120.1

df1=60.0
df=120.0

--Link1--
%chk=cfc114a
# rhf/6-31G* freq geom=checkpoint test

cfc114a hf/6-31G* freq vib114a

0 1
```

CFC115

```
%chk=cfc115
# rhf/6-31G*  Opt test

cfc115 optimisation

0 1
C
C2  C   cc
F   C   fc   C2  fcc
F2  C   fc   C2  fcc   F   df
F3  C   fc   C2  fcc   F   -df
Cl  C2  clc  C   clcc  F   dcl
F4  C2  fc2  C   fcc2  Cl  -df1
F5  C2  fc2  C   fcc2  Cl  df1

cc=1.555
clc=1.74
fc=1.33
fc2=1.34
clcc=110.6
fcc=110.9
fcc2=108.0
df1=121.7

df=-120.0
dcl=60.0

--Link1--
%chk=cfc115
# rhf/6-31G* freq geom=checkpoint test

cfc115 hf/6-31G* freq vib115

0 1
```

FC116

```
%chk=cfc116
# rhf/6-31G*  Opt test

fc116 optimisation

0 1
C
C2  C   cc
F   C   fc   C2  fcc
F2  C   fc   C2  fcc   F   120.0
F3  C   fc   C2  fcc   F   -120.0
F4  C2  fc   C   fcc   F   60.0
F5  C2  fc   C   fcc   F   -60.0
F6  C2  fc   C   fcc   F   180.0

cc=1.545
fc=1.326
fcc=109.8

--Link1--
```

```
%chk=cfc116
# rhf/6-31G* freq geom=checkpoint test

fc116 hf/6-31G* freq vib116

0 1
```

HFC170

```
%chk=hfc170
# rhf/6-31G*  Opt test

hfc170 optimisation

0 1
C
C2  C   cc
H   C   hc   C2   hcc
H2  C   hc   C2   hcc  Cl   120.0
H3  C   hc   C2   hcc  Cl   -120.0
H4  C2  hc   C    hcc  Cl   60.0
H5  C2  hc   C    hcc  Cl   -60.0
H6  C2  hc   C    hcc  Cl   180.0

cc=1.5324
hc=1.1068
hcc=111.0

--Link1--
%chk=hfc170
# rhf/6-31G* freq geom=checkpoint test

hfc170 hf/6-31G* freq vib170

0 1
```

HFC161

```
%chk=hfc161
# rhf/6-31G*  Opt test

hfc161 optimisation

0 1
C
C2  C   cc
H   C   hc   C2  hcc
H2  C   hc   C2  hcc    H  dh
H3  C   hc   C2  hcc    H  -dh
F   C2  fc   C   fcc    H  df1
H4  C2  hc2  C   hcc2   H  -dh1
H5  C2  hc2  C   hcc2   H  dh2

cc=1.505
hc=1.090
hc2=1.095
fc=1.398
hcc=109.65
```

```
fcc=109.75
hcc2=112.9
dh1=-58.0
dh2=178.0

dh=120.0
df1=60.0

--Link1--
%chk=hfc161
# rhf/6-31G* freq geom=checkpoint test

hfc161 hf/6-31G* freq vib161

0 1
```

HFC152

```
%chk=hfc152
# rhf/6-31G*  Opt test

hfc152 optimisation

0 1
C
C2  C   cc
F   C   fc    C2  fcc
H   C   hc    C2  hcc    F  df
H2  C   hc    C2  hcc    F  -df
F2  C2  fc    C   fcc    F  df1
H3  C2  hc    C   hcc    F  -dh
H4  C2  hc    C   hcc    F  dh

cc=1.5033
hc=1.1034
fc=1.3892
hcc=111.0
fcc=110.3

df=119.6
df1=180.0
dh=60.4

--Link1--
%chk=hfc152
# rhf/6-31G* freq geom=checkpoint test

hfc152 hf/6-31G* freq vib152

0 1
```

HFC152a

```
%chk=hfc152a
# rhf/6-31G*  Opt test

hfc152a optimisation
```

```
0 1
C
C2  C   cc
H   C   hc    C2  hcc
H2  C   hc    C2  hcc   H    dh
H3  C   hc    C2  hcc   H    -dh
H4  C2  hc2   C   hcc2  H    dh1
F   C2  fc    C   fcc   H4   -df
F2  C2  fc    C   fcc   H4   df

cc=1.54
hc=1.10
hc2=1.09
fc=1.345
hcc=108.7
hcc2=109.8
fcc=109.4
df=120.3

dh=120.0
dh1=60.0

--Link1--
%chk=hfc152a
# rhf/6-31G* freq geom=checkpoint test

hfc152a hf/6-31G* freq vib152a

0 1
```

HFC143

```
%chk=hfc143
# rhf/6-31G*  Opt test

hfc143 optimisation

0 1
C
C2  C   cc
H   C   hc    C2  hcc
H2  C   hc    C2  hcc   H    dh
F   C   fc    C2  fcc   H    df
F2  C2  fc2   C   fcc2  F    df1
F3  C2  fc2   C   fcc2  F    df2
H3  C2  hc2   C   hcc2  F    dh1

cc=1.50
hc=1.0881
hc2=1.09
fc=1.3878
fc2=1.3534
hcc=108.9
hcc2=108.8
fcc=109.1
fcc2=109.2
df=-113.15
```

```
df2=63.5
dh=133.7
dh1=-58.2

df1=180.0

--Link1--
%chk=hfc143
# rhf/6-31G* freq geom=checkpoint test

hfc143 hf/6-31G* freq vib143

0 1
```

HFC143a

```
%chk=hfc143a
# rhf/6-31G*  Opt test

hfc143a optimisation

0 1
C
C2  C   cc
F   C   fc   C2  fcc
F2  C   fc   C2  fcc   F    120.0
F3  C   fc   C2  fcc   F    -120.0
H   C2  hc   C   hcc   F    60.0
H2  C2  hc   C   hcc   F    -60.0
H3  C2  hc   C   hcc   F    180.0

cc=1.530
hc=1.085
fc=1.335
hcc=108.3
fcc=111.0

--Link1--
%chk=hfc143a
# rhf/6-31G* freq geom=checkpoint test

hfc143a hf/6-31G* freq vib143a

0 1
```

HFC134

```
%chk=hfc134
# rhf/6-31G*  Opt test

hfc134 optimisation

0 1
C
C2  C   cc
H   C   hc   C2  hcc
F   C   fc   C2  fcc   Cl   df
F2  C   fc   C2  fcc   Cl   -df
```

```
F3  C2  fc   C   fcc   Cl   -df1
F4  C2  fc   C   fcc   Cl   df1
H2  C2  hc   C   hcc   Cl   dh

cc=1.518
hc=1.098
fc=1.35
hcc=110.3
fcc=108.2

df=-122.0
df1=58.0
dh=180.0

--Link1--
%chk=hfc134
# rhf/6-31G* freq geom=checkpoint test

hfc134 hf/6-31G* freq vib134


0 1
```

HFC134a

```
%chk=hfc134a
# rhf/6-31G*  Opt test

hfc134a optimisation

0 1
C
C2  C   cc
F   C   fc    C2  fcc
F2  C   fc    C2  fcc   F    df
F3  C   fc    C2  fcc   F    -df
F4  C2  fc2   C   fcc2  F    df1
H   C2  hc    C   hcc   F4   -df2
H2  C2  hc    C   hcc   F4   df2

cc=1.525
hc=1.09
fc=1.335
fc2=1.39
hcc=109.8
fcc=110.9
fcc2=109.7
df2=120.2

df1=60.0
df=120.0

--Link1--
%chk=hfc134a
# rhf/6-31G* freq geom=checkpoint test

hfc134a hf/6-31G* freq vib134a

0 1
```

HFC125

```
%chk=hfc125
# rhf/6-31G*  Opt test

hfc125 optimisation

0 1
C
C2  C   cc
F   C   fc   C2  fcc
F2  C   fc   C2  fcc   F    df
F3  C   fc   C2  fcc   F    -df
H   C2  hc   C   hcc   F    dh
F4  C2  fc2  C   fcc2  H    -df2
F5  C2  fc2  C   fcc2  H    df2

cc=1.52
hc=1.10
fc=1.335
fc2=1.345
hcc=110.0
fcc=110.8
fcc2=109.6
df2=120.2

df=-120.0
dcl=60.0

--Link1--
%chk=hfc125
# rhf/6-31G* freq geom=checkpoint test

hfc125 hf/6-31G* freq vib125

0 1
```

HFC170 (MP2 version).

```
%chk=hfc170
# mp2=fulldirect/6-31G*  Opt test

hfc170 optimisation

0 1
C
C2  C   cc
H   C   hc   C2   hcc
H2  C   hc   C2   hcc  Cl  120.0
H3  C   hc   C2   hcc  Cl  -120.0
H4  C2  hc   C    hcc  Cl  60.0
H5  C2  hc   C    hcc  Cl  -60.0
H6  C2  hc   C    hcc  Cl  180.0

cc=1.5324
hc=1.1068
```

```
hcc=111.0

--Link1--
%chk=hfc170
# mp2=fulldirect/6-31G* freq geom=checkpoint guess=checkpoint scf=direct test

hfc170 mp2/6-31G* freq vib170

0 1
```

HFC161

```
%chk=hfc161
# mp2=fulldirect/6-31G*  Opt test

hfc161 optimisation

0 1
C
C2  C   cc
H   C   hc    C2  hcc
H2  C   hc    C2  hcc    H  dh
H3  C   hc    C2  hcc    H  -dh
F   C2  fc    C   fcc    H  df1
H4  C2  hc2   C   hcc2   H  -dh1
H5  C2  hc2   C   hcc2   H  dh2

cc=1.505
hc=1.090
hc2=1.095
fc=1.398
hcc=109.65
fcc=109.75
hcc2=112.9
dh1=-58.0
dh2=178.0

dh=120.0
df1=60.0

--Link1--
%chk=hfc161
# mp2=fulldirect/6-31G* freq geom=checkpoint guess=checkpoint scf=direct test

hfc161 mp2/6-31G* freq vib161

0 1
```

HFC152

```
%chk=hfc152
# mp2=fulldirect/6-31G*  Opt test

hfc152 optimisation

0 1
C
```

```
C2  C   cc
F   C   fc    C2  fcc
H   C   hc    C2  hcc    F  df
H2  C   hc    C2  hcc    F  -df
F2  C2  fc    C   fcc    F  df1
H3  C2  hc    C   hcc    F  -dh
H4  C2  hc    C   hcc    F  dh

cc=1.5033
hc=1.1034
fc=1.3892
hcc=111.0
fcc=110.3

df=119.6
df1=180.0
dh=60.4

--Link1--
%chk=hfc152
# mp2=fulldirect/6-31G* freq geom=checkpoint guess=checkpoint scf=direct test

hfc152 mp2/6-31G* freq vib152

0 1
```

HFC152a

```
%chk=hfc152a
# mp2=fulldirect/6-31G*  Opt test

hfc152a optimisation

0 1
C
C2  C   cc
H   C   hc    C2  hcc
H2  C   hc    C2  hcc    H    dh
H3  C   hc    C2  hcc    H    -dh
H4  C2  hc2   C   hcc2   H    dh1
F   C2  fc    C   fcc    H4   -df
F2  C2  fc    C   fcc    H4   df

cc=1.54
hc=1.10
hc2=1.09
fc=1.345
hcc=108.7
hcc2=109.8
fcc=109.4
df=120.3

dh=120.0
dh1=60.0

--Link1--
%chk=hfc152a
```

```
# mp2=fulldirect/6-31G* freq geom=checkpoint guess=checkpoint scf=direct test

hfc152a mp2/6-31G* freq vib152a

0 1
```

Appendix D

Listing of the fortran program CALST.

```
        DIMENSION S(9,12),T(9,12),R(7),ALP(12),Q(12),MOLNAM(10)
        WRITE(9,999)
999     FORMAT(' ENTER NAME OF COMPOUND')
        READ(9,998)MOLNAM
998     FORMAT(10A2)
C
C    7 bonds lengths are entered interactively in the atom number sequence used by
C    OVER and NORCORD
C
        WRITE(9,99)
99      FORMAT('ENTER BOND LENGTHS')
        WRITE(9,990)
990     FORMAT(' X.XXXX X.XXXX X.XXXX X.XXXX X.XXXX X.XXXX
X.XXXX')
        READ(9,98)R
98      FORMAT(7F7.4)
C
C    12 angles are entered, 6 for the CCX angles and 6 for the XCX angles.
C
        WRITE(9,97)
97      FORMAT('ENTER ANGLES',/,' XXX.X XXX.X XXX.X XXX.X
XXX.X  XXX.X')
        READ(9,96) ALP
96      FORMAT(6F6.1)
C
C    12 non-bonded distances are entered, 6 for the C...X distances
C     and 6 for the X...X distances
C
        WRITE(9,95)
95      FORMAT(' ENTER NON-BONDED DISTANCES')
        WRITE(9,950)
950     FORMAT(' X.XXXX X.XXXX X.XXXX X.XXXX X.XXXX
X.XXXX')
        READ(9,94)Q
94      FORMAT(6F7.4)
C
C    check input
C
        WRITE(9,89)R
89      FORMAT(7(F6.4,2X))
        WRITE(9,88)ALP
88      FORMAT(6(F5.1,2X))
        WRITE(9,87)Q
87      FORMAT(6(F6.4,2X))
C
C    clear s and t arrays
C
        DO 25 J=1,9
        DO 25 K=1,12
        S(J,K)=0
        T(J,K)=0
```

```
25      CONTINUE
C
C     calculate s and t values for each atom combination
C
C
C     initiate pointers for atoms 1 and 2
C
        I=1
        J=2
        DO 100 K=1,12
        CALL SANDT(S(1,K),T(1,K),R(I),R(J),ALP(K),Q(K))
        J=J+1
        KK=K-5
        IF(KK) 100,100,5
5       GOTO  (10,20,30,40,50,60),KK
C
C     reset pointers to next atoms for the calculations.
C
10      I=2
        J=3
        GOTO 100
20      I=2
        J=4
        GOTO 100
30      I=3
        J=4
        GOTO 100
40      I=5
        J=6
        GO TO 100
50      I=5
        J=7
        GO TO 100
60      I=6
        J=7
100     CONTINUE
C
C      output results
C
        WRITE(6,305)MOLNAM
305     FORMAT(' COMPOUND:',10A2)
        WRITE(6,310)R
310     FORMAT(' BOND LENGTHS:',7(F6.4,1X))
        WRITE(6,320)ALP
320     FORMAT(' ANGLES:',12(F5.1,1X))
        WRITE(6,330)Q
330     FORMAT(' Qs:',12(F6.4,1X),/)
C
C     output 6 columns of data for combinations of each X with each C.
C
        WRITE(6,200)
200     FORMAT(1H ,12X,'S/T12    S/T13    S/T14    S/T15    S/T16
       1S/T17')
        M=1
        N=6
        DO 300 II=1,2
        WRITE(6,210)(S(1,I),I=M,N),(T(1,I),I=M,N)
210     FORMAT(' S(IJ)     ',6(F7.4,3X),/,' T(IJ)     ',6(F7.4,3X))
```

```
      WRITE(6,220)(S(2,I),I=M,N),(T(2,I),I=M,N)
220   FORMAT(' S(JI)     ',6(F7.4,3X),/,' T(JI)     ',6(F7.4,3X))
      WRITE(6,225)
225   FORMAT(1H ,/,' I/J STRETCH')
      WRITE(6,230)(S(3,I),I=M,N),(T(3,I),I=M,N)
230   FORMAT(' S(IJ)**2  ',6(F7.4,3X),/,' T(IJ)**2  ',6(F7.4,3X))
      WRITE(6,235)
235   FORMAT(1H ,/,' J/I STRETCH')
      WRITE(6,240)(S(4,I),I=M,N),(T(4,I),I=M,N)
240   FORMAT(' S(JI)**2  ',6(F7.4,3X),/,' T(JI)**2  ',6(F7.4,3X))
      WRITE(6,245)
245   FORMAT(1H ,/,' OFF-DIAGONAL STRETCH')
      WRITE(6,250)(S(5,I),I=M,N),(T(5,I),I=M,N)
250   FORMAT(' S(IJ)S(JI)',6(F7.4,3X),/,' S(IJ)S(JI)',6(F7.4,3X))
      WRITE(6,255)
255   FORMAT(1H ,/,' I/J STRETCH-BEND')
      WRITE(6,260)(S(6,I),I=M,N),(T(6,I),I=M,N)
260   FORMAT('           ',6(F7.4,3X),/,11X,6(F7.4,3X))
      WRITE(6,265)
265   FORMAT(1H ,/,' J/I STRETCH-BEND')
      WRITE(6,270)(S(7,I),I=M,N),(T(7,I),I=M,N)
270   FORMAT('           ',6(F7.4,3X),/,11X,6(F7.4,3X))
      WRITE(6,275)
275   FORMAT(1H ,/,' I/J BEND-BEND')
      WRITE(6,280)(S(8,I),I=M,N),(T(8,I),I=M,N)
280   FORMAT('           ',6(F7.4,3X),/,11X,6(F7.4,3X))
      WRITE(6,285)
285   FORMAT(1H ,/,' J/I BEND-BEND')
      WRITE(6,290)(S(9,I),I=M,N),(T(9,I),I=M,N)
290   FORMAT('           ',6(F7.4,3X),/,11X,6(F7.4,3X))
      M=7
      N=12
      IF(II=2) GO TO 300
C
C   output 6 columns of data for each combination of each pair of X's
C
      WRITE(6,205)
205   FORMAT(1H ,/,/,1H ,12X,'S/T23    S/T24    S/T34    S/T56
     1S/T57    S/T67',/)
300   CONTINUE
      PAUSE
      END
C
C   subroutine to calculate appropriate s and t.
C
      SUBROUTINE SANDT(SS,TS,R1,R2,A,Q)
      DIMENSION SS(9),TS(9)
C
C   convert degrees to radians
C
      AR=A*0.017453292
C
C   calculate s and t as defined by Overend and Scherer 1960)
C
      SS(1)=(R1-(R2*COS(AR)))/Q
      TS(1)=(R2*SIN(AR))/Q
      SS(2)=(R2-(R1*COS(AR)))/Q
      TS(2)=(R1*SIN(AR))/Q
```

```
C
C     s and t squared
C
          SS(3)=SS(1)*SS(1)
          TS(3)=TS(1)*TS(1)
          SS(4)=SS(2)*SS(2)
          TS(4)=TS(2)*TS(2)
C
C     adjacent bonds stretch-stretch interaction
C
          SS(5)=SS(1)*SS(2)
          TS(5)=-TS(1)*TS(2)
C
C     adjacent stretch and bend interactions
C
          TEMP1=(TS(1)*TS(2))**0.5
          TEMP2=(R2/R1)**0.5
          SS(6)=SS(1)*TEMP1*TEMP2
          TS(6)=TS(1)*SS(2)*(R2/R1)
          TEMP2=(R1/R2)**0.5
          SS(7)=SS(2)*TEMP1*TEMP2
          TS(7)=TS(2)*SS(1)*(R1/R2)
C
C     adjacent angles interactions
C
          SS(8)=TS(1)*TS(2)*(R2/R1)
          TS(8)=-SS(1)*SS(2)*(R2/R1)
          SS(9)=TS(2)*TS(1)*(R1/R2)
          TS(9)=-SS(2)*SS(1)*(R1/R2)

          RETURN
          END
```

Appendix E

Potential energy matrices from the UB calculations.

Potential energy distribution for the molecule for each force constant (rows) for each fundamental frequency in symmetry group sequence (columns).

CFC110

C-C	0.426310	0.015825	0.133826	0.000000	0.000000	0.000000
0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
0.000000	0.000000	0.000000	0.000000	0.000000		
C-Cl	0.099454	0.368563	0.002629	0.000000	0.245182	0.204157
0.332039	0.332254	0.339536	0.339282	0.075413	0.075439	0.602008
0.602014	0.138945	0.138943	0.002693	0.002682		
CCCl	0.031763	0.002989	0.055328	0.000000	0.052154	0.035526
0.104487	0.104542	0.019669	0.019677	0.067815	0.067959	0.002441
0.002441	0.001090	0.001089	0.182259	0.182454		
ClCCl	0.055410	0.005215	0.096523	0.000000	0.090983	0.061974
0.045676	0.045702	0.074687	0.074791	0.159958	0.159829	0.078414
0.078423	0.172151	0.172152	0.000583	0.000584		
Cl~Cl	0.000000	0.000000	0.000000	1.000000	0.000000	0.000000
0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.041294
0.041300	0.065283	0.065285	0.028072	0.028102		
Cl...Cl	0.149362	0.499322	0.250673	0.000000	0.293116	0.585618
0.275272	0.274839	0.390136	0.390189	0.339933	0.339635	0.134433
0.134444	0.462169	0.462163	0.353470	0.352822		
	0.042655	-0.004156	0.056076	0.000000	0.074454	0.016278
0.050531	0.050557	0.005243	0.005288	0.085241	0.085249	0.018953
0.018957	0.040140	0.040141	0.069082	0.069157		
Cl...C	0.192595	0.108526	0.398245	0.000000	0.223980	0.076137
0.147232	0.147310	0.162199	0.162218	0.236535	0.236751	0.115748
0.115753	0.102656	0.102658	0.304863	0.305157		
	0.002450	0.003716	0.006700	0.000000	0.020130	0.020311
0.044763	0.044796	0.008529	0.008555	0.035105	0.035138	0.006709
0.006667	0.017566	0.017570	0.058977	0.059043		

CFC111

C-C	0.020943	0.410376	0.022949	0.000568	0.012664	0.009027
0.000059	0.003298	0.036419	0.076303	0.034977	0.000000	0.000000
0.000000	0.000000	0.000000	0.000000	0.000000		
C-Cl	0.077877	0.114492	0.378708	0.285875	0.257813	0.227732
0.284850	0.128643	0.002035	0.025691	0.004903	0.331160	0.557915
0.269231	0.260320	0.150594	0.002222	0.000502		
C-F	0.504399	0.003675	0.173775	0.002869	0.136261	0.014689
0.033690	0.002809	0.000830	0.001108	0.000001	0.000000	0.000000
0.000000	0.000000	0.000000	0.000000	0.000000		
CCCl	0.051048	0.022607	0.024629	0.038628	0.019245	0.024660
0.021550	0.004522	0.026377	0.078288	0.149887	0.109476	0.004234
0.003360	0.014967	0.098386	0.221837	0.000444		
CCF	0.023074	0.031736	0.007165	0.026267	0.000032	0.007095
0.049319	0.000992	0.050415	0.013726	0.033837	0.000000	0.000000
0.000000	0.000000	0.000000	0.000000	0.000000		
ClCCl	0.017434	0.040668	0.059958	0.076235	0.007212	0.027667
0.043866	0.179954	0.159088	0.126901	0.019923	0.019583	0.047023
0.000104	0.123944	0.094958	0.000017	0.000876		
ClCF	0.020447	0.021190	0.003321	0.029010	0.048419	0.038495
0.003552	0.015400	0.051276	0.000847	0.014684	0.055914	0.066214
0.196865	0.000020	0.017271	0.000575	0.000411		

```
Cl~F      0.000000  0.000000  0.000000  0.000000  0.000000  0.000000
0.000000  0.000000  0.000000  0.000000  0.000000  0.000963  0.022504
0.022285  0.009170  0.000862  0.012280  0.247211
Cl~Cl     0.001965  0.000101  0.021005  0.004588  0.008708  0.001624
0.009585  0.059555  0.000803  0.011837  0.019811  0.000082  0.012314
0.001459  0.007442  0.004742  0.010934  0.746468
Cl...Cl   0.099078  0.094888  0.135850  0.192880  0.188582  0.482452
0.279382  0.417914  0.235206  0.218004  0.243293  0.207111  0.114651
0.102358  0.421502  0.269175  0.284316  0.001790
          0.022252  0.027391  0.025685  0.050978  0.014485  0.008353
0.003296  0.033554  0.050973  0.055211  0.050622  0.034631  0.012858
0.012104  0.020771  0.061886  0.056855  0.000433
Cl...C    0.073954  0.139716  0.068795  0.170974  0.077245  0.070059
0.143393  0.093591  0.155222  0.276308  0.275415  0.100198  0.090169
0.060528  0.118498  0.216815  0.239654  0.000705
          0.020015  0.003591  0.012516  0.015273  0.007613  0.012399
0.011768  0.015579  0.025505  0.022329  0.033622  0.031820  0.005586
0.007035  0.009816  0.025610  0.045530  0.000174
F...Cl    0.042694  0.046643  0.013627  0.059571  0.177059  0.050316
0.070119  0.030319  0.108258  0.048854  0.062820  0.047734  0.033347
0.235453  0.008016  0.026440  0.045401  0.000547
          0.007677  0.010975  0.001234  0.012979  0.000775  0.004806
0.011337  0.006179  0.022215  0.009819  0.012899  0.011928  0.009612
0.017522  0.000498  0.005318  0.009222  0.000069
F...C     0.012156  0.027174  0.052108  0.029085  0.039841  0.017346
0.038557  0.006525  0.069649  0.034599  0.033296  0.041137  0.019630
0.059703  0.004194  0.023269  0.059255  0.000308
          0.004987  0.004777  -0.001326 0.004219  0.004046  0.003280
0.002270  0.001166  0.005727  0.000175  0.010009  0.008263  0.003943
0.011993  0.000842  0.004674  0.011902  0.000062

                              CFC112
C-C       0.027579  0.406979  0.030909  0.001108  0.079521  0.111562
0.000000  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000
0.000000  0.000000  0.000000  0.000000  0.000000
C-F       0.553015  0.000865  0.255225  0.049218  0.000411  0.003555
0.000000  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000
0.754670  0.000773  0.082130  0.014340  0.001334
C-Cl      0.041359  0.111735  0.126408  0.263862  0.004904  0.022508
0.494378  0.306739  0.003085  0.001421  0.325265  0.214957  0.265903
0.035787  0.296243  0.170247  0.059342  0.001335
CCF       0.043538  0.054648  0.019088  0.082370  0.025493  0.000019
0.000000  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000
0.000137  0.047720  0.022931  0.002781  0.143069
CCCl      0.035640  0.006256  0.025876  0.008647  0.000001  0.081070
0.001992  0.001367  0.248412  0.001660  0.107240  0.005838  0.143368
0.004062  0.025962  0.010919  0.009011  0.105374
FCCl      0.025506  0.038972  0.024815  0.001611  0.159335  0.009974
0.163197  0.175045  0.000221  0.000641  0.101423  0.217350  0.031109
0.034408  0.059149  0.118010  0.031190  0.004045
ClCCl     0.012357  0.031266  0.005476  0.016028  0.099610  0.160688
0.000000  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000
0.011267  0.062683  0.004059  0.216034  0.003072
F~F       0.000000  0.000000  0.000000  0.000000  0.000000  0.000000
0.010719  0.012219  0.005210  0.120586  0.000000  0.000000  0.000000
0.000000  0.000000  0.000000  0.000000  0.000000
```

Cl~Cl	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
0.010449	0.001801	0.011275	0.870064	0.000000	0.000000	0.000000
0.013597	0.005219	0.012796	0.071329	0.029634		
F…C	0.016360	0.054228	0.115393	0.068204	0.101933	0.065985
0.042777	0.045562	0.103855	0.000858	0.070878	0.058303	0.067902
0.062851	0.041484	0.033591	0.015911	0.102353		
	0.007769	0.009194	0.000485	0.003611	0.006616	0.005537
0.008597	0.009157	0.020872	0.000172	0.014245	0.011718	0.013646
0.001188	0.008997	0.010177	0.002257	0.019017		
Cl…C	0.044225	0.086284	0.037645	0.083470	0.089820	0.216448
0.054047	0.041603	0.159430	0.000770	0.052102	0.036748	0.169739
0.009199	0.116058	0.035931	0.068146	0.145329		
	0.013402	0.000969	0.009500	0.008700	0.010602	0.009527
0.002891	0.003496	0.029735	0.000248	0.018560	0.005667	0.012781
0.002057	0.009989	0.007068	0.014287	0.028210		
F…Cl	0.097280	0.118357	0.252219	0.151583	0.199995	0.130798
0.103649	0.296686	0.114677	0.001127	0.114736	0.304246	0.105691
0.036366	0.157372	0.326145	0.144661	0.245789		
	0.018694	0.026602	0.004177	0.020878	0.042317	0.026516
0.029826	0.017618	0.023202	0.000270	0.028445	0.025558	0.018893
0.005595	0.032411	0.014458	0.028906	0.049691		
Cl…Cl	0.050291	0.038696	0.082045	0.244539	0.156256	0.114895
0.076473	0.081303	0.233374	0.001852	0.147068	0.104840	0.148852
0.023741	0.103166	0.135239	0.306026	0.100985		
	0.012986	0.014949	0.010740	-0.003829	0.023187	0.040918
0.001004	0.007404	0.046653	0.000330	0.020039	0.014775	0.022115
0.007453	0.032776	0.016299	0.015778	0.020762		

CFC113

C-C	0.004275	0.126168	0.203048	0.085706	0.018294	0.007591
0.012862	0.017683	0.000031	0.004222	0.000223	0.000205	0.070563
0.004785	0.054186	0.050304	0.009232	0.000063		
C-Cl	0.014673	0.048306	0.140248	0.066151	0.353340	0.268734
0.044458	0.102817	0.058702	0.295266	0.253245	0.139353	0.038690
0.134635	0.071693	0.009460	0.005720	0.000151		
C-F	0.622488	0.424617	0.179966	0.547743	0.103713	0.035489
0.269303	0.172339	0.127735	0.001869	0.001141	0.031438	0.004195
0.014757	0.002334	0.001904	0.000402	0.000078		
CCCl	0.015476	0.047052	0.021532	0.002382	0.022215	0.013272
0.010223	0.022235	0.004094	0.009932	0.003107	0.003200	0.003940
0.044478	0.096503	0.098291	0.212856	0.002671		
CCF	0.049736	0.001094	0.030093	0.022179	0.009288	0.041372
0.014952	0.024578	0.019805	0.004370	0.001077	0.075255	0.042338
0.076201	0.048899	0.079968	0.027173	0.000599		
ClCCl	0.003865	0.000007	0.001609	0.019492	0.003967	0.031359
0.003578	0.003061	0.000519	0.000003	0.000028	0.024705	0.081697
0.073017	0.043417	0.036430	0.004179	0.000471		
ClCF	0.038535	0.018288	0.077918	0.023557	0.113723	0.108512
0.001645	0.056160	0.207038	0.097098	0.196858	0.091043	0.119079
0.029682	0.038090	0.019370	0.010045	0.008134		
FCF	0.001122	0.059683	0.008135	0.012979	0.009284	0.000001
0.106728	0.030309	0.000108	0.046896	0.001491	0.000179	0.011211
0.004803	0.000444	0.001093	0.000956	0.001110		
Cl~Cl	0.000445	0.002262	0.000294	0.000000	0.026051	0.007319
0.005461	0.002446	0.018491	0.004799	0.021225	0.001674	0.001379
0.000376	0.001645	0.000560	0.030535	0.446207		

Cl~F	0.000387	0.000423	0.000778	0.002746	0.002221	0.000118
0.000107	0.000509	0.007561	0.000019	0.000038	0.003312	0.003178
0.005615	0.008077	0.002786	0.000023	0.313553		
F~F	0.000187	0.000126	0.001626	0.002061	0.001136	0.002748
0.001063	0.001393	0.004495	0.002665	0.000208	0.004394	0.002035
0.001803	0.002455	0.004791	0.001143	0.200581		
C…Cl	0.030063	0.022090	0.041522	0.022653	0.034378	0.079057
0.016652	0.027429	0.041961	0.032656	0.037567	0.062107	0.064622
0.091606	0.140444	0.147402	0.122943	0.002531		
	0.007443	0.007230	0.003193	0.001292	0.006083	0.006968
0.002790	0.007357	0.006573	0.003523	0.004393	0.008626	0.010365
0.011012	0.011495	0.016723	0.018783	0.000444		
C…F	0.026669	0.069659	0.078582	0.065021	0.077702	0.079621
0.091819	0.099556	0.083291	0.057025	0.051538	0.095353	0.136972
0.120633	0.127996	0.111670	0.142737	0.004484		
	0.015034	0.006262	0.012253	0.006366	0.008447	0.010528
0.015038	0.009207	0.011086	0.011130	0.010124	0.013752	0.007845
0.017228	0.017189	0.018600	0.029948	0.000928		
Cl…Cl	0.019255	0.029026	0.034400	0.012908	0.078497	0.052137
0.010406	0.095526	0.042259	0.008361	0.101881	0.165356	0.126891
0.093664	0.074207	0.109406	0.116777	0.004174		
	0.004719	0.005353	0.006360	0.007154	0.006128	0.016154
0.002000	0.012490	0.002924	0.001281	0.012077	-0.003597	0.017703
0.009273	0.017066	0.026961	0.023839	0.000890		
Cl…F	0.078735	0.091470	0.089240	0.060778	0.088940	0.140529
0.169349	0.261319	0.242322	0.343740	0.283723	0.158290	0.190228
0.157190	0.162240	0.177935	0.175879	0.008844		
	0.020400	0.016188	0.020827	0.009637	0.022734	0.035167
0.022139	0.009356	0.022155	0.010911	0.016949	0.028989	0.035792
0.028608	0.034358	0.036669	0.036138	0.001669		
F…F	0.043137	0.012691	0.039427	0.023652	0.010741	0.054008
0.199357	0.038206	0.083544	0.053450	0.002529	0.080289	0.025305
0.066701	0.039605	0.041376	0.025568	0.001994		
	0.003358	0.012003	0.008950	0.005541	0.003120	0.009315
0.000071	0.006025	0.015305	0.010784	0.000576	0.016076	0.005972
0.013932	0.007657	0.008303	0.005123	0.000426		

CFC114

C-C	0.069893	0.356176	0.031914	0.021978	0.061385	0.114816
0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
0.000000	0.000000	0.000000	0.00			
C-Cl	0.082972	0.137928	0.046960	0.241938	0.152046	0.069271
0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
0.101321	0.289231	0.005520	0.331148	0.001143		
C-F	0.412924	0.003169	0.358547	0.000699	0.015786	0.004011
0.839685	0.076948	0.002054	0.000644	0.671645	0.241870	0.006435
0.556989	0.038579	0.188736	0.000177	0.000020		
CCCl	0.064994	0.001118	0.018565	0.013743	0.031692	0.141322
0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
0.004347	0.008443	0.006176	0.005829	0.245273		
CCF	0.004463	0.046677	0.000007	0.002385	0.070964	0.000222
0.001003	0.004231	0.183350	0.000874	0.049693	0.071426	0.071468
0.001523	0.038649	0.023596	0.008321	0.050533		
ClCF	0.003703	0.089970	0.003588	0.068166	0.019452	0.115168
0.053536	0.349310	0.002999	0.002655	0.046540	0.116319	0.264959
0.006366	0.163241	0.001486	0.117579	0.006501		

FCF	0.083784	0.000715	0.076566	0.120910	0.035152	0.003065
0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
0.095464	0.000001	0.182902	0.035130	0.000908		
Cl~Cl	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
0.008089	0.022737	0.020604	0.646814	0.000000	0.000000	0.000000
0.000000	0.000000	0.000000	0.000000	0.000000		
F~F	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
0.001881	0.012661	0.006044	0.342258	0.000000	0.000000	0.000000
0.005107	0.003380	0.004839	0.005963	0.005529		
C...Cl	0.006167	0.041079	0.004128	0.024656	0.035255	0.138557
0.005576	0.035555	0.065650	0.000570	0.022250	0.036798	0.051301
0.004479	0.061994	0.009005	0.028793	0.075495		
	0.007202	0.000151	0.002365	0.003711	0.005858	0.001919
0.001164	0.007424	0.013706	0.000119	0.004645	0.007683	0.010711
0.000544	0.004884	0.002157	0.003167	0.014679		
C...F	0.132086	0.137008	0.166617	0.211539	0.308993	0.223576
0.051768	0.163454	0.273424	0.001933	0.050824	0.237929	0.213184
0.119958	0.144897	0.169219	0.174634	0.300386		
	0.017756	0.023912	0.015065	0.022082	0.023165	0.032352
0.005158	0.026558	0.050864	0.000512	0.026096	0.018814	0.040714
0.008723	0.026843	0.036266	0.013707	0.058802		
Cl...F	0.068569	0.046771	0.079909	0.174860	0.117298	0.079277
0.008935	0.124292	0.115323	0.000988	0.037119	0.115317	0.103257
0.046672	0.067293	0.112703	0.193276	0.141138		
	0.009913	0.013197	0.009669	0.011033	0.014027	0.020252
0.006444	0.014139	0.024090	0.000289	0.011954	0.010061	0.024470
0.003614	0.020353	0.018810	0.004067	0.029889		
F...F	0.018557	0.085769	0.189444	0.068013	0.088992	0.047828
0.021458	0.137457	0.203390	0.001974	0.072508	0.123007	0.179559
0.025090	0.112391	0.230857	0.065435	0.058623		
	0.017017	0.016361	-0.003343	0.014288	0.019933	0.008363
0.004697	0.025232	0.038502	0.000367	0.006726	0.020775	0.033942
0.019804	0.019821	0.007728	0.012775	0.011082		

CFC115

C-C	0.010954	0.338005	0.015244	0.035917	0.030925	0.001806
0.000166	0.015049	0.017977	0.171605	0.018229	0.000000	0.000000
0.000000	0.000000	0.000000	0.000000	0.000000		
C-F	0.561698	0.256431	0.482963	0.227748	0.409796	0.244513
0.166074	0.001028	0.046437	0.004470	0.001750	0.633126	0.806908
0.184867	0.150616	0.029252	0.001744	0.000072		
C-Cl	0.026566	0.002241	0.116512	0.143305	0.033759	0.004284
0.000728	0.260385	0.099713	0.006801	0.012223	0.000000	0.000000
0.000000	0.000000	0.000000	0.000000	0.000000		
CCF	0.022474	0.018579	0.004876	0.029540	0.009416	0.018266
0.000998	0.003741	0.083309	0.051324	0.053244	0.036846	0.001729
0.004819	0.037340	0.072045	0.144705	0.000026		
CCCl	0.025222	0.001901	0.007288	0.001277	0.001150	0.007389
0.003205	0.009583	0.025516	0.003385	0.176046	0.000000	0.000000
0.000000	0.000000	0.000000	0.000000	0.000000		
FCF	0.071707	0.076672	0.090506	0.031720	0.050576	0.144093
0.258670	0.075233	0.043389	0.051027	0.005015	0.044369	0.028634
0.244684	0.017703	0.024843	0.000005	0.000271		
FCCl	0.002812	0.010384	0.018444	0.088709	0.006711	0.001174
0.001012	0.092601	0.000623	0.062736	0.017614	0.016278	0.034855
0.000060	0.190545	0.174825	0.002141	0.000205		

F~Cl	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
0.000000	0.000000	0.000000	0.000000	0.000000	0.000493	0.005185
0.008123	0.005874	0.000354	0.011218	0.428537		
F~F	0.000661	0.000581	0.006349	0.001333	0.000707	0.001648
0.010641	0.003753	0.000060	0.002114	0.008125	0.000081	0.002372
0.002621	0.006442	0.002654	0.006422	0.569982		
F...C	0.071021	0.109930	0.092268	0.142118	0.086835	0.088124
0.125270	0.078074	0.239760	0.306419	0.202707	0.050135	0.049461
0.127246	0.145026	0.180222	0.241337	0.000182		
	0.021036	0.005939	0.010049	0.011790	0.011547	0.022071
0.022804	0.012403	0.032343	0.015173	0.040676	0.022823	0.003538
0.021660	0.019120	0.029792	0.046844	0.000042		
Cl...C	0.001960	0.011829	0.002399	0.018306	0.004931	0.003230
0.000949	0.018140	0.017189	0.027878	0.057976	0.007725	0.003228
0.001410	0.018782	0.029212	0.025749	0.000024		
	0.001897	0.000202	0.000310	0.002399	0.000380	0.001041
0.000159	0.002458	0.001508	0.001561	0.005999	0.001614	0.000674
0.000295	0.003924	0.006104	0.005381	0.000005		
F...F	0.104664	0.099309	0.053941	0.132324	0.296617	0.285936
0.361799	0.076874	0.235248	0.184344	0.137049	0.120478	0.038142
0.356124	0.166863	0.220435	0.310984	0.000366		
	0.023576	0.029787	0.021839	0.027110	0.004074	0.012387
0.041443	0.013876	0.048007	0.036504	0.026057	0.021293	0.002181
0.039555	0.031272	0.043455	0.058837	0.000076		
F...Cl	0.046242	0.030012	0.071431	0.081582	0.046832	0.143144
0.004988	0.323534	0.097964	0.059069	0.195114	0.034597	0.014261
0.007233	0.192201	0.150894	0.119621	0.000188		
	0.007508	0.008196	0.005582	0.024821	0.005743	0.020896
0.001093	0.013270	0.010960	0.015589	0.042175	0.010140	0.008832
0.001304	0.014291	0.035913	0.025011	0.000024		

CFC112a

C-C	0.027982	0.370467	0.032021	0.008269	0.004318	0.027532
0.001394	0.003259	0.033189	0.123728	0.018314	0.000000	0.000000
0.000000	0.000000	0.000000	0.000000	0.000000		
C-Cl	0.122259	0.113299	0.377134	0.313354	0.043501	0.329156
0.291448	0.278179	0.053926	0.041468	0.004042	0.021865	0.437694
0.039933	0.221915	0.034131	0.027081	0.000357		
C-F	0.371468	0.017321	0.112699	0.029216	0.221732	0.000074
0.000426	0.003134	0.007817	0.001015	0.000024	0.618687	0.127234
0.150002	0.010628	0.003923	0.001506	0.000108		
CCCl	0.056198	0.015902	0.033158	0.028170	0.011562	0.007412
0.016753	0.026288	0.060825	0.082454	0.206707	0.025333	0.028512
0.010514	0.004771	0.000613	0.153451	0.000058		
CCF	0.004807	0.043566	0.008632	0.021487	0.013235	0.002479
0.008135	0.010540	0.031011	0.009558	0.021161	0.039416	0.015663
0.011759	0.109454	0.028146	0.049737	0.000054		
ClCCl	0.004231	0.021439	0.061843	0.056593	0.005953	0.011716
0.016438	0.105238	0.143115	0.067787	0.005605	0.003189	0.061171
0.003068	0.005951	0.219847	0.011886	0.001464		
ClCF	0.008827	0.050852	0.000404	0.063830	0.000093	0.009437
0.080663	0.000364	0.000234	0.032363	0.015802	0.042237	0.006039
0.224084	0.072934	0.015784	0.009605	0.000290		
FCF	0.075213	0.003454	0.011407	0.000026	0.131581	0.036201
0.018362	0.001147	0.010822	0.001424	0.002382	0.000000	0.000000
0.000000	0.000000	0.000000	0.000000	0.000000		

```
Cl~Cl     0.000000  0.000000  0.000000  0.000000  0.000000  0.000000
0.000000  0.000000  0.000000  0.000000  0.000000  0.002156  0.014726
0.018348  0.001196  0.027982  0.009190  0.453849
Cl~F      0.003580  0.000041  0.012938  0.008758  0.007932  0.002639
0.006418  0.011416  0.009208  0.000693  0.015580  0.001445  0.005182
0.019286  0.003390  0.004649  0.015532  0.540068
C...Cl    0.030867  0.078924  0.049016  0.092091  0.021437  0.059816
0.035103  0.089958  0.111731  0.212152  0.164983  0.036004  0.055131
0.052609  0.075464  0.071319  0.184944  0.000577
          0.010571  0.002049  0.010562  0.008898  0.002384  0.004413
0.006485  0.006947  0.015765  0.012605  0.024087  0.009108  0.011373
0.008313  0.007901  0.014590  0.032558  0.000100
C...F     0.068719  0.065483  0.070179  0.064289  0.086731  0.039588
0.047769  0.029559  0.093309  0.079056  0.112563  0.024364  0.036126
0.097843  0.113750  0.029045  0.036271  0.000105
          0.011731  0.009101  0.000904  0.005562  0.018900  0.004073
0.008613  0.003570  0.007389  0.001181  0.023666  0.012162  0.000074
0.011745  0.017752  0.004319  0.007811  0.000027
Cl...Cl   0.056409  0.061785  0.149516  0.142226  0.027496  0.348353
0.164529  0.375824  0.262471  0.228969  0.176738  0.053197  0.146130
0.027428  0.105884  0.424066  0.306667  0.001981
          0.010634  0.015736  0.027450  0.033802  0.005167 -0.002059
0.003325  0.012836  0.057645  0.050131  0.034281  0.009929  0.022702
0.003913 -0.008610  0.058689  0.059903  0.000503
Cl...F    0.086532  0.045817  0.019606  0.046028  0.144173  0.089623
0.229418  0.027444  0.060314  0.020686  0.118673  0.034436  0.012468
0.174979  0.092145  0.022257  0.034273  0.000225
          0.010038  0.014234  0.002250  0.014315  0.022105  0.004248
0.004317  0.003973  0.009909  0.006117  0.025680  0.013812  0.003331
0.012493  0.022472  0.005534  0.007642  0.000025
F...F     0.021541  0.058751  0.015720  0.054285  0.229881  0.021015
0.050368  0.008503  0.025194  0.024286  0.024946  0.050804  0.015167
0.113984  0.120350  0.029559  0.043690  0.000178
          0.018393  0.011780  0.004560  0.008800  0.001818  0.004280
0.010036  0.001821  0.006126  0.004329  0.004766  0.001855  0.001275
0.019698  0.022652  0.005547  0.008253  0.000032
```

CFC113a

```
C-C       0.390355  0.083959  0.001919  0.032881  0.178742  0.000000
0.000000  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000
0.000000  0.000000  0.000000  0.000000  0.000000
C-F       0.158370  0.231748  0.284127  0.000004  0.001358  0.574658
0.574653  0.096332  0.096323  0.172598  0.172579  0.032567  0.032563
0.005282  0.005282  0.001962  0.001961  0.000000
C-Cl      0.018633  0.109535  0.041995  0.303090  0.002888  0.013429
0.013428  0.450258  0.450253  0.006475  0.006475  0.260502  0.260507
0.027822  0.027823  0.025002  0.025002  0.000000
FCC       0.030135  0.010152  0.031500  0.005644  0.013976  0.028861
0.028859  0.016253  0.016254  0.000036  0.000036  0.102604  0.102604
0.018848  0.018847  0.051384  0.051383  0.000000
ClCC      0.006041  0.028608  0.006770  0.010619  0.050258  0.022600
0.022599  0.034560  0.034561  0.001180  0.001180  0.013090  0.013090
0.002069  0.002068  0.165937  0.165938  0.000000
FCF       0.066260  0.022321  0.069262  0.012410  0.030732  0.071213
0.071222  0.007871  0.007871  0.238194  0.238202  0.016995  0.016994
0.002147  0.002147  0.003290  0.003290  0.000000
```

```
ClCCl     0.011140  0.052756  0.012484  0.019583  0.092677  0.001982
0.001982  0.061737  0.061743  0.000646  0.000646  0.001418  0.001418
0.248516  0.248518  0.005817  0.005817  0.000000
F~Cl      0.000000  0.000000  0.000000  0.000000  0.000000  0.000000
0.000000  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000
0.000000  0.000000  0.000000  0.000000  1.000000
F...C     0.083751  0.139035  0.055459  0.033527  0.133274  0.055977
0.055980  0.042487  0.042486  0.124088  0.124092  0.154937  0.154935
0.027737  0.027735  0.060846  0.060846  0.000000
          0.007625  0.000695  0.017937  0.001284  0.000936  0.017212
0.017212  0.002590  0.002590  0.021697  0.021697  0.023604  0.023604
0.004275  0.004274  0.013071  0.013071  0.000000
Cl...C    0.041476  0.032121  0.022037  0.049136  0.155217  0.016420
0.016419  0.051486  0.051488  0.002553  0.002553  0.051640  0.051641
0.066838  0.066839  0.165812  0.165812  0.000000
         -0.001167  0.007103  0.001264  0.005187  0.006835  0.004574
0.004574  0.010951  0.010951  0.000164  0.000164  0.000205  0.000205
0.014021  0.014021  0.028946  0.028946  0.000000
F...F     0.117301  0.090029  0.386491  0.024731  0.055928  0.115121
0.115122  0.037625  0.037625  0.383380  0.383384  0.196711  0.196710
0.035322  0.035319  0.094683  0.094682  0.000000
          0.035394  0.015089  0.016065  0.004986  0.012942  0.026262
0.026264  0.007321  0.007321  0.045151  0.045153  0.041834  0.041834
0.007425  0.007424  0.019561  0.019561  0.000000
Cl...Cl   0.027027  0.139396  0.043078  0.499060  0.216308  0.043518
0.043515  0.156527  0.156530  0.003361  0.003361  0.111627  0.111631
0.470909  0.470913  0.305159  0.305160  0.000000
          0.007658  0.037451  0.009611 -0.002143  0.047930  0.008171
0.008171  0.024001  0.024004  0.000479  0.000479 -0.007735 -0.007735
0.068790  0.068790  0.058531  0.058531  0.000000
```

CFC114a

```
C-C       0.008550  0.387094  0.014125  0.061425  0.009771  0.000974
0.017455  0.000423  0.073454  0.079230  0.040331  0.000000  0.000000
0.000000  0.000000  0.000000  0.000000  0.000000
C-F       0.600569  0.223083  0.682517  0.233489  0.318826  0.198193
0.129131  0.058874  0.005937  0.004813  0.002315  0.596253  0.086217
0.172710  0.001225  0.035235  0.001673  0.000019
C-Cl      0.006621  0.006277  0.049812  0.130273  0.045714  0.000423
0.138145  0.151202  0.003580  0.000979  0.007168  0.014890  0.392490
0.002585  0.204806  0.174124  0.024226  0.000082
CCF       0.034847  0.021627  0.009573  0.030345  0.028251  0.003379
0.015703  0.083624  0.030629  0.078543  0.080493  0.022861  0.009759
0.000241  0.002604  0.106729  0.048205  0.000021
CCCl      0.011872  0.004613  0.004789  0.009213  0.000897  0.003984
0.019455  0.004985  0.001290  0.005333  0.097637  0.023350  0.028499
0.002273  0.004523  0.023034  0.177134  0.000119
FCF       0.060681  0.057548  0.023979  0.025409  0.066011  0.227858
0.037619  0.020090  0.023507  0.020281  0.008569  0.069277  0.007578
0.248922  0.002081  0.021820  0.002572  0.000173
FCCl      0.003293  0.014643  0.012166  0.025706  0.004004  0.001489
0.050436  0.000070  0.108713  0.000776  0.006222  0.003733  0.103303
0.001370  0.190168  0.006769  0.002351  0.000122
ClCCl     0.002089  0.001909  0.015809  0.033334  0.006529  0.000008
0.003058  0.020630  0.091203  0.125811  0.027833  0.000000  0.000000
0.000000  0.000000  0.000000  0.000000  0.000000
```

```
F~F       0.000000  0.000000  0.000000  0.000000  0.000000  0.000000
0.000000  0.000000  0.000000  0.000000  0.000000  0.001026  0.005561
0.006120  0.006725  0.000405  0.004495  0.260049
F~Cl      0.001686  0.000480  0.004834  0.000665  0.000110  0.009141
0.004252  0.002055  0.005075  0.012946  0.006633  0.000876  0.002392
0.004082  0.000360  0.000087  0.004608  0.738380
F...C     0.054334  0.090951  0.059673  0.130498  0.067961  0.129256
0.084633  0.134499  0.128125  0.181264  0.132055  0.061278  0.068319
0.126669  0.054342  0.200002  0.128844  0.000174
          0.018743  0.004974  0.004584  0.006790  0.017381  0.020398
0.011102  0.018600  0.008572  0.015401  0.024851  0.018459  0.009018
0.022361  0.010685  0.032298  0.026994  0.000037
C...Cl    0.012469  0.026475  0.009744  0.032944  0.017451  0.002554
0.019277  0.048673  0.058059  0.069029  0.119395  0.008968  0.031299
0.002139  0.033138  0.042183  0.109662  0.000057
          0.003626  0.000055  0.001567  0.004974  0.001020  0.000760
0.005020  0.004565  0.010308  0.009088  0.013745  0.002831  0.006267
0.000209  0.004896  0.000680  0.016915  0.000017
F...F     0.100446  0.088103  0.034625  0.081342  0.349126  0.343987
0.076916  0.134512  0.041651  0.128618  0.103404  0.104521  0.027373
0.361404  0.007142  0.237952  0.102243  0.000207
          0.021993  0.026221  0.008902  0.015017  0.012925  0.038759
0.014184  0.028598  0.009275  0.026694  0.021139  0.022938  0.005337
0.042673  0.001569  0.049578  0.020660  0.000047
F...Cl    0.032311  0.020398  0.032632  0.090314  0.028798  0.011410
0.233521  0.082882  0.185487  0.126531  0.140488  0.013473  0.090358
0.001876  0.306525  0.037260  0.084109  0.000226
          0.006335  0.006769  0.001943  0.019135  0.004705  0.000802
0.002235  0.011786  0.038593  0.025709  0.028500  0.002943  0.024660
0.000494  0.025760  0.003171  0.016768  0.000028
Cl...Cl   0.015821  0.015237  0.020481  0.051041  0.016727  0.005588
0.124193  0.197653  0.153479  0.070571  0.112177  0.027366  0.096045
0.003303  0.125482  0.028954  0.191131  0.000205
          0.003713  0.003542  0.008243  0.018086  0.003793  0.001036
0.013666 -0.003720  0.023063  0.018384  0.027045  0.004958  0.005525
0.000571  0.017968 -0.000282  0.037411  0.000038
```

<u>FC116</u>

```
C-C       0.469573  0.049185  0.199800  0.000000  0.000000  0.000000
0.000000  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000
0.000000  0.000000  0.000000  0.000000  0.000000
C-F       0.165216  0.553637  0.003969  0.000000  0.454173  0.258510
0.616052  0.616051  0.219637  0.219635  0.065137  0.065138  0.750128
0.750128  0.149561  0.149561  0.000762  0.000762
CCF       0.013184  0.002729  0.025697  0.000000  0.018622  0.022506
0.026565  0.026565  0.004255  0.004254  0.086828  0.086828  0.000609
0.000609  0.000598  0.000598  0.115170  0.115170
FCF       0.083214  0.017226  0.162190  0.000000  0.117534  0.142054
0.079104  0.079105  0.250387  0.250389  0.068595  0.068593  0.091745
0.091745  0.297088  0.297088  0.000122  0.000122
F~F       0.000000  0.000000  0.000000  1.000000  0.000000  0.000000
0.000000  0.000000  0.000000  0.000000  0.000000  0.000000  0.006593
0.006593  0.015645  0.015645  0.011310  0.011310
C...F     0.125005  0.077931  0.319989  0.000000  0.160131  0.089321
0.068396  0.068396  0.132646  0.132646  0.292548  0.292549  0.063150
0.063150  0.118370  0.118370  0.305558  0.305558
```

```
          0.005812  0.006152  0.015571  0.000000  0.012153  0.026882
0.026164  0.026164  0.019306  0.019306  0.046772  0.046772  0.006516
0.006516  0.023637  0.023637  0.060660  0.060660
F...F     0.105986  0.294605  0.223878  0.000000  0.187836  0.432082
0.151848  0.151848  0.337389  0.337390  0.363816  0.363815  0.066467
0.066466  0.351363  0.351363  0.422980  0.422980
          0.032009 -0.001465  0.048907  0.000000  0.049552  0.028645
0.031870  0.031871  0.036380  0.036381  0.076305  0.076305  0.014792
0.014792  0.043739  0.043739  0.083438  0.083438
```

HFC170

```
C-C       0.002500  0.156155  0.472816  0.000000  0.000000  0.000000
0.000000  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000
0.000000  0.000000  0.000000  0.000000  0.000000
C-H       0.942466  0.002260  0.013641  0.000000  0.924577  0.014606
0.955632  0.955631  0.002886  0.002886  0.002072  0.002073  0.947195
0.947195  0.005353  0.005352  0.007848  0.007848
CCH       0.000442  0.141217  0.020153  0.000000  0.000664  0.156877
0.000880  0.000880  0.012714  0.012717  0.324225  0.324228  0.000000
0.000000  0.019263  0.019266  0.314085  0.314087
HCH       0.000222  0.071077  0.010144  0.000000  0.000334  0.078960
0.000432  0.000432  0.143156  0.143155  0.005509  0.005508  0.000506
0.000506  0.135050  0.135049  0.006638  0.006637
H~H       0.000000  0.000000  0.000000  1.000000  0.000000  0.000000  -
0.000000  0.000000  0.000000  0.000000  0.000000  0.000000  0.000168
0.000168  0.033409  0.033408  0.025909  0.025911
H...H     0.017055  0.049140  0.008315  0.000000  0.016457  0.056906
0.003899  0.003899  0.062846  0.062846  0.043250  0.043249  0.003696
0.003696  0.060625  0.060625  0.042266  0.042266
          0.000178  0.008807  0.001154  0.000000  0.000224  0.009577  -
0.000575 -0.000575  0.011450  0.011450  0.008140  0.008140 -0.000576  -
0.000576  0.010932  0.010932  0.008004  0.008003
H...C     0.042837  0.449865  0.474425  0.000000  0.062689  0.555116
0.040705  0.040706  0.629832  0.629831  0.503537  0.503535  0.052274
0.052274  0.603318  0.603318  0.482549  0.482546
         -0.005700  0.121479 -0.000647  0.000000 -0.004945  0.127958  -
0.000973 -0.000973  0.137116  0.137116  0.113268  0.113268 -0.003263  -
0.003263  0.132049  0.132049  0.112702  0.112701
```

HFC161

```
C-C       0.000003  0.000546  0.001663  0.044381  0.023849  0.115784
0.000367  0.274772  0.148173  0.02944   0.012740  0.000000  0.000000
0.000000  0.000000  0.000000  0.000000  0.000000
C-H       0.954337  0.933452  0.938367  0.005800  0.003066  0.003323
0.005202  0.004582  0.006140  0.002378  0.001374  0.949217  0.957151
0.003948  0.002608  0.002629  0.003065  0.000004
C-F       0.000009  0.001052  0.000111  0.000267  0.028232  0.089032
0.162231  0.093199  0.260114  0.287327  0.009455  0.000000  0.000000
0.000000  0.000000  0.000000  0.000000  0.000000
CCH       0.000325  0.000257  0.000488  0.083882  0.039410  0.096089
0.114141  0.095559  0.068625  0.205498  0.025607  0.000071  0.001029
0.016538  0.211996  0.235687  0.186478  0.000320
CCF       0.000328  0.000693  0.000025  0.002603  0.000520  0.000929
0.003894  0.052363  0.001101  0.000086  0.432673  0.000000  0.000000
0.000000  0.000000  0.000000  0.000000  0.000000
HCH       0.000338  0.000253  0.000148  0.070053  0.084768  0.044450
0.029264  0.004881  0.002541  0.003038  0.001662  0.000104  0.000233
0.099428  0.000155  0.003570  0.000863  0.000287
```

```
HCF       0.000000  0.000001  0.000001  0.000026  0.003473  0.015517
0.025547  0.003474  0.024496  0.001343  0.004410  0.000137  0.000042
0.000217  0.034927  0.034713  0.043112  0.001819
H~F       0.000000  0.000000  0.000000  0.000000  0.000000  0.000000
0.000000  0.000000  0.000000  0.000000  0.000000  0.000112  0.000023
0.020837  0.000004  0.003236  0.008908  0.484562
H~H       0.000077  0.000026  0.000002  0.012253  0.016050  0.001610
0.002945  0.003473  0.010182  0.003359  0.005843  0.000042  0.000003
0.006181  0.003812  0.004375  0.045965  0.496328
H...H     0.004301  0.009415  0.018799  0.027414  0.063889  0.042812
0.037658  0.016576  0.012980  0.029089  0.003940  0.001190  0.003201
0.072328  0.022218  0.039698  0.027265  0.000576
         -0.000634  0.000175  0.000199  0.004795  0.012184  0.007949
0.006949  0.003090  0.002529  0.005729  0.000780 -0.000562 -0.000602
0.013765  0.004358  0.007840  0.005371  0.000113
H...C     0.042733  0.051232  0.044753  0.450199  0.567792  0.401239
0.370235  0.360502  0.270837  0.313087  0.178333  0.047684  0.037344
0.632781  0.267806  0.420060  0.307109  0.006423
         -0.002124 -0.003684 -0.005128  0.112361  0.120673  0.097232
0.082784  0.032137  0.028253  0.063987  0.041684 -0.002965 -0.001004
0.131358  0.064791  0.091789  0.071528  0.001438
F...H     0.000063  0.006965  0.000393  0.084512  0.005577  0.017746
0.019016  0.011833  0.041374  0.010473  0.035907  0.004715  0.001955
0.000375  0.053210  0.022090  0.040130  0.001133
          0.000005 -0.000590 -0.000040  0.015199  0.001244  0.004380
0.005107  0.001061  0.002602 -0.000184  0.006657 -0.000285 -0.000103
0.000059  0.009164  0.003796  0.007482  0.000200
F...C     0.000207  0.000089  0.000213  0.071887  0.024769  0.053655
0.112550  0.030514  0.102808  0.044647  0.212013  0.000449  0.000605
0.001817  0.270383  0.108599  0.210280  0.005654
          0.000033  0.000116  0.000005  0.014371  0.004503  0.008255
0.022108  0.011985  0.017245  0.000694  0.026921  0.000091  0.000122
0.000367  0.054570  0.021919  0.042441  0.001141
```

HFC152

```
C-C       0.001714  0.171028  0.000002  0.424423  0.028470  0.034275
0.000000  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000
0.000000  0.000000  0.000000  0.000000  0.000000
C-F       0.001626  0.155194  0.136655  0.049694  0.495698  0.101303
0.000000  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000
0.001342  0.014487  0.268523  0.639558  0.007310
C-H       0.944821  0.000133  0.002136  0.002439  0.003385  0.000388
0.953051  0.005930  0.001257  0.000001  0.959366  0.000923  0.000120
0.933427  0.006358  0.001502  0.001865  0.000130
CCF       0.001349  0.000560  0.024323  0.095585  0.022943  0.352410
0.000000  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000
0.000202  0.001299  0.001742  0.000531  0.485576
CCH       0.000001  0.158930  0.000904  0.028300  0.037787  0.007416
0.000003  0.178702  0.155808  0.001421  0.001315  0.283785  0.055129
0.000273  0.075815  0.103299  0.027079  0.023847
FCH       0.000000  0.013412  0.018362  0.000410  0.025986  0.004945
0.000165  0.045429  0.044546  0.002636  0.000139  0.016118  0.082494
0.000001  0.002507  0.037898  0.017153  0.003216
HCH       0.000099  0.007078  0.039299  0.001252  0.000907  0.000635
0.000000  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000
0.000124  0.043705  0.000614  0.002071  0.000814
```

```
F~F       0.000000  0.000000  0.000000  0.000000  0.000000  0.000000
0.000080  0.000203  0.003580  0.525848  0.000000  0.000000  0.000000
0.000000  0.000000  0.000000  0.000000  0.000000
H~H       0.000000  0.000000  0.000000  0.000000  0.000000  0.000000
0.000039  0.012574  0.087514  0.443226  0.000000  0.000000  0.000000
0.000052  0.021283  0.015091  0.009738  0.005951
F...C     0.000082  0.172884  0.066100  0.063162  0.118937  0.281598
0.000602  0.291073  0.271720  0.010580  0.001433  0.258654  0.338630
0.000188  0.062606  0.237064  0.121180  0.158348
          0.000209  0.028654  0.016962  0.019886  0.025316  0.014937
0.000124  0.060097  0.056101  0.002185  0.000296  0.053399  0.069921
0.000067  0.013097  0.041766  0.015030  0.038613
H...C     0.036260  0.173423  0.474984  0.293043  0.151881  0.140798
0.044639  0.258527  0.245340  0.009049  0.033698  0.253303  0.291530
0.051160  0.513998  0.193858  0.091372  0.191183
         -0.003495  0.056323  0.102487  0.004517  0.025273  0.030453 -
0.003059  0.059985  0.054720  0.001944 -0.000978  0.056735  0.062465 -
0.003766  0.113600  0.043418  0.020614  0.041428
F...H     0.005954  0.031496  0.068581  0.011598  0.047177  0.023040
0.005254  0.046248  0.040684  0.001660  0.005528  0.038867  0.053200
0.005811  0.076993  0.024363  0.042193  0.033590
         -0.000487  0.006967  0.014423  0.001913  0.002567  0.004743 -
0.000270  0.008132  0.007970  0.000312 -0.000266  0.007208  0.009947 -
0.000455  0.014832  0.006974  0.001559  0.006181
H...H     0.011684  0.020118  0.029595  0.003253  0.011409  0.002590
0.000054  0.027785  0.025819  0.000956  0.000141  0.026027  0.030690
0.011368  0.033823  0.020013  0.008360  0.003187
          0.000181  0.003800  0.005186  0.000526  0.002265  0.000469 -
0.000682  0.005314  0.004941  0.000183 -0.000670  0.004981  0.005874
0.000207  0.005596  0.003876  0.001697  0.000626
```

HFC143

```
C-C       0.000001  0.000248  0.000875  0.011411  0.163575  0.001447
0.015773  0.000000  0.302382  0.003836  0.083664  0.004140  0.035206
0.007732  0.013663  0.027999  0.007482  0.000281
C-H       0.962150  0.950959  0.943072  0.000300  0.000234  0.004789
0.000587  0.003658  0.002573  0.001023  0.001357  0.001531  0.000144
0.000290  0.000611  0.000252  0.000180  0.000013
C-F       0.000005  0.001906  0.000994  0.226280  0.112518  0.038293
0.279967  0.097651  0.152714  0.602217  0.318904  0.545588  0.125743
0.085526  0.034824  0.091706  0.002621  0.000771
CCH       0.000695  0.000331  0.000172  0.028365  0.153666  0.102392
0.088757  0.224590  0.076499  0.006690  0.010984  0.034475  0.107006
0.033559  0.022386  0.001800  0.010165  0.003035
CCF       0.000225  0.000514  0.000469  0.014298  0.003663  0.009275
0.009585  0.006172  0.033432  0.022428  0.035583  0.013645  0.006206
0.032904  0.247283  0.231410  0.379029  0.007916
HCH       0.000000  0.000001  0.000054  0.001511  0.001540  0.018846
0.001572  0.000050  0.000451  0.000001  0.000028  0.000943  0.000003
0.000026  0.000022  0.000031  0.000271  0.000001
HCF       0.000139  0.000080  0.000000  0.033952  0.013192  0.006602
0.029958  0.020293  0.003623  0.015853  0.027734  0.021380  0.037638
0.008700  0.002544  0.000984  0.002048  0.006173
FCF       0.000001  0.000410  0.000008  0.000219  0.011812  0.001106
0.001087  0.007277  0.013017  0.008975  0.017635  0.000011  0.001197
0.183139  0.066637  0.054101  0.012238  0.000118
```

H~H	0.000022	0.000009	0.000000	0.000082	0.000026	0.000003
0.000000	0.000105	0.000068	0.000011	0.000149	0.000006	0.001088
0.002520	0.000116	0.000316	0.002909	0.196205		
H~F	0.000013	0.000000	0.000022	0.028550	0.001490	0.002310
0.016797	0.000034	0.001597	0.013207	0.007101	0.005564	0.022715
0.002599	0.003969	0.000878	0.024502	0.321935		
F~F	0.000017	0.000029	0.000017	0.000765	0.000042	0.007412
0.010378	0.001794	0.000213	0.005440	0.004189	0.009222	0.025936
0.020976	0.007892	0.000087	0.000362	0.375119		
C...H	0.032844	0.035170	0.037594	0.158757	0.097671	0.431150
0.176123	0.202189	0.189590	0.064854	0.142904	0.120269	0.208900
0.047057	0.088939	0.062248	0.149336	0.024802		
	-0.001885	-0.002706	-0.003581	0.033453	0.030465	0.088685
0.037006	0.042667	0.007076	0.012487	0.020737	0.023163	0.038530
0.010098	0.017154	0.011715	0.030241	0.004994		
C...F	0.001279	0.001014	0.000359	0.170148	0.239638	0.111717
0.209228	0.224729	0.131435	0.104511	0.174870	0.126620	0.259112
0.263483	0.246809	0.304809	0.226168	0.034128		
	0.000248	0.000297	0.000113	0.034817	0.040654	0.023068
0.037595	0.045457	0.021176	0.019015	0.037796	0.022582	0.042815
0.040140	0.044659	0.032345	0.039282	0.006315		
H...H	0.000066	0.000135	0.014547	0.003350	0.004190	0.028660
0.012893	0.015064	0.002843	0.001363	0.007459	0.008783	0.016203
0.000495	0.001090	0.000289	0.001363	0.001693		
	-0.000509	0.000005	0.000181	0.000738	0.001043	0.005074
0.003765	0.004599	0.000725	0.000419	0.002291	0.002668	0.004987
0.000145	0.000330	0.000076	0.000385	0.000522		
H...F	0.004804	0.011343	0.005538	0.027928	0.035710	0.074859
0.033524	0.044381	0.020570	0.028949	0.035798	0.051533	0.045834
0.020555	0.023864	0.013939	0.031226	0.006352		
	-0.000278	-0.000689	-0.000504	0.007745	0.008089	0.013336
0.007981	0.006651	0.003116	0.002338	0.004633	0.002880	0.007395
0.004937	0.004611	0.002818	0.005445	0.001098		
F...F	0.000139	0.000736	0.000057	0.185652	0.066651	0.026158
0.023066	0.043753	0.029588	0.075943	0.054862	0.004253	0.012483
0.216342	0.150267	0.137281	0.062628	0.007223		
	0.000025	0.000208	0.000012	0.031680	0.014132	0.004819
0.004357	0.008885	0.007312	0.010437	0.011321	0.000745	0.000860
0.018776	0.022331	0.024917	0.012119	0.001307		

HFC134

C-C	0.000830	0.204225	0.380420	0.010926	0.018710	0.078401
0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
0.000000	0.000000	0.000000	0.000000	0.000000		
C-H	0.957049	0.000024	0.000895	0.003354	0.000201	0.000276
0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
0.951148	0.003656	0.003395	0.000022	0.000023		
C-F	0.002045	0.145211	0.013329	0.497466	0.170913	0.008830
0.287012	0.669358	0.000030	0.001694	0.359849	0.428609	0.169690
0.001811	0.068114	0.660470	0.096179	0.000042		
CCH	0.000451	0.163735	0.108250	0.002299	0.015865	0.003670
0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
0.000043	0.210158	0.014949	0.000004	0.066959		
CCF	0.000942	0.002275	0.044347	0.044768	0.022733	0.141655
0.000502	0.001433	0.339000	0.000169	0.045527	0.038545	0.258755
0.000123	0.006274	0.002569	0.056770	0.185611		

HCF	0.000040	0.006671	0.000784	0.009041	0.005202	0.000682
0.026582	0.010815	0.000002	0.000115	0.020616	0.017881	0.000071
0.000054	0.012395	0.002604	0.000258	0.006536		
FCF	0.000484	0.025027	0.003481	0.041188	0.184980	0.168376
0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
0.000435	0.008736	0.065770	0.298671	0.035764		
H~H	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
0.019670	0.010633	0.003303	0.144243	0.000000	0.000000	0.000000
0.000000	0.000000	0.000000	0.000000	0.000000		
F~F	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
0.001107	0.000771	0.002000	0.850591	0.000000	0.000000	0.000000
0.000089	0.000078	0.004549	0.012087	0.029305		
C...H	0.027016	0.035262	0.170926	0.054430	0.030825	0.036810
0.132597	0.054189	0.067317	0.000609	0.111798	0.096779	0.051728
0.037920	0.111374	0.015622	0.012558	0.086890		
	-0.001950	0.019712	0.002484	0.011708	0.007535	0.006835
0.027890	0.011398	0.014158	0.000128	0.023515	0.020356	0.010879
0.002974	0.026238	0.003982	0.002642	0.018402		
C...F	0.001370	0.246767	0.181603	0.103572	0.237701	0.336306
0.178999	0.096236	0.254578	0.000770	0.141732	0.123027	0.273621
0.000666	0.310010	0.120628	0.192472	0.267546		
	0.000448	0.036898	0.029272	0.029317	0.028964	0.033502
0.031399	0.012054	0.054821	0.000181	0.035797	0.031173	0.033037
0.000152	0.056363	0.009525	0.043954	0.054651		
H...F	0.010713	0.031621	0.019236	0.030292	0.016048	0.013439
0.029452	0.030762	0.012116	0.000236	0.023300	0.040560	0.010233
0.010432	0.046646	0.020332	0.015026	0.027078		
	-0.000633	0.007631	0.003849	0.002632	0.004071	0.002666
0.008827	0.002385	0.001957	0.000032	0.007233	0.004801	0.001501
0.000614	0.010500	0.001293	0.003116	0.005484		
F...F	0.000946	0.059882	0.034250	0.130237	0.242116	0.137892
0.218288	0.089575	0.211633	0.001052	0.197471	0.170685	0.162106
0.000546	0.108156	0.055241	0.247576	0.181936		
	0.000252	0.015061	0.006874	0.028769	0.014134	0.030660
0.037677	0.010391	0.039085	0.000179	0.033163	0.027584	0.028379
0.000170	0.021301	0.019070	0.018665	0.033773		

HFC125

C-C	0.000394	0.235250	0.162574	0.034354	0.004285	0.131080
0.007687	0.014748	0.001390	0.069782	0.047133	0.000000	0.000000
0.000000	0.000000	0.000000	0.000000	0.000000		
C-F	0.001469	0.214622	0.461688	0.337552	0.548392	0.406406
0.188787	0.170372	0.100406	0.024796	0.003571	0.402443	0.599652
0.558803	0.179606	0.121930	0.000779	0.000510		
C-H	0.956668	0.000041	0.000163	0.001358	0.003476	0.000010
0.000029	0.000074	0.000046	0.000245	0.000043	0.000000	0.000000
0.000000	0.000000	0.000000	0.000000	0.000000		
CCF	0.000554	0.015719	0.037826	0.019723	0.011149	0.043569
0.097517	0.019861	0.011461	0.119855	0.195572	0.042423	0.019095
0.012841	0.011350	0.194255	0.291037	0.000211		
CCH	0.000057	0.118806	0.015939	0.098253	0.028543	0.024456
0.019182	0.001289	0.005232	0.000159	0.024666	0.000000	0.000000
0.000000	0.000000	0.000000	0.000000	0.000000		
FCF	0.000408	0.042846	0.065305	0.053745	0.062020	0.001979
0.090082	0.242563	0.294689	0.171631	0.015925	0.009496	0.056054
0.002238	0.248040	0.046639	0.000457	0.000057		

FCH	0.000046	0.004571	0.000001	0.005759	0.006147	0.000664
0.001532	0.000984	0.001209	0.000014	0.003654	0.017919	0.006761
0.014692	0.000009	0.000043	0.000018	0.000514		
F~H	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
0.000000	0.000000	0.000000	0.000000	0.000000	0.013873	0.016253
0.017277	0.005094	0.000024	0.007611	0.297867		
F~F	0.000047	0.000095	0.001574	0.001431	0.002346	0.001872
0.001323	0.000176	0.021452	0.004874	0.012747	0.000110	0.001497
0.000512	0.002781	0.001121	0.003820	0.688246		
F...C	0.000939	0.176370	0.080533	0.171578	0.116859	0.156770
0.145747	0.163274	0.153245	0.283497	0.288642	0.116236	0.085412
0.096870	0.136352	0.255806	0.250744	0.002850		
	0.000230	0.026478	0.016622	0.028393	0.016901	0.013972
0.031386	0.026024	0.031895	0.034961	0.040497	0.030939	0.017161
0.018278	0.022980	0.036840	0.049884	0.000584		
H...C	0.031308	0.024680	0.030347	0.067978	0.038212	0.042867
0.027787	0.005282	0.006829	0.011087	0.043763	0.094833	0.035027
0.075634	0.001970	0.018189	0.048983	0.002594		
	-0.002425	0.013302	0.000177	0.010636	0.008086	0.002600
0.004706	0.001150	0.001547	0.000979	0.010833	0.019742	0.007292
0.015746	0.000410	0.003786	0.010197	0.000540		
F...F	0.000940	0.079739	0.100508	0.116227	0.097286	0.156364
0.344448	0.316876	0.323691	0.222086	0.248301	0.190994	0.121396
0.127124	0.350270	0.264104	0.272740	0.004236		
	0.000243	0.020601	0.023539	0.027442	0.026178	0.009451
0.031698	0.030422	0.038011	0.048031	0.048578	0.034766	0.023762
0.020173	0.040612	0.052773	0.052837	0.000834		
F...H	0.009755	0.022000	0.002676	0.021104	0.027808	0.006795
0.006676	0.005637	0.007276	0.006681	0.013398	0.020261	0.008514
0.036413	0.000455	0.003820	0.009075	0.000812		
	-0.000633	0.004881	0.000528	0.004466	0.002312	0.001145
0.001416	0.001266	0.001621	0.001321	0.002677	0.005963	0.002123
0.003398	0.000070	0.000671	0.001816	0.000145		

HFC152a

C-C	0.000008	0.000265	0.001231	0.188120	0.016537	0.031056
0.196658	0.094124	0.089980	0.017196	0.041837	0.000000	0.000000
0.000000	0.000000	0.000000	0.000000	0.000000		
C-H	0.955920	0.945517	0.937803	0.001068	0.003085	0.007077
0.007463	0.002588	0.002379	0.000781	0.000594	0.957104	0.000247
0.003098	0.000173	0.002067	0.001679	0.000010		
C-F	0.000053	0.001485	0.000040	0.084963	0.010624	0.012661
0.240616	0.135899	0.266289	0.057814	0.014614	0.000000	0.255861
0.008490	0.450557	0.191908	0.049647	0.000412		
CCH	0.000387	0.000361	0.000546	0.136142	0.026734	0.215391
0.067551	0.194768	0.185255	0.053012	0.006629	0.000307	0.016191
0.012116	0.058533	0.303940	0.013837	0.000200		
CCF	0.000081	0.000677	0.000000	0.006809	0.001437	0.000008
0.007026	0.041678	0.002537	0.089313	0.166305	0.000527	0.016451
0.003182	0.034008	0.001077	0.370037	0.000675		
HCH	0.000255	0.000007	0.000095	0.008967	0.075030	0.030702
0.002974	0.002992	0.001842	0.000184	0.000314	0.000261	0.002095
0.078922	0.000442	0.002380	0.000542	0.000181		
HCF	0.000006	0.000114	0.000000	0.015487	0.000509	0.004096
0.008967	0.004593	0.000381	0.013119	0.000203	0.000000	0.050247
0.002222	0.023898	0.000682	0.000047	0.000236		

FCF	0.000012	0.000337	0.000008	0.013170	0.001741	0.001415
0.027948	0.009662	0.006607	0.119179	0.197092	0.000000	0.000000
0.000000	0.000000	0.000000	0.000000	0.000000		
H~H	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
0.000000	0.000000	0.000000	0.000000	0.000000	0.000038	0.012579
0.005143	0.009391	0.001814	0.001592	0.213384		
H~F	0.000126	0.000019	0.000000	0.001166	0.023780	0.000072
0.000045	0.000870	0.010572	0.020948	0.000355	0.000035	0.000972
0.007626	0.000007	0.004304	0.004485	0.779100		
C...H	0.040790	0.038897	0.043583	0.151764	0.616378	0.430094
0.208953	0.307614	0.261450	0.078984	0.048818	0.039134	0.171595
0.639152	0.137694	0.351964	0.079749	0.002376		
	-0.002398	-0.002779	-0.004958	0.040477	0.123592	0.096396
0.011620	0.049403	0.043000	0.017157	0.006900	-0.002063	0.035433
0.127526	0.028300	0.073071	0.016938	0.000483		
C...F	0.000293	0.000733	0.000295	0.184365	0.006243	0.065990
0.104339	0.047101	0.060774	0.249078	0.240083	0.000268	0.141773
0.006705	0.073878	0.017307	0.225217	0.000860		
	0.000048	0.000234	-0.000005	0.033131	0.000996	0.010838
0.015935	0.013875	0.003211	0.035917	0.040586	0.000053	0.030320
0.001677	0.019039	-0.000675	0.032756	0.000213		
H...H	0.004543	0.000299	0.021075	0.010994	0.073604	0.051219
0.005012	0.024641	0.022741	0.001823	0.000686	0.004702	0.003865
0.075904	0.007107	0.036922	0.002018	0.000187		
	-0.000635	-0.000013	0.000194	0.002246	0.014789	0.009826
0.000882	0.005054	0.004688	0.000377	0.000137	-0.000655	0.000778
0.015249	0.001474	0.007677	0.000438	0.000040		
H...F	0.000457	0.013818	0.000096	0.039047	0.001134	0.012554
0.032391	0.012285	0.005192	0.029940	0.021082	0.000019	0.035481
0.001704	0.038857	0.003926	0.013775	0.000274		
	-0.000016	-0.000877	-0.000008	0.008568	0.000278	0.002589
0.003946	0.001226	0.000100	0.006684	0.004127	0.000004	0.009947
0.000453	0.003497	-0.000038	0.002691	0.000044		
F...F	0.000057	0.000705	0.000001	0.059430	0.002667	0.014856
0.044270	0.042262	0.029749	0.186895	0.182681	0.000223	0.182476
0.009110	0.097885	0.002837	0.157008	0.001110		
	0.000013	0.000200	0.000002	0.014086	0.000841	0.003162
0.013403	0.009366	0.003254	0.021600	0.026957	0.000044	0.033688
0.001720	0.015259	-0.001163	0.030544	0.000215		

HFC143a

C-C	0.001074	0.295458	0.114711	0.160326	0.123896	0.000000
0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
0.000000	0.000000	0.000000	0.000000	0.000000		
C-F	0.000011	0.065275	0.154858	0.471454	0.036975	0.000000
0.000000	0.013021	0.013044	0.629549	0.629560	0.110789	0.110742
0.124501	0.124486	0.025072	0.025070	0.000000		
C-H	0.928592	0.000513	0.005770	0.000790	0.000504	0.958498
0.958497	0.002252	0.002252	0.000001	0.000001	0.001672	0.001673
0.000063	0.000063	0.001585	0.001585	0.000000		
CCF	0.000002	0.011244	0.021946	0.000169	0.068007	0.000324
0.000324	0.000000	0.000000	0.030385	0.030384	0.001681	0.001683
0.003191	0.003192	0.218535	0.218536	0.000000		
CCH	0.000468	0.124061	0.100025	0.004698	0.002012	0.000338
0.000338	0.025503	0.025531	0.032121	0.032090	0.340135	0.340138
0.002004	0.002005	0.012777	0.012777	0.000000		

```
FCF      0.000004  0.022598  0.044109  0.000339  0.136685  0.000000
0.000000 0.001163  0.001165  0.052110  0.052116  0.004494  0.004493
0.257964 0.257968  0.018757  0.018754  0.000000
HCH      0.000075  0.019793  0.015959  0.000750  0.000321  0.000237
0.000237 0.075641  0.075633  0.002952  0.002956  0.002841  0.002844
0.000033 0.000033  0.000637  0.000638  0.000000
F~H      0.000000  0.000000  0.000000  0.000000  0.000000  0.000000
0.000000 0.000000  0.000000  0.000000  0.000000  0.000000  0.000000
0.000000 0.000000  0.000000  0.000000  1.000000
F...C    0.000334  0.044109  0.039751  0.122510  0.197025  0.000337
0.000337 0.001278  0.001280  0.047872  0.047875  0.013854  0.013854
0.145817 0.145820  0.260670  0.260668  0.000000
        -0.000011  0.002106  0.006820  0.000653  0.025005  0.000072
0.000072 0.000083  0.000084  0.015599  0.015600  0.000017  0.000017
0.027214 0.027214  0.047451  0.047451  0.000000
H...C    0.038850  0.240668  0.301796  0.062830  0.042109  0.034806
0.034809 0.606837  0.606803  0.055481  0.055482  0.359847  0.359874
0.002176 0.002176  0.016484  0.016488  0.000000
        -0.004478  0.059542  0.040568 -0.000075 -0.000603 -0.001899 -
0.001900 0.119797  0.119791  0.010846  0.010846  0.073353  0.073358
0.000468 0.000468  0.003752  0.003753  0.000000
F...F    0.000007  0.036929  0.075932  0.173641  0.323398  0.000461
0.000460 0.001065  0.001067  0.092402  0.092404  0.009062  0.009062
0.386049 0.386051  0.326992  0.326990  0.000000
         0.000002  0.010896  0.021836 -0.000814  0.043471  0.000087
0.000087 0.000224  0.000224  0.017784  0.017785  0.000749  0.000750
0.050015 0.050016  0.063313  0.063312  0.000000
H...H    0.034788  0.055575  0.047066  0.002324  0.001023  0.007795
0.007795 0.127325  0.127317  0.010686  0.010687  0.067432  0.067437
0.000419 0.000419  0.003260  0.003261  0.000000
         0.000284  0.011234  0.008854  0.000407  0.000172 -0.001056 -
0.001056 0.025810  0.025808  0.002213  0.002213  0.014073  0.014074
0.000089 0.000089  0.000715  0.000716  0.000000
```

HFC134a

```
C-C      0.000799  0.170175  0.051020  0.162338  0.035644  0.000024
0.161455 0.065612  0.011965  0.029180  0.017794  0.000000  0.000000
0.000000 0.000000  0.000000  0.000000  0.000000
C-F      0.001598  0.103337  0.243139  0.479726  0.393235  0.579745
0.455613 0.101971  0.125127  0.091592  0.000810  0.000000  0.597236
0.101823 0.048092  0.132384  0.023004  0.000492
C-H      0.940164  0.000753  0.001149  0.000480  0.001206  0.001774
0.000308 0.000109  0.000025  0.000226  0.000072  0.961842  0.000094
0.002004 0.000005  0.000024  0.001257  0.000034
CCF      0.000455  0.007788  0.018839  0.037720  0.014063  0.014944
0.016447 0.104320  0.005794  0.184109  0.324204  0.000299  0.025906
0.001909 0.012203  0.001855  0.196886  0.005864
CCH      0.000049  0.114418  0.005677  0.004154  0.084467  0.039085
0.010878 0.008285  0.000218  0.000780  0.015215  0.000401  0.059283
0.196844 0.122236  0.001154  0.013113  0.003067
FCF      0.000002  0.017163  0.010289  0.064468  0.044850  0.000206
0.000184 0.124333  0.262802  0.041553  0.006615  0.000000  0.055763
0.006662 0.001931  0.269731  0.017599  0.000223
FCH      0.000000  0.000440  0.022480  0.000322  0.012469  0.021763
0.000023 0.000311  0.000000  0.001266  0.004996  0.000145  0.000792
0.039181 0.053164  0.000012  0.00
```

```
HCH        0.000129   0.029829   0.030623   0.000476   0.000985   0.001647
0.000052   0.000034   0.000069   0.000088   0.001133   0.000000   0.000000
0.000000   0.000000   0.000000   0.000000   0.000000
F~F        0.000000   0.000000   0.000000   0.000000   0.000000   0.000000
0.000000   0.000000   0.000000   0.000000   0.000000   0.000042   0.001641
0.000160   0.003454   0.007252   0.002518   0.376513
F~H        0.000051   0.008880   0.023343   0.003737   0.006201   0.010162
0.000339   0.000006   0.010292   0.000058   0.010699   0.000039   0.001370
0.009100   0.076502   0.007808   0.052818   0.537861
F...C      0.000390   0.088009   0.081769   0.061698   0.131785   0.097289
0.130649   0.159677   0.141433   0.270650   0.223526   0.000905   0.074187
0.203683   0.226482   0.136217   0.255036   0.023831
           0.000091   0.012064   0.017288   0.014226   0.020193   0.018481
0.003766   0.027853   0.025386   0.035446   0.036220   0.000186   0.020073
0.041225   0.042812   0.025402   0.046603   0.004697
C...H      0.035319   0.249127   0.294034   0.045950   0.119683   0.103033
0.055251   0.048315   0.003022   0.024957   0.162663   0.031959   0.036763
0.229107   0.232898   0.000671   0.013541   0.018621
          -0.003199   0.061963   0.060324   0.001089   0.018257   0.021659
0.001248   0.005154   0.000033   0.004641   0.034841  -0.001857   0.007846
0.048751   0.047153   0.000156   0.003190   0.003771
F...F      0.000179   0.025520   0.029482   0.096500   0.061957   0.009841
0.158459   0.310171   0.366697   0.257285   0.091099   0.000444   0.085830
0.009641   0.020976   0.370170   0.306275   0.008877
           0.000034   0.006785   0.006334   0.022914   0.016123   0.001844
0.000152   0.034698   0.046872   0.050956   0.017601   0.000084   0.016844
0.001410   0.003504   0.046855   0.059358   0.001700
F...H      0.007290   0.055737   0.053315   0.002522   0.016120   0.057102
0.003166   0.006601   0.000157   0.005132   0.039057   0.006703   0.007394
0.051710   0.051785   0.000139   0.002910   0.004268
          -0.000588   0.011285   0.013021   0.000539   0.004316   0.002838
0.000637   0.001368   0.000023   0.001131   0.007884  -0.000318   0.001480
0.010008   0.010484   0.000029   0.000667   0.000883
H...H      0.016971   0.031024   0.032053   0.000984   0.015512   0.015458
0.001158   0.000987   0.000074   0.000803   0.004650   0.000113   0.006280
0.039181   0.038792   0.000121   0.002453   0.003107
           0.000264   0.005703   0.005822   0.000157   0.002933   0.003105
0.000215   0.000195   0.000011   0.000146   0.000921  -0.000989   0.001218
0.007599   0.007526   0.000023   0.000475   0.000603
```

Appendix F

Frequencies (cm^{-1}) and intensities ($kmmole^{-1}$) calculated using the HF method for the CFCs.

110		111		112		112a		113		113a		114		114a		115		116	
Freq.	Intens.	Freq.	Intens.	Freq.	Intens.	Freq.	Intens.	Freq.	Intens.	Freq.	Intens.	Feq.	Intens.	Freq.	Intens.	Freq.	Intens.	Freq.	Intens.
983	0	1155	113.16	1205	0	1227	144.90	1249	101.05	1277	208.93	1308	0	1322	187.33	1386	86.44	1458	0
882	0	1035	28.99	1173	316.13	1202	168.67	1234	161.19	1277	208.93	1233	424.49	1282	261.53	1283	334.08	1283	619.88
882	0	919	48.96	1084	0	1058	146.52	1157	234.82	1266	269.17	1228	0	1276	210.00	1278	244.69	1283	619.88
793	202.42	860	135.99	925	0	870	98.35	1080	92.77	909	50.19	1158	451.01	1148	174.73	1234	189.09	1277	0
793	202.42	816	245.00	842	389.36	862	157.00	914	226.08	865	156.70	1098	0	943	151.53	1147	287.74	1277	0
676	66.25	723	118.71	749	192.58	780	187.56	811	295.09	865	156.70	849	419.18	918	280.60	981	327.58	1113	369.29
423	0	493	2.89	567	0	612	19.37	640	14.23	698	52.57	693	0	720	56.42	746	40.32	795	0
372	1.38	401	1.99	459	4.77	447	2.08	521	5.48	547	7.98	594	18.89	577	5.51	631	20.96	693	51.64
335	0	390	0.61	406	0	435	0.74	450	1.73	547	7.98	534	0	546	9.31	583	1.61	603	0
335	0	378	0.05	388	0	412	1.51	433	1.30	418	0.66	437	0	492	3.93	541	9.56	603	0
276	0.15	311	0.54	373	1.78	327	0.001	387	1.49	360	0.002	429	4.13	395	0.42	441	3.09	505	8.61
276	0.15	281	0.04	292	0	326	0.47	346	0.63	360	0.002	365	1.33	390	0.69	430	1.12	505	8.61
222	0	262	0.40	291	0.33	265	0.53	306	0.58	262	0.68	352	0	323	1.31	356	0.04	371	0
222	0	229	0.001	254	0	258	0.32	285	0.19	262	0.68	318	0	304	0.32	327	0.10	371	0
218	0	221	0.02	225	0	227	0.04	236	0.22	255	0.0003	250	0	259	0.74	304	1.47	338	0
163	0.25	171	0.43	198	1.41	179	0.70	197	1.39	177	1.02	212	2.42	194	1.59	211	3.11	206	3.79
163	0.25	161	0.35	160	0.44	160	0.60	162	0.91	177	1.02	166	1.63	178	1.42	179	1.94	206	3.79
83	0	79	0.08	72	0.31	81	0.10	73	0.22	83	0	67	0.29	74	0.07	68	0.07	63	0

Frequencies (cm^{-1}) and intensities (kmmole^{-1}) for the HFCs calculated using the HF method.

170		161		152		152a		143		143a		134		134a		125	
Freq.	Intens.	Freq.	Intens.	Freq.	Intens.	Freq.	Intens.	Freq.	Intens.	Freq.	Intens.	Freq.	Intens	Freq.	Intens.	Freq.	Intens.
2931	101.69	2954	94.09	2978	92.62	2976	78.79	2994	69.82	2981	11.11	3011	59.75	2997	23.95	3002	30.39
2931	101.69	2940	48.28	2954	0	2959	22.16	2977	9.07	2981	11.11	3002	0	2942	16.96	1470	2.66
2909	0	2931	1.41	2922	74.39	2956	5.69	2929	23.87	2906	2.23	1480	0	1490	9.17	1389	27.05
2909	0	2904	39.20	2921	0	2891	6.56	1491	5.05	1457	0.19	1385	0	1451	19.52	1318	206.58
2870	0	2877	20.91	1513	3.44	1462	0.50	1460	15.78	1457	0.19	1358	92.66	1313	194.05	1267	389.50
2864	72.56	1507	0.54	1506	0	1459	11.87	1403	40.11	1433	94.16	1304	54.43	1302	193.42	1222	238.46
1477	5.70	1473	2.14	1450	0	1435	73.44	1339	41.21	1280	178.68	1158	399.94	1233	303.87	1173	141.34
1477	5.70	1456	3.00	1343	29.56	1395	48.70	1240	15.69	1266	281.34	1145	0	1201	56.06	1133	146.36
1472	0	1421	36.01	1271	0	1380	8.09	1152	132.71	1266	281.34	1131	0	1104	107.32	861	61.96
1472	0	1385	4.43	1213	6.92	1162	160.70	1132	173.54	980	47.06	1125	284.31	983	64.20	708	44.80
1415	0	1272	0.31	1158	0	1149	94.40	1117	36.73	980	47.06	1098	0	831	20.03	571	1.92
1386	0.14	1172	6.48	1073	0	1121	57.13	1086	81.48	813	4.24	613	0	648	42.45	560	19.03
1198	0	1110	55.65	1070	251.87	961	56.53	897	39.99	579	30.08	530	13.82	530	13.07	506	12.02
1198	0	1046	63.53	1048	0	849	11.47	558	6.27	524	2.68	478	0	518	4.24	407	1.80
951	0	869	16.82	786	0.67	549	8.46	474	24.27	524	2.68	412	63.04	395	0.93	351	0.12
796	2.50	787	0.03	445	0	450	16.29	411	7.09	351	0.45	352	0	346	1.18	239	5.25
796	2.50	393	7.23	275	23.41	365	0.006	234	9.54	351	0.45	194	3.06	210	3.98	201	3.20
292	0	244	0.92	130	15.77	231	0.09	120	9.37	225	0	85	3.16	107	6.96	73	1.14

Frequencies (cm^{-1}) and intensities ($kmmole^{-1}$) for HFC170, HFC161, HFC152, HFC152a calculated using the MP2 method.

170		161		152		152a	
Freq.	Intens.	Freq.	Intens.	Freq.	Intens.	Freq.	Intens.
3024	54.72	3034	27.80	3028	58.99	3051	9.86
3024	54.72	3031	18.30	3007	0	3047	7.69
3006	0	2994	29.51	2960	52.83	2981	49.80
3006	0	2942	12.21	2955	0	2953	2.09
2934	45.20	2941	35.48	1510	2.12	1463	0.30
2933	0	1504	0.11	1502	0	1461	4.83
1483	8.61	1476	2.70	1424	0	1412	77.92
1483	8.61	1460	4.88	1318	17.94	1370	41.11
1479	0	1403	33.24	1260	0	1363	5.09
1479	0	1370	4.66	1189	2.94	1137	126.55
1406	0	1260	0.03	1145	0	1133	29.75
1381	1.77	1162	4.89	1070	0	1120	86.02
1198	0	1102	25.26	1053	170.10	942	52.84
1198	0	1052	57.70	1043	0	853	9.60
990	0	874	13.63	789	0.09	537	6.85
801	4.66	790	0.52	440	0	440	13.00
801	4.66	389	6.29	263	19.81	363	0.07
312	0	262	0.67	133	13.04	252	0.10

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