The Out-of-Plane Vibrations of the Fluorinated Benzenes

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It is a capital mistake to theorize before one has data.

(Sir Arthur Conan Doyle)

Abstract

From the fundamental frequencies of the out-of-plane vibrations of Benzene and nineteen Fluorine substituted Benzenes, a number of force fields have been calculated using the perturbation method. Of these fields, only a 23 parameter force field fitted to the frequencies of all the molecules, which reproduces the observed frequencies to within 19cm^{-1} with an average error of 5.85cm^{-1}, is found to be acceptable. This field is in agreement with Scherer's similar field for the Chlorine substituted Benzene and those force constants which overlap with Benzene are in agreement with the values calculated by Whiffen. The fact, that the diagonal force constants for the C-H and C-F out-of-plane angle bends decrease with increasing Fluorine substitution at the ring position adjacent to the moving substituent, is discussed.

Reassignments of the fundamentals were made for most of the molecules and, for some of them, the gas phase far infrared spectra were recorded for the first time. The a_{2u} fundamental of Hexafluoro Benzene is discussed in some detail with particular reference to the use of time correlation functions in making vibrational assignments.

Also, the absolute infrared intensities of the out-of-plane vibrations of 1,4 difluoro Benzene and 1,3,5 trifluoro Benzene have been measured. The results were interpreted assuming that the rehybridization moment of +0.3 D.rad^{-1}, which Steele and Wheatley suggested is acting during both C-H and C-F out-of-plane angle bends of Benzene and Hexafluoro Benzene respectively, acts also in these molecules. Therefore, bond moments of +0.29 D (C-H) and -0.92 D (C-F) in 1,4 difluoro Benzene and +0.42 D (C-H) and -1.05 D (C-F) in 1,3,5 trifluoro Benzene, which are in reasonable agreement with currently accepted values, were calculated. In analysing the results, the electro-optical theory of Gribov was used.

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PART I

The Force Fields

INTRODUCTION.

An experimentally observed infrared absorption band has, in general, three characteristics. They are:-

i. Position or Frequency,

ii. Size or Intensity,

iii. Shape.

Taking these characteristics either singly, or in pairs, or altogether, much useful information about the molecule being studied can be obtained.

Band frequencies are used normally to provide analytical information to help in the identification of molecules or certain groups of atoms in molecules. However, they can also be used to calculate the force field and the eigen vectors, which describe the complex form of a vibration in terms of bond parameters, of a molecule.

From bond intensities the changes in the dipole of a molecule with respect to the changes in the normal coordinates (or dipole moment derivatives) can be calculated. Using the eigen vectors calculated from the band frequencies, the dipole moment derivatives can be interpreted in terms of bond properties, i. e. the dipole moment of a bond (the bond moment) or the change in dipole moment with respect to the deformation (either stretching or bending) of a bond (the bond moment derivative).

The information supplied by the band shape is perhaps that least used. In the gas phase the band shape depends on, amongst other things, the resolution of the spectrometer (as to a lesser extent do band frequencies and intensities), and the higher the resolution the greater the amount of detailed information that can be obtained. However, this information is normally only obtainable for light molecules but for all molecules the overall band shape of a particular vibration in the gas phase can provide information as to which symmetry species of the molecule being studied this vibration belongs. In all phases the shape of an infrared band is directly connected with its time correlation function, which considers an infrared band from a time development approach.

All three characteristics are dependant, to some degree, on whether the molecule being studied is in the gas, liquid (pure or solution) or solid (amorphous or crystalline) phase. In the dilute gas phase intermolecular interactions are minimised so it is in this phase that the most 'pure' information can be obtained. This does not mean that information derived from other phases is inferior; it is simply different.

In Part I the band frequencies of the out-of-plane vibrations of twenty Fluorine substituted Benzenes are used to calculate a number of force fields for these molecules. The Fluorine substituted Benzenes form an ideal system for studying the effect of increasing substitution of the Benzene ring. They are readily available (except for 1,2,3 trifluoro Benzene), all are volatile so they can be studied in the gas phase and some vibrational data are reported for all of them in the literature.

The inequality rule of Steele and Whiffen (37) predicts that, on replacing a Hydrogen atom in molecule A with a Fluorine atom to produce molecule B, then the ith highest frequency of B lies below the ith highest but above the i+1 th highest frequency of A provided there is only one internal coordinate involving the altered atom, provided that there is no change in the force field on going from molecule A to molecule B. On going through the series of molecules from Benzene to Hexafluoro Benzene the fundamental frequencies decrease. If this decrease can be explained on the basis of the inequality rule alone then there will be no force field changes on going through the series. However, if it cannot, then allowance will have to be made for this in the force fields.

Radcliffe and Steele (24) fitted a 15 parameter force field to the fundamental frequencies of the out-of-plane vibrations of Benzene, Fluoro Benzene, 1,4 difluoro Benzene and their fully deuterated analogues, which formed the starting field for all the calculations reported here. When Radcliffe and Steele tried to fit a field to the above molecules plus Hexafluoro Benzene, the accuracy of the fit of the force field to the observed frequencies got worse. This suggests that there are changes in the force field with increasing Fluorine substitution, which Radcliffe and Steele did not allow for.

Scherer (115) fitted a 23 parameter force field to the out-of-plane vibrations of twenty five Chlorine substituted Benzenes. Scherer found that the diagonal force constants for the C-H and C-Cl out-of-plane angle bends decrease on substituting a Fluorine atom for a Chlorine atom at the ring postion adjacent to the moving substituent. This means that there is a change in force field on going through the Chlorine substituted Benzenes.

In Chapter One the general methods involved in calculating frequencies, eigen vectors and force constants are outlined. In Chapter Two the fundamental frequencies of the out-of-plane vibrations of the Fluorine substituted Benzenes considered here are determined and assigned to their symmetry species. In Chapter Three force fields and force constants are considered, first in general, then in particular with reference to the Fluorine substituted Benzenes. The force fields for these molecules are then calculated and discussed. Finally, in Chapter Four the computer programs used in making these calculations are outlined.

CHAPTER ONE General Theory of Normal Coordinate Analysis.

SECTION 1.1 A diatomic molecule.

A simple diatomic molecule is considered, first using the classical model of two particles of masses m_1 and m_2 joined by a spring. Hooke's law states that when the spring is displaced from its equilibrium position a restoring force f is induced which is proportional to the displacement Δx but acts in the opposite direction.

Therefore $f = -k\Delta x$

where k is the force constant - the restoring force per unit displacement from the equilibrium position.

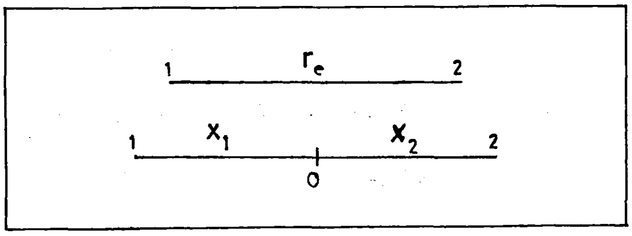


FIGURE 1.1

The force, which acts on both particles, produces an acceleration.

By Newton's second law of motion,

$$k\Delta x = -m_1 \ddot{x}_1 = -m_2 \ddot{x}_2 \qquad 1$$

If the equilibrium distance is r_e and the instantaneous separation r

$$r = x_1 + x_2 \qquad 2$$

and $$\Delta x = r - r_e \qquad 3$$

If the centre of gravity is taken as the origin,

$$m_1 x_1 = m_2 x_2$$

substituting for x_2 using equation 2,

$$x_1 = \frac{m_2}{m_1 + m_2} r$$

Therefore $$\ddot{x}_1 = \frac{m_2}{m_1 + m_2} \ddot{r} \qquad 4$$

substituting in 1 using 3 and 4,

$$k (r - r_e) = -M\ddot{r} \qquad 5$$

where M is the reduced mass given by

$$M = \frac{m_1 m_2}{m_1 + m_2}$$

Equation 5 is that of Simple Harmonic Motion and its solution is

$$r - r_e = A \cos 2\pi vt \qquad 6$$

$$\ddot{r} = 4\pi^2 v^2 A \cos 2\pi vt$$

Therefore $k = 4\pi^2 v^2 M$

and the frequency v is given by

$$v = 1/2\pi . (k/M)^{1/2} \qquad 7$$

Equation 7 is an important classical result. It shows that two particles of reduced mass M, joined by a spring of force constant k, vibrate according to equation 6 with frequency given by equation 7.

When a diatomic molecule is displaced from its equilibrium position, its electron cloud is distorted and exerts a restoring force in the same manner as the spring. Therefore it vibrates at a frequency v, determined by its reduced mass and force constant. The vibration is accompanied by the absorption of electromagnetic radiation of frequency v and energy hv. This absorption for molecular vibrations occurs in the Infra Red (IR) region of the electromagnetic spectrum (100 - 5000 cm.^{-1}).

This mathematical treatment of the diatomic molecule cannot be generalized to polyatomics. For convenience the general method to be derived later is now applied to the diatomic molecule.

This requires the solving of the equation $GFL = L\Lambda$ for one internal coordinate, a bond stretch.

$$\begin{aligned} G &= BM^{-1}B^t \\ &= (1 \; -1) \begin{vmatrix} 1/m_1 & 0 \\ 0 & 1/m_2 \end{vmatrix} \begin{vmatrix} 1 \\ -1 \end{vmatrix} \\ &= 1/m_1 + 1/m_2 = 1/M \end{aligned}$$

$F = k$ the force constant

Therefore the eigen value λ is

$$\lambda = k/M$$

The eigen value L is arbitrarily given the value unity.

λ is related to the frequency v by $\lambda = 4\pi^2 v^2$.

Therefore $v = 1/2\pi \; (k/M)^{\frac{1}{2}}$

Example: Hydrogen Fluoride.

$$\bar{v} = 3958.4 \text{ cm}^{-1}$$

$\bar{v}$ denotes the frequency in wave numbers (cm^{-1}).

Therefore $\bar{v} = 1/\lambda = v/c$.

From Kaye and Laby (1),

H = 1.00797 qmu and F = 18.9984 qmu

Avagadro's Number $N = 6.02252.10^{23}$ mol.^{-1}

Velocity of Light $c = 2.997925.10^{10}$ cm.S^{-1}

$\pi = 3.14159$

Therefore $M = .95719/N$ g

and $v = c\bar{v} = 1.18670.10^{14}$Hz

Therefore $k = 4\pi^2 v^2 M$

$= 8.836.10^5$ dyn.cm^{-1}

Alternative units are millidynes per Angstrom (mdyn.A^{-1}).

Since 1A = 10^{-5} cm and 1 mdyn = 10^{-3} dyn

1 dyn.cm^{-1} = 10^{-5} mdyn. A^{-1}

Therefore k (for HF) = 8.836 mdyn.A^{-1}

This unit ideally expresses force constants on a molecular scale and is used throughout.

In S.I. units a force constant is expressed in Newtons per metre (N.m^{-1}).

Since 1N = 10^5 dyn = 10^8 mdyn

and 1M = 10^2 cm = 10^{10} A

1 N.M^{-1} = 10^2 mdyn. A^{-1}

Therefore k (for HF) = $8.836.10^2$ N.M^{-1}

Barrow (2), Chapter 2, is a general reference to this section.

SECTION 1.2 The Kinetic and Potential Energy Expressions.

The general problem is now considered in classical mechanics.

The Kinetic Energy T of a particle in motion is given by

$$T = mv^2/2$$

where m is its mass and v its velocity.

Its momentum p is given by

$$p = mv$$

Therefore $T = p^2/2m$

The Kinetic Energy of a system of particles or atoms (i.e. a molecule) in motion is now considered. The instantaneous position of each atom is defined by three Cartesian coordinates denoted generally by q. The Kinetic Energy of the molecule is

$$T = \tfrac{1}{2}\sum_k m_k \dot{q}_k{}^2 \qquad 8$$

where the summation is over all the 3n Cartesian coordinates associated with a molecule containing n atoms. m_k is the mass of the atom associated with the k th Cartesian coordinate q_k and $\dot{q}_k$ is the instantaneous velocity given by

$$\dot{q}_k = dq_k/dt$$

The Cartesian coordinate system is not a convenient system to define the internal vibrations of a molecule. The 3n degrees of freedom (i.e. one independent motion along each coordinate) can be redefined as 3 corresponding to translation of the molecule as a whole, as 3 corresponding to rotation of the molecule as a whole, and the remaining 3n-6 degrees of freedom as internal changes in the positions of the atoms in the molecule with no overall translation or rotation. These internal changes are known as the Internal Coordinates of the molecule (for a fuller discussion see Section 1.11) and this is the coordinate system in which the Kinetic Energy must be expressed.

Equation 8 is differentiated with respect to $\dot{q}_k$

$$dT/d\dot{q}_k = m_k\dot{q}_k = p_k \qquad 9$$

where p_k is the momentum conjugate with q_k. p_k is expanded as a series of partial derivatives.

$$p_k = \Sigma_i \, \delta T/\delta \dot{R}_i \, \delta R_i/\delta q_k \qquad 10$$

where R_i is the ith Internal Coordinate and the summation is over all 3n-6 Internal Coordinates.

A further term must be included to take account of changes in Kinetic Energy due to translation or rotation of the molecule as a whole.

Therefore $+ \dfrac{\delta T}{\delta(\text{Tr,Rot})} \times \dfrac{\delta(\text{Tr,Rot})}{\delta T}$

However, if the molecule is assumed to be moving in a coordinate system whose origin is at, and moves with, the centre of gravity of the molecule, and which rotates with the molecule, the momentum associated with translation and rotation is zero.

If, by comparison with equation 9

$$P_i = \delta T/\delta \dot{R}_i$$

where P_i is the internal momentum conjugate with the ith Internal Coordinate R_i, and

$$b_{ik} = \delta R_i/\delta q_k$$

where b_{ik} relates the change in the ith Internal Coordinate with the change in kth Cartesian Coordinate, then equation 10 becomes

$$p_k = \Sigma_i \; P_i b_{ik}$$

substituting in equation 8

$$T = \tfrac{1}{2}\Sigma_k(\Sigma_i P_i b_{ik})^2/m_k \qquad 11$$

The term $(\Sigma_i P_i b_{ik})^2$ can be alternatively expressed, without any change of meaning as $\Sigma_i P_i b_{ik} \cdot \Sigma_j P_j b_{jk}$. In both cases the expansion is performed before the multiplication and the summation over i and j is over all 3n-6 Internal Coordinates.

Equation 11 becomes

$$T = \tfrac{1}{2}\sum_k \sum^2{}_{i,j} (b_{ik}b_{jk})/m_k . P_i P_j$$

$$= \tfrac{1}{2}\sum_i{}^2{}_{,j}\ g_{i,j}\ P_i P_j \qquad 12$$

where $g_{i,j} = \sum_k (b_{ik}b_{jk})/m_k$

In matrix notation

$$2T = P^t GP \qquad 13$$

where P is a column matrix, dimension 3n-6, whose ith element is the Internal Momentum p_i. G is a square matrix, dimension (3n-6) by (3n-6) defined by

$$G = BM^{-1}B^t \qquad 14$$

where B is a rectangular matrix, dimension (3n-6) by 3n, whose i,k th element is b_{ik}. M^{-1} is a square diagonal matrix, dimension 3n by 3n, whose k,k th element is $1/M_k$ and whose off diagonal elements are zero.

For a discussion of matrix notation and algebra see Appendix I.

The potential Energy of a molecule is a function of the positions of the atoms. In terms of the Internal Coordinates, the Potential Energy V $(R_1 \ldots R_{3n-6})$ represents the internal energy as a function of the relative positions of the atoms, and is not affected by translational or rotational motions of the rigid molecule, (Duinker (3), p.20). It is represented by a hypersurface in $3n-5$ dimensional space, (i.e. $3n-6$ internal coordinate variables and one Potential Energy variable), with a minimum at the equilibrium configuration. When the molecule is displaced from its equilibrium position the electron cloud is distorted and exerts a force which tends to restore the molecule to its equilibrium position.

Since V is a continuous function of the Internal Coordinates it can be expanded as a Taylor Series, (4), p.283. The general expansion is

$$f(b) = f(a) + (b-a)\, f'(a) + (b-a)^2\, f''(a)/2! + (b-a)^3\, f'''(a)/3! + \ldots$$

Therefore if b represents the instantaneous Internal Coordinate R_i, and a the Internal Coordinate at the equilibrium position R_i^e

$$\begin{aligned} V(R_1 \ldots R_{3n-6}) = {} & V(R^e 1 \ldots R^e{}_{3n-6}) + \\ & \sum_i (R_i - R_i^e) \left| \frac{\partial V}{\partial R_i} \right|_e \\ & + \frac{1}{2} \sum_{i,j}^{2} (R_i - R_i^e)(R_j - R_j^e) \left| \frac{\partial V}{\partial R_i \partial R_j} \right|_e \\ & + \frac{1}{6} \sum_{i,j,k}^{3} (R_i - R_i^e)(R_j - R_j^e) \\ & x \; (R_k - R_k^e) \left| \frac{\partial V}{\partial R_i \partial R_j \partial R_k} \right|_e + \ldots \end{aligned} \qquad 15$$

where the summations i,j,k ... are over all $3n-6$ Internal Coordinates and the subscript e indicates that the expansion is about the equilibrium position.

$Vo = V(R^e{}_1 \ldots R^e{}_{3n-6})$ is the zero point energy and is arbitrarily given the value zero.

It is usually assumed that $\sum_i(\partial V/\partial R_i)_e = 0$. This assumption is further considered in Section 1.14.

Provided that the displacements from the equilibrium position are small, the third and higher order terms can be neglected. This follows from the fact that $dR_i dR_j$ is much greater than $dR_i dR_j dR_k$ (where dR_i is the change in the ith internal coordinate from the equilibrium position i.e. $R_i - R_i^e$) although

$$\left|\frac{\partial^2 V}{\partial R_i \partial R_j}\right|_e \sim \left|\frac{\partial^3 V}{\partial R_i \partial R_j \partial R_k}\right|_e$$

Therefore equation 15 reduces to

$$V(R_1 \ldots R_{3n-6}) = \frac{1}{2}\sum_{i,j}^{2}\left|\frac{\partial^2 V}{\partial R_i \partial R_j}\right|_e dR_i dR_j$$

$$= \frac{1}{2}\sum_{i,j}^{2} f_{i,j}\ dR_i dR_j \qquad 16$$

where $f_{i,j} = \left|\frac{\partial^2 V}{\partial R_i \partial R_j}\right|_e$

and are the force constants.

Equation 16 is the Harmonic Oscillator approximation in which the Potential Energy is expressed as the sum of a series of quadratic (second order) terms. In matrix form it becomes

$$2V = R^t F R \qquad 17$$

where R is a column matrix, dimension 3n-6, whose ith element is dR_i, the displacement of the ith Internal Coordinate from the equilibrium position. F is a square matrix, dimension (3n-6) by (3n-6), whose i,j th element is $f_{i,j}$.

The diagonal elements $f_{i,i}$ of the F matrix are the primary force constants and are often correlated with the strength of a particular chemical bond. They are always positive in sign, since if R_i is displaced V increases according to

$$2V = f_{ii}\, dR_i^2$$

dR_i^2 is always positive, therefore f_{ii} is always positive.

The off diagonal elements $f_{i,j}$ are the interaction force constants. They can be either positive or negative. They are understood by the following argument, Duinker (3), p.21.

If only dR_1 is not equal to zero

$$2V = f_{11}\, dR_1^2$$

A new relative minimum can be achieved by displacing R_2.

$$2V = f_{11}\, dR_1^2 + 2f_{12} dR_1 dR_2 + f_{22} dR_2^2 \qquad 18$$

The new minimum is given by

$$(\partial V/\partial dR_1) = 0 = f_{11} dR_1 + f_{12} dR_2$$

$$dR_2 = - f_{11}/f_{12}\, dR_1 \qquad 19$$

Substituting for dR_2 in equation 18

$$2V = (- 1 + f_{11} f_{22}/f_{12}^2)\, f_{11}\, dR_1^2$$

This is only equal to zero if the two minima coincide

$$\text{when } f_{11} = 0$$

$$\text{or } f_{12}^2 = f_{11}\, f_{12}$$

Equation 19 shows that if to achieve a new minimum following an increase in R_1 ($dR_1 > 0$) it is necessary to:

increase R_2 ($dR_2 > 0$) the interaction force constant

f_{12} is negative,

decrease R_2 ($dR_2 < 0$) the interaction force constant

f_{12} is positive.

SECTION 1.3 Equations of Motion in Hamiltonian form.

For general coordinates the momentum p_i associated with coordinate q_i is given by, (Eyring, Walter and Kimball (5), p.14).

$$p_i = dL/d\dot{q}_i$$

where L is the total energy of the system under consideration, i.e. $L = T + V$.

The Hamiltonian Equations of Motion are

$$d(T + V)/dp_i = \dot{q}_i \qquad d(T + V)/dq_i = - \dot{p}_i$$

Since the coordinates q_i and momenta p_i are independent variables

$$dV/dp_i = 0 \qquad dT/dq_i = 0$$

i.e. the Potential Energy V is not a function of momentum and the Kinetic Energy T is not a function of position.

Therefore

$$dT/dp_i = \dot{q}_i \qquad dV/dq_i = - \dot{p}_i \qquad 20$$

In terms of the Internal Momenta P_i and the change in the Internal Coordinates dR_i, the Hamiltonian Equations of Motion are

$$dT/dP_i = \dot{R}_i \qquad dV/d(dR_i) = - \dot{P}_i \qquad 21$$

From Equations 12 and 16

$$2T = \sum_{i,j}^{2} g_{i,j} P_i P_j \qquad 2V = \sum_{i,j}^{2} f_{i,j} dR_i dR_j$$

Differentiating

$$dT/dP_i = \sum_j g_{i,j} P_j \qquad dV/d(dR_i) = \sum_j f_{i,j} dR_j$$

(The loss of the terms $\frac{1}{2}$ occur since $g_{i,j} = g_{j,i}$ and $f_{i,j} = f_{j,i}$.)

Therefore

$$\sum_j g_{i,j} P_j = \dot{R}_i \qquad \sum_j f_{i,j} dR_j = -\dot{P}_i$$

where

$$\dot{R}_i = d(R_i)/dt \qquad \dot{P}_i = d(P_i)/dt$$

In matrix form

$$GP = \dot{R} \quad 22 \qquad FR = -\dot{P} \quad 23$$

where $\dot{R}$ is a column matrix, dimension 3n-6, whose ith element is $\dot{R}_i$, and $\dot{P}$ is a column matrix, dimension 3n-6, whose ith element is $\dot{P}_i$.

By strict analogy with equation 20, the Hamiltonian Equations should be expressed in terms of Pi and R_i.

i.e. $dV/dR_i = -\dot{P}_i$ 24

However $dR_i = R_i - R_e$

$d(dR_i) = dR_i$

since R_e is a constant.

Therefore equations 21 and 24 are equivalent.

SECTION 1.4 Normal Coordinates

It is necessary to introduce a new set of coordinates Q. They are known as the Normal Coordinates and are defined in terms of the internal coordinates by the linear transformation

$$dR_i = \sum_j l_{i,j}\, dQ_j \quad \text{or} \quad dR_i/dQ_j = l_{i,j}$$

where the summation j is over all 3n-6 normal coordinates (again, one for each degree of vibrational freedom).

In matrix form

$$R = LQ \qquad 25$$

where Q is a column matrix, dimension 3n-6, whose jth element, dQ_j, is the change in the jth Normal Coordinate. L is a square matrix, dimension (3n-6) by (3n-6), whose i,j th element is $l_{i,j}$, the coefficient which relates the change in the ith Internal Coordinate with that in the jth Normal Coordinate.

The coefficients $l_{i,j}$ are chosen such that the Kinetic and Potential Energy expressions have the form

$$2T = \sum_i \dot{Q}_i^{\,2} \qquad 26 \qquad 2V = \sum_i \lambda_i\, dQ_i^{\,2} \qquad 27$$

where the summation i is over all 3n-6 Normal Coordinates. λ_k is a constant related to the k th vibrational frequency, and $\dot{Q}_i = dQ_i/dt$.

In equation 26 the Kinetic Energy expression contains no cross terms involving $\dot{Q}_i\,\dot{Q}_j$ and equation 27 the Potential Energy expression contains no cross terms involving $dQ_i\,dQ_j$. This means that when expressed in Normal Coordinates the Kinetic and Potential expressions can be expanded in a series of separate terms, each term corresponding to one vibrational degree of freedom. Therefore, with each Normal Coordinate is associated only one fundamental vibration (or Normal Mode), which is associated with only this Normal Coordinate.

In matrix form equations 26 and 27 are

$$2T = \dot{Q}^t\dot{Q} \qquad 28 \qquad 2V = Q^t \Lambda Q \qquad 29$$

where $\dot{Q}$ is a column matrix, dimension 3n-6, whose ith element is $\dot{Q}_i$. Λ is a square diagonal matrix, dimension(3n-6) by (3n-6), whose i,i th element is λ_i and whose off diagonal elements are zero.

The relationship between the constants λ and the fundamental frequencies is given by substituting for T and V in Lagrange's Equation of Motion

$$d/dt.\ (dT/d\dot{Q}_i) + dV/dQ_i = 0$$

Substituting for T using equation 26

$$\begin{aligned} d/dt.\ (dT/d\dot{Q}_i) &= d/dt.\ \dot{Q}_i \\ &= \ddot{Q}_i \end{aligned}$$

Substituting for V using equation 27

$$V = \sum_i \lambda_i\, dQ_i^2 = \sum_i \lambda_i\, (Q_i - Q_i^e)^2$$

where Q_i^e is the ith equilibrium normal coordinate and $dQ_i = Q_i - Q_i^e$.

Therefore $dV/dQ_i = \lambda_i\, (Q_i - Q_i^e)$

Therefore $\ddot{Q}_i + \lambda_i\, (Q_i - Q_i^e) = 0$

This is the equation for simple harmonic motion and the solution is

$$Q_i - Q_i^e = Q_i^e \sin 2\pi v_i t$$

$$\ddot{Q}_i = -4\pi^2 v_i^2\, Q_i^e \sin 2\pi v_i t$$

Therefore $\lambda_i = 4\pi^2\, v_i^2$ 30

SECTION 1.5 The Secular Equation

In Sections 1.2, 1.3 and 1.4 the following matrix equations have been derived

$2T = P^t G P$ 13 $2V = R^t F R$ 17

$2T = \dot{Q}^t \dot{Q}$ 28 $2V = Q^t \Lambda Q$ 29

$\dot{R} = GP$ 22 $-\dot{P} = FR$ 23

also be definition $R = LQ$ 25

A method is required to calculate λ - the constants, which are related to the vibrational frequencies and L, the matrix whose elements related the Normal Coordinates to the Internal Coordinates.

From equation 22

$$P = G^{-1}\dot{R}$$

substituting in equation 13

$$\begin{aligned} 2T &= (G^{-1}\dot{R})^t \, G(G^{-1}\dot{R}) \\ &= \dot{R}^t G^{-1} \dot{R} \qquad 31 \end{aligned}$$

Since $GG^{-1} = E$ by definition

and $(G^{-1})^t = (G^t)^{-1} = G^{-1}$

Since G is a symmetric matrix i.e. $G = G^t$

Equation 31 gives the Kinetic Energy in terms of the time derivates of the Internal Coordinates and G^{-1}, the therefore G is sometimes referred to as the Inverse Kinetic Energy Matrix.

It can be shown from equation 25 that

$$\dot{R} = L\dot{Q}$$

provided L is invariant with time.

Substituting for $\dot{R}$ in equation 31

$$2T = \dot{Q}^tL^tG^{-1}L\dot{Q}$$

Therefore by comparison with equation 28

$$L^tG^{-1}L = E$$

$$G^{-1} = (LL^t)^{-1}$$

or $$G = LL^t \qquad 32$$

Substituting for R in equation 17 using equation 25

$$2V = Q^tL^tFLQ$$

Therefore by comparison with equation 29

$$L^tFL = \Lambda \qquad 33$$

Combining equations32 and 33

$$LL^tFL = L\Lambda$$

$$GFL = L\Lambda \qquad 34$$

If $$H = GF$$

$$HL = L\Lambda$$

where H is the Vibrational Secular Matrix with eigen vectors L and eigen values Λ. Therefore, provided G and F are known, L and Λ can be calculated.

The elements of the G matrix are determined from the B matrix and the masses. The calculation of the B matrix is considered in Section 1.11.

The elements of the F matrix are the individual force constants. In general, they cannot be known prior to the calculation of the frequencies, as they are calculated from the frequencies. The method of calculation is considered in Section 1.7.

The eigen values λ_i are the diagonal elements of the matrix Λ. It follows from equation 34 that λ_i has the same units as GF.

The units of G are a.m.u.$^{-1}$ $=$ $(g/N)^{-1}$
The units of F are mdyn. A^{-1} $=$ 10^5 dyn.cm^{-1}

Therefore the units of GF are

$$(\text{a.m.u})^{-1}.\ (\text{mdyn.A}^{-1}) = 10^5 N\ \text{dyn.cm.}^{-1}\text{g.}^{-1}$$
$$= 10^5 N\ s^{-2}$$

Therefore to express λ_i in (seconds)$^{-2}$ the derived values are multiplied by 10^5N.

The units of the frequency v_i are (seconds)$^{-1}$. However vibrational frequencies are usually expressed in wavenumbers (or cm^{-1}) and are obtained by

$$\bar{v}_i = v_i/c$$

where $\bar{v}_i$ denotes the frequency in wavenumbers.

The eigen value λ_i and frequency v_i are related by equation 30.

$$\lambda_i = 4\pi^2 v_i^2$$
or
$$v_i = \lambda_i^{\frac{1}{2}}/2\pi$$

Therefore if λ_i is the calculated eigen value in (a.m.u)$^{-1}$ (mdyn.A^{-1}), the calculated frequency in wavenumbers is given by

$$\bar{v}_i = \frac{(N.10^5)^{\frac{1}{2}}}{2\pi C} \lambda_i^{\frac{1}{2}}$$

Using the values for N, π and C given in section 1.1.

$$\bar{v}_i = 1302.83\,\lambda_i^{\frac{1}{2}} \qquad 35$$

SECTION 1.6 The Φ and Z matrices

Before considering the calculation of the force constants it is necessary to consider further how they constitute the F matrix. For a F matrix of dimension n by n, there are n^2 elements. However since F is a symmetric matrix, i.e. $f_{i,j} = f_{j,i}$ (this follows from the definition of $f_{i,j}$, section 1.2), only $n(n + 1)/2$ elements need be considered (i.e. the n diagonal and $(n^2 - n)/2$ off-diagonal elements. These are not necessarily all different since a number of internal coordinates may refer to the same type of bond and therefore the force constants involving these internal coordinates are identical.

For H_2O there are two internal coordinates (R_1 and R_2) which refer to the OH bond stretches. The diagonal force constant for an OH bond stretch is denoted fr and is obviously the same for R_1 and R_2. There is a third internal coordinate (R_3) which refers to the HOH angle bend and the associated force constant is denoted fA. There is one bond stretch/bond stretch interaction, for which the force constant is denoted ffRR. There are two bond stretch/angle bend interactions, between R_1 and R_3, and R_2 and R_3 but there is only one force constant denoted by ffRA.

The F matrix for H_2O is

	R_1	R_2	R_3
R_1	fR	ffRR	ffRA
R_2	ffRR	fR	ffRA
R_3	ffRA	ffRA	fA

Therefore, for H_2O, there are only four independent force constants out of a possible total of six.

In general, a column matrix Φ is set up to contain the independent force constants, each occurring once only. The ith element of Φ is ϕ_i.

If there are M independent force constants required in constructing the F matrix, dimension n by n, it is necessary to define M Z matrices, each of dimension n by n, one for each force constant. These Z matrices are known as specification matrices and are evaluated as follows.

If the F matrix has the same force constant ϕ_i in positions $f_{j,k}$ (and $f_{k,j}$) and $f_{l,m}$ (and $f_{m,l}$), the ith Z matrix Z^i will have non zero values at $z_{j,k}$ (and $z_{k,j}$) and $z_{l,m}$ (and $z_{m,l}$) and zeros in all other positions. The non zero values are the factors with which ϕ_i appears in F. Multiplying the scalar ϕ_i by the matrix Z^i gives the contribution of ϕ_i to the F matrix.

Therefore $$F = \Sigma_i \phi_i Z^i \qquad 36$$

where the summation i is over all force constants.

For H_2O the $\mathbf{\Phi}$ matrix is

$$\begin{matrix} \phi_1 & fR \\ \phi_2 & fA \\ \phi_3 & ffRR \\ \phi_4 & ffRA \end{matrix}$$

and the $\mathbf{Z}$ matrices are

$$\mathbf{Z}^1 = \begin{matrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{matrix} \qquad \mathbf{Z}^2 = \begin{matrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{matrix}$$

$$\mathbf{Z}^3 = \begin{matrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{matrix} \qquad \mathbf{Z}^4 = \begin{matrix} 0 & 0 & 1 \\ 0 & 0 & 1 \\ 1 & 1 & 0 \end{matrix}$$

and $F = \phi_1 \mathbf{Z}^1 + \phi_2 \mathbf{Z}^2 + \phi_3 \mathbf{Z}^3 + \phi_4 \mathbf{Z}^4$

In this example the non-zero elements are simply + 1.0. In some cases they can be - 1.0 (e.g. when $f_{j,k} = - f_{l,m}$). Other values are also possible and will be mentioned when they arise.

The set of independent force constants defined by matrix $\mathbf{\Phi}$ are known generally as a Force Field.

SECTION 1.7 The Iterative Refinement of Force Constants

As stated in Section 1.5 it is necessary to evaluate the force constants from a prior knowledge of the frequencies. An iterative method of calculating force constants is presented.

An initial force field $\bar{\Phi}^1$ is postulated and a set of initial eigen values calculated. A function X^1 is defined which is a measure of the lack of agreement between the observed eigen values λ_i^{obs} and the calculated ones λ_i^{1}(6).

$$X^1 = \Sigma_i W_i (\lambda_i^{obs} - \lambda_i^{1})^2$$

where the summation i is over all n eigen values and w_i is the weighting factor for the ith eigen value (see Section 1.9).

Changes $\Delta \bar{\Phi}^1$ are made in the $\bar{\Phi}^1$ force field such that

$$\bar{\Phi}^1 \rightarrow \bar{\Phi}^2 = \bar{\Phi}^1 + \Delta \bar{\Phi}^1$$

so that on calculating a new set of eigen values Λ^2

$$X^2 < X^1$$

The process is repeated until $X^n = X^{n+1}$.

At this point X^{n+1} is not necessarily equal to zero. This follows from the fact that equation 16 is not an exact relationship but only a harmonic approximation. Therefore the calculated harmonic eigen values will not be exactly equal to the observed unharmonic eigen values but only at the best a harmonic approximation. (The approximation is still valid however since the differences are small). A residual vector r_i is defined so that

$$r_i = \lambda_i^{obs} - \lambda_i^{c}$$

where the set of eigen values Λ^c are the calculated set of "correct" eigen values - the closest approach to the observed eigen values.

Therefore if $\lambda_i^{n} = \lambda_i^{c}$

$$X^n = \Sigma_i w_i r_i^2$$ and is a minimum.

Since the eigen values are functions of the force constants, λ_i^n the ith eigen value calculated from the nth set of force constants Φ^n can be expanded as a Taylor power series in them.

$$\lambda_i^n(\phi_1^n \ldots \phi_m^n) = \lambda_i^c(\phi_1^c \ldots \phi_m^c) + \sum_j \left|\frac{\partial\lambda_i}{\partial\phi_j}\right|_c (\phi_j^n - \phi_j^c) + \frac{1}{2}\sum_{j,k}^{2}\left|\frac{\partial^2\lambda_i}{\partial\phi_j\partial\phi_k}\right|_c (\phi_j^n-\phi_j^c)(\phi_k^n-\phi_k^c) + \text{higher order terms.} \qquad 37$$

where the summations j and k are over all m force constants. The set of force constants Φ^c are the final "correct" set from which Λ^c is calculated.

$$\text{If } J^c_{i,j} = \left|\frac{\partial\lambda_i}{\partial\phi_j}\right|_c$$

where J^c is the Jacobian matrix, dimension n by m, whose i,j th element $J^c_{i,j}$ relates the change in the ith eigen value to that in the jth force constant. The superscript c indicates it is calculated for the values Φ^c and Λ^c.

$$\text{And} \qquad d\phi_j^n = \phi_j^c - \phi_j^n$$

and second and higher order terms are neglected, equation 37 becomes (noting the sign change)

$$\lambda_i^n = \lambda_i^c - \sum_j J^c_{i,j}\ d\phi_j^n \qquad 38$$

If $$\phi_j^{n+1} = \phi_j^n + d\phi_j^n$$

$$= \phi_j^n + \phi_j^c - \phi_j^n = \phi_j^c$$

$$\lambda_i^{n+1} = \lambda_i^c - \sum_j J_{i,j}^c (\phi_j^c - \phi_j^{n+1})$$

Therefore $\lambda_i^{n+1} = \lambda_i^c$

This implies that the correct set of eigen values Λ^c are reached after one stage of refinement. However, equation 38 is only an approximation, also the Jacobian J^c cannot be calculated until Φ^c is known. It can be calculated for Φ^n (see Section 1.8) and provided that the initial set of force constants Φ^1 is chosen carefully and the changes are small so that $J^n \sim J^{n+1}$ it can be stated that

$$\lambda_i^n = \lambda_i^{n+1} - \sum_j J_{i,j}^n \; d\phi_j^n \qquad 39$$

and $$\phi_j^{n+1} = \phi_j^n + d\phi_j^n \qquad 40$$

Assuming Φ^n is known Λ^n can be calculated (from equations 34 and 36). Therefore X^n can be calculated, but until $\Delta\Phi^n$ is known X^{n+1} cannot be calculated. By definition

$$X^{n+1} = \sum_i w_i(\lambda_i^{obs} - \lambda_i^{n+1})^2$$

substituting for λ_i^{n+1} from equation 39

$$X^{n+1} = \sum_i w_i (\lambda_i^{obs} - \lambda_i^n - \sum_j J_{i,j}^n \; d\phi_j^n)^2$$

$$= \sum_i w_i (\Delta\lambda_i^n - \sum_j J_{i,j}^n \, d\phi_j^n)^2 \qquad 41$$

where $\Delta\lambda_i^n = \lambda_i^{obs} - \lambda_i^n$

J^n is calculated from Φ^n and the values of $d\phi_j$ required are those which minimise X^{n+1}.

i.e. $$\frac{dX^{n+1}}{d(d\phi_j^{\,n})} = 0 \qquad \text{for all } j$$

Expanding equation 41 and dropping the superscript n so that normal power notation can be used,

$$\frac{d}{d(d\phi_j)} \left| \sum_i w_i \Delta\lambda_i^2 - 2\sum_i w_i \Delta\lambda_i \sum_j J_{i,j}\, d\phi_j + \sum_i w_i \left(\sum_j J_{i,j}\, d\phi_j \right)^2 \right| = 0 \qquad 42$$

Considering each differential separately

$$\frac{d}{d(d\phi_j)} \sum_i w_i \Delta\lambda_i^2 = 0$$

since neither λ_i^{obs} nor $\lambda_i^{\,n}$ is a function of $d\phi_j^{\,n}$.

$$\frac{d}{d(d\phi_j)} \sum_i w_i \Delta\lambda_i \sum_j J_{i,j}\, d\phi_j = \sum_i w_i \Delta\lambda_i J_{i,j}$$

If $$\sum_j J_{i,j} d\phi_j = J_{i,j}\, d\phi_j + \sum_k J_{i,k} d\phi_k$$

where the summation k is over all m force constants except j.

$$\frac{d}{d(d\phi_j)} \sum_i w_i \left(\sum_j J_{i,j}\, d\phi_j \right)^2$$

$$= \frac{d}{d(d\phi_j)} \sum_i w_i \left(J^2_{i,j}\, d\phi_j^{\,2} + 2J_{i,j} d\phi_j \sum_k J_{i,k} d\phi_k + \left(\sum_k J_{i,k} d\phi_k \right)^2 \right)$$

$$= \sum_i w_i \left(2J^2_{i,j} d\phi_j + 2J_{i,j} \sum_k J_{i,k} d\phi_k \right)$$

$$= 2 \sum_i w_i J_{i,j} \sum_k J_{i,k}\, d\phi_k$$

where summation k is now over all m force constants.

Therefore equation 42 becomes

$$- 2 \sum_i w_i \Delta \lambda_i J_{i,j} + 2 \sum_i w_i J_{i,j} \sum_k J_{i,k} d\phi_k = 0 \qquad 43$$

The differentiation has so far only been performed for one force constant $d\phi_j$. Therefore considering differentiation over all j, equation 43 becomes

$$\sum^2_{i,j} J_{i,j} w_i \Delta \lambda_i = \sum^3_{i,j,k} J_{i,j} w_i J_{i,k} d\phi_k \qquad 44$$

In matrix notation

$$J^t W \Delta \Lambda = J^t W J \Delta \Phi \qquad 45$$

where W is a square diagonal matrix, dimension n by n, whose i,i th element is w_i the weighting factor for the ith eigen value and whose off diagonal elements are zero.

$\Delta \Lambda$ is a column matrix, dimension n, whose ith element is $\Delta \lambda_i$.

$\Delta \Phi$ is a column matrix, dimension m, whose kth element is $d\phi_k$.

where n is the number of eigen values and m the number of force constants.

That equations 44 and 45 are the same can be proved by expansion of equation 45.

Since $J^t WJ$ must be a square matrix it can be inverted provided it is non-singular.

i.e. determinant $(J^t WJ) = 0$ 46

Therefore from equation 45

$$\Delta \Phi = (J^t WJ)^{-1} J^t W \Delta \Lambda \qquad 47$$

It follows that starting from Φ^1, J^1 and $\Delta \Lambda^1$ are calculated and hence $\Delta \Phi^1$. Then $\Phi^2 = \Phi^1 + \Delta\Phi^1$ and the process continues iteratively. Since the changes in the force constants $\Delta\Phi^n$ are chosen so as to minimise X^{n+1}, eventually $X^{n+1} = X^n$ i.e. $\Delta\Phi^n = 0$. Then X^n is a minimum, $X^n = X^c$, and $\Phi^n = \Phi^c$ the required set of force constants.

SECTION 1.8 Calculation of the Jacobian Matrix.

By definition the Jacobian matrix relates the changes in the eigen values to those in the force constants (see Section 1.7). The method of calculation is as described by Long, Gravenor and Woodger (6a).

Equation 34 states that

$$GFL = L\Lambda$$

If λ_i is the ith element of Λ and associated with it is L_i the ith column of L, the eigen vector matrix, then

$$GFL_i = \lambda_i L_i \qquad 48$$

If an arbitary change $\Delta\Phi$ is made in the force constant matrix so that

$$F \rightarrow F + \Delta F$$

and if the ith eigen value associated with $G(F + \Delta F)$ is $\lambda_i + d\lambda_i$, and the eigen vector is $L_i + \sum_j e_{i,j} L_j$ where $e_{i,j}$ is a constant, equation 48 becomes

$$G(F + \Delta F)(L_i + \sum_j e_{i,j} L_j) = (\lambda_i + d\lambda_i)(L_i + \sum_j e_{i,j} L_j) \qquad 49$$

where the summation j is over all n rows of the eigen vector matrix. Since G is a function of mass and geometry only it does not change.

Expanding equation 49

$$GFL_i + G\Delta FL_i + GF\sum_j e_{i,j} L_j + G\Delta F\sum_j e_{i,j} L_j$$
$$= \lambda_i L_i + d\lambda_i L_i + \lambda_i \sum_j e_{i,j} L_j + d\lambda_i \sum_j e_{i,j} L_j \qquad 50$$

From equation 48 $GFL_i = \lambda_i L_i$ is cancelled.

Also $\quad GF\sum_j e_{i,j} L_j = \sum_j \lambda_j e_{i,j} L_j$

Substituting in equation 50 and rearranging

$$G\Delta FL_i + G\Delta F\sum_j e_{i,j} L_j$$
$$= d\lambda_i L_i + \sum_j e_{i,j} (\lambda_i - \lambda_j) L_j + d\lambda_i \sum_j e_{i,j} L_j \qquad 51$$

Since by definition (equation 32),

$$LL^t = G$$
$$L^t = L^{-1}G$$

Therefore $\quad (L^t)_i = (L^{-1}G)_i$

$$(L_i)^t = L_i^{-1}G$$

or the ith row of L^t (the ith column of L)

equals the ith row of L^{-1} multiplied by G.

Also since $\quad LL^{-1} = E$

$L_i L_j^{-1} = \delta_{i,j}$ $\quad$ i.e. L is orthornomal.

Equation 51 is premultiplied by L_i^{-1}.

Considering each term in turn

$$L_i^{-1} G\Delta FL_i = L_i^t \Delta FL_i$$
$$L_i^{-1} G\Delta F\sum_j e_{i,j} L_j = L_i^t \Delta F\sum_j e_{i,j} L_j$$
$$L_i^{-1} d\lambda_i L_i = d\lambda_i$$
$$L_i^{-1} \sum_j e_{i,j} (\lambda_i - \lambda_j) L_j = 0$$

Since if $i = j \quad \lambda_i - \lambda_j = o$

$$i \neq j \quad L_i^{-1} L_j = 0$$

$$L_i^{-1} d\lambda_i \sum_j e_{i,j} L_j = e_{i,i} d\lambda_i$$

Therefore equation 51 becomes

$$L_i^t \Delta F L_i + \sum_j e_{i,j} L_i^t \Delta F L_j = d\lambda_i + e_{i,i} d\lambda_i \qquad 52$$

This equation is exact, no assumptions are made in deriving it and no limitations are placed on the size of the displacement. However since the $e_{i,j}$ coefficients cannot be easily evaluated the limitation is imposed that the change $\Delta\Phi$ is small. Then $d\lambda_i$, ΔF and $e_{i,j}$ are small and terms which are the product of two small quantities are neglected. Equation 52 becomes

$$L_i^t \Delta F L_i = d\lambda_i \qquad 53$$

From equation 36

$$F = \sum_j Z^j \phi_j$$

Since Z does not change

$$\Delta F = \sum_j Z^j d\phi_j$$

Therefore $\quad d\lambda_i = \sum_j L^t_i Z^j L_i d\phi_j$

and $\quad J_{i,j} = \dfrac{d\lambda_i}{d\phi_j} = L^t_i Z^j L^i \qquad 54$

Changing from matrix to algebraic notation

$$J_{i,j} = \sum{}^2_{k,l} l_{k,i} l_{l,i} Z^j_{k,l} \qquad 55$$

where the summations k and l are over all n rows of the eigen vector matrix.

Since F and therefore all the Z^j matrices are symmetric it is not necessary to calculate elements for both $Z^j_{k,l}$ and $Z^j_{l,k}$ as they will be identical. Remembering that there is only one element where $k = 1$, equation 55 becomes

$$J_{i,j} = \sum_k (l_{k,i})^2 Z^j_{k,k} + 2\sum_k^2 {}_{l(l>k)} l_{k,i}\, l_{l,i}\, Z^j_{k,l} \qquad 56$$

The only approximation made in deriving the Jacobian is that the changes are small. No conditions are imposed on the direction of the change.

SECTION 1.9 The weighting matrices P and W.

The eigen value weight matrix W is introduced to account for random errors in the observed frequencies. From section 1.7 the error X for any set of calculated eigen values is

$$X = \sum_i w_i \left(\lambda_i^{obs} - \lambda_i \right)^2$$

Since X is the sum of the weighted square errors (WSQER) and the refinement process is essentially a least squares fit, the individual $w_i^{\frac{1}{2}} d\lambda_i$ are the quantities considered, where $d\lambda_i = \lambda_i^{obs} - \lambda_i$. From equation 35

$$v_i = k\, \lambda_i^{\frac{1}{2}} \quad \text{and} \quad \lambda_i = c\, v_i^2$$

where $k = 1/c^2 = 1302.8$

Therefore $$d\,\lambda_i = c\,((v_i^{obs})^2 - v_i^2)$$

$$= c\,(v_i^{obs} - v_i)\,(v_i^{obs} + v_i)$$

If $dv_i = v_i^{obs} - v_i$ and is small so that $v_i^{obs} \sim v_i$

$$d\,\lambda_i \sim 2\,c\,v_i^{obs}\,d\,v_i$$

If $$w_i = (\lambda_i^{obs})^{-1}$$

$$w_i^{\frac{1}{2}}\, d\lambda_i = \frac{2\,c\,v_i^{obs}\,dv_i}{c^{\frac{1}{2}}\,v_i^{obs}}$$

$$= 2\,c^{\frac{1}{2}}\,dv_i \qquad 57$$

Therefore refinement continues until $\sum_i (dv_i)^2$ is a minimum. This assumes that the random errors are independent of the observed frequencies and the refinement gives an ABSOLUTE fit to them.

If $$w_i = (\lambda_i^{obs})^{-2}$$

$$w_i^{\frac{1}{2}}\, d\lambda_i = \frac{2\,c\,v_i^{obs}\,dv_i}{c\,(v_i^{obs})^2}$$

$$= \frac{2\,dv_i}{v_i^{obs}} \qquad 58$$

Therefore refinement continues until $\sum_i (dv_i/v_i^{obs})^2$ is a minimum. This assumes that the random errors are proportional to the observed frequencies and the refinement gives a PERCENTAGE fit to them.

The differences between the two weighting methods are understood by considering an example of a molecule with two observed frequencies at 1000 $cm.^{-1}$ and 200 cm^{-1}.

If the dv are ± 10 at 200 (5%)
and ± 20 at 1000 (2%)
Then $\sum_i (dv_i)^2 = 500$
$\sum_i (dv_i/v_i)^2 = 29.10^{-4}$

If changes are made in the force constants so that the dv are now

$\pm$ 4 at 200 (2%)

$\pm$ 40 at 1000 (4%)

Then $\sum_i (dv_i)^2 = 1616$

$\sum_i (dv_i/v_i)^2 = 20.10^{-4}$

Therefore if the weighting is absolute the new set of force constants gives a worse fit.

But if the weighting is percentage the new set of force constants gives a better fit.

If a larger than average error is suspected in a frequency it can be allowed for by a fractional entry, instead of unity, in the denominator of w_i, e.g. $w_i = 0.5/\lambda_i^{obs}$. If there is no observed band which corresponds to a particular calculated frequency then $w_i = o$ for that band and obviously has no effect on the calculations.

Sometimes it is required that one or more of the force constants are held at a fixed value (not necessarily zero). This is achieved by introduction of a matrix P, dimension m by mr, where mr is the number of force constants to be refined. If the ith force constant is to be held, P can be thought of as an identity matrix, dimension m by m, with the ith column removed. P is unitary, i.e. $PP^t = E$, and from equation 45

$$J^tW \Delta\Lambda = J^tWJ \; \Delta\Phi$$

Therefore $P^tJ^tW\Delta\Lambda = P^tJ^tWJPP^t \; \Delta\Phi$

$P^tJ^tW\Delta\Lambda$ is a column matrix, dimension mr.

P^tJ^tWJP is a square matrix, dimension mr by mr, and can be inverted.

$P^t\Delta\Phi$ is a column matrix, dimension mr.

Therefore $P^t\Delta\Phi = (P^tJ^tWJP)^{-1} \; P^tJ^tW \; \Delta\Lambda$

and $$\Delta\Phi = P(P^tJ^tWJP)^{-1} \; P^tJ^tW \; \Delta\Lambda \tag{59}$$

if the ith force constant is held constant then $d\phi_i = o$.

In the actual calculation a simpler but equivalent method is used which does not involve forming P explicitly. PJ is formed simply by removing the ith column from J and the corresponding element in $\Delta\Phi$ is set equal to zero.

If the calculated changes $d\phi_j$ in the force constants are large then equation 38, the condition of linearity, does not necessarily hold. The changes are therefore reduced by the introduction of a, a constant scalar, so that

$$\Phi^{n+1} = \Phi^n + a\Delta\Phi^n \tag{60}$$

where $o < a < 1$.

This method of force constant calculation is usually known as the Force Constant Perturbation Method. In Chapter 3 some of the problems which can be encountered are discussed and other methods of calculation reviewed.

SECTION 1.10 The Overlay Procedure.

The foregoing discussion has considered the refinement of a force field to the observed frequencies of one molecule. However, if a series of chemically similar molecules is under consideration the procedure can be extended to fit one force field to all these molecules. This is known as the overlay procedure (7).

If in equation 45

$$C = J^tWJ \quad \text{and} \quad D = J^tW\Delta\Lambda \qquad 61$$

where C is a square matrix, dimension m by m, and D is a column matrix, dimension m, i.e. neither has a dimension depending on the number of frequencies, then the C and D matrices are calculated for each molecule in turn and summed, so that

$$\Delta\bar{\Phi} \sum_n C^n = \sum_n D^n$$

where C^n and D^n are the C and D matrices for the nth molecule and the summation is over all molecules. Since $\sum_n C^n$ is square it can be inverted.

Therefore $\Delta\bar{\Phi} = (\sum_n C^n)^{-1} \sum_n D^n$ 62

The force constant weight matrix P can be included and by comparison with equation 59, equation 61 becomes

$$\Delta\bar{\Phi} = P(P^t(\sum_n C^n)\ P)^{-1}\ (P^t \sum_n D^n) \qquad 63$$

All this involves in the computation is that at each cyle, for each molecule in turn the Jacobian and $\Delta\Lambda$ matrices are calculated, using the common force field. Composite C and D matrices are formed by summing the individual C and D matrices for all molecules.

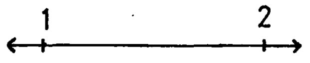
It is obviously necessary that the force field is of a type transferable among molecules. It is for this reason that it is expressed in terms of the internal coordinates of the molecules.

SECTION 1.11 Internal Coordinates and the B matrix.

In section 1.2 the concept of Internal Coordinates was introduced. In this section the forms these coordinates take are explained. Also the method of calculating the elements of the B matrix are developed.

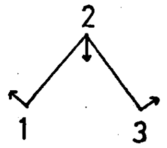
Changes in the Internal Coordinates of a molecule refer to changes in the bond parameters (usually bond lengths and bond angles) and are more convenient to use when describing the vibrations of a molecule than displacements of the atoms in x, y or z directions. There are six types of Internal Coordinate which are described below. The arrows on the atoms show the directions of motion to produce an increase (or positive change) in the Internal Coordinate. Wilson, Decius and Cross (8), Chapter 4, defined the first four as follows.

1. Bond Strech dr



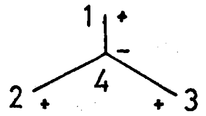
The atoms move so that the bond length r_{12} increases.

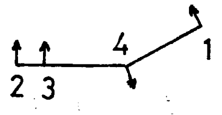
2. Angle Bend dα



The atoms move so that the angle 1 2 3 (α) increases.

3. Out of Plane Angle Bend dy



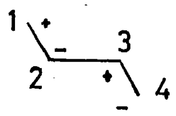


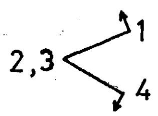
Note: + indicates an upward motion out of the plane.

\- indicates a downward motion out of the plane.

The atoms move so that the angle between the bond 1,4 and the plane 2,4,3 increases.

4. Bond Torsion dτ

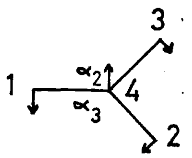




The atoms move so that the dihedral angle between the planes 1,2,3 and 2,3,4 increases.

This set will completely define the internal motions of a molecule but two more Internal Coordinates are usually introduced.

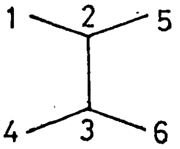
5. In Plane Angle Bend dβ



The atoms move so that the angle between bond 1,4 and the bisector of the angle 2,4,3 increases. An alternative description is $d\alpha_2 - d\alpha_3$.

It is complementary to the out of plane angle bend and they are used usually when atoms 1,2,3,4 are coplanar. In this case the alternative description of changes in angles α_3 and α_2 implies no out of plane motion.

6. Special or Bell Torsion $d\phi$



This Internal Coordinate was introduced by Bell (9) specifically to remove an inconsistency in applying Torsion $d\tau$ to Benzene. If atoms 1,2,3,4 are in the carbon ring and atoms 5 and 6 are the substituents (in Benzene, Hydrogen) a torsion defined by atoms 1,2,3,4 with atoms 5 and 6 not moving implies a y deformation of bonds 2,5 and 3,6. In Bell's Torsion the atoms move so that the dihedral angle between planes 1,2,5 and 3,4,6 increases. It is equivalent to $d\phi$ (cccc) + $d\phi$(HCCH) where $d\phi$(cccc) is a torsion of atoms 1,2,3,4 and $d\phi$(HCCH) is a torsion of atoms 5,2,3,6.

For consistency all the Internal Coordinates involving a change of angle are scaled by an appropriate bond length so that all the Internal Coordinates have dimensions of length (A). The scaling factors are

1. For an angle bend $d\alpha$, $(r_{12}\, r_{23})^{\frac{1}{2}}$

2. For out of plane $d\gamma$ and in plane $d\beta$ angle bends, r_{14}
3. For torsions $d\tau$ and $d\phi$, r_{23}

This scaling means that all force constants are expressed in units of force per unit length (mdyn. $Å^{-1}$). This follows from equation 16

$$2V = \sum_{i,j}^{2} f_{i,j}\, dR_i\, dR_j$$

since dR_i and dR_j are expressed in Angstroms and V, the Potential Energy, in millidyne Angstroms.

In Section 1.2 the concept of the B matrix was introduced. The i,k th element, $b_{i,k}$ was defined as

$$b_{i,k} = \delta R_i / \delta q_k$$

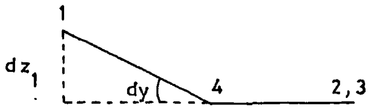
To calculate the numerical values of the G matrix elements it is necessary to calculate the numerical values of these B matrix elements. As this thesis is concerned with out of plane vibrations, only the analytical expressions for these types of Internal Coordinates will be derived.

The Out of Plane Angle Bend

Since all the molecules under consideration are planar only the expressions for the planar case are required

If the four atoms lie in the xy plane, for each atom the cartesian displacements in the z direction required to change the angle between the bond 1,4 and the plane defined by atoms 2,3,4 by dy is calculated. By definition the change occurs so that atom 1 can be considered to have moved in the positive z direction.

A. For atom 1



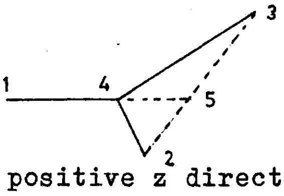
Since the displacements are small $dz_1 = r_{14}\ dy$

Therefore the B matrix element is

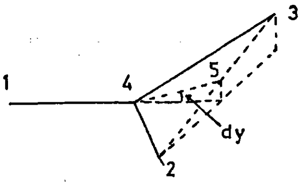
$$\frac{r_{14}\ dy}{dz_1} = 1 \qquad 64$$

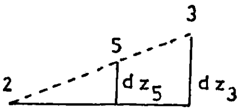
and the scaling factor r_{14} is included on the left hand side of the equation.

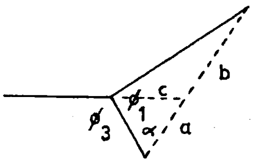
B. For atoms 2 and 3



The angle between 1,4 and 4,5 is dy. By definition 2 and 3 move in a positive z direction.







Since all the displacements are small,

$$\frac{dz_5}{dz_3} = \frac{a}{a+b} \qquad 65$$

and $\quad dz_5 = c\ d\ y$

By the sine rule

$$\frac{\sin \phi_1}{a + b} = \frac{\sin \alpha}{r_{34}}$$

and

$$\frac{\sin (\pi - \phi_3)}{a} = \frac{\sin \alpha}{c}$$

Substituting in equation 65

$$\frac{dy}{dz_3} = \frac{a}{c(a+b)}$$

$$= \frac{\sin \phi_3}{\sin \alpha} \quad \frac{\sin \alpha}{r_{34} \sin \phi_1}$$

$$= \frac{1}{r_{34}} \quad \frac{\sin \phi_3}{\sin \phi_1}$$

Therefore the B matrix element for atom 3 is

$$r_{14} \frac{dy}{dz_3} = \frac{r_{14}}{r_{34}} \quad \frac{\sin \phi_3}{\sin \phi_1} \qquad 66$$

Similarly the B matrix element for atom 2 is

$$r_{14} \frac{dy}{dz_2} = \frac{r_{14}}{r_{24}} \quad \frac{\sin \phi_2}{\sin \phi_1} \qquad 67$$

C. For atom 4 (the apex atom).

If the apex atom is displaced by dz_4, a rigid displacement of the atom in the opposite direction by an equal amount returns the apex atom to the original position but displaces 1,2 and 3 by $-dz_4$. The change in angle for simultaneous displacement of 1,2 and 3 by $-dz_4$ is given by

$$dy = - r_{14}dz_4 - \frac{dz_4}{r_{34}} \frac{\sin \phi_3}{\sin \phi_1} - \frac{dz_4}{r_{24}} \frac{\sin \phi_2}{\sin \phi_1}$$

Therefore the B matrix element for atom 4 is

$$\frac{r_{14}\, dy}{dz_4} = - 1 + \frac{r_{14} \sin \phi_3}{r_{34} \sin \phi_1} + \frac{r_{14} \sin \phi_2}{r_{24} \sin \phi_1} \qquad 68$$

For Benzene $\phi_1 = \phi_2 = \phi_3 = 120^\circ$ and if $r_{14} = r$ and $r_{24} = r_{34} = R$ then

$$r \frac{dy}{dz_1} = 1$$

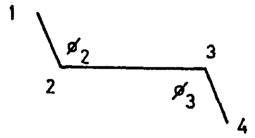
$$r \frac{dy}{dz_2} = r \frac{dy}{dz_3} = \frac{r}{R}$$

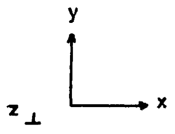
$$r \frac{dy}{dz_4} = - 1 - \frac{2r}{R}$$

These values agree with those given by Whiffen (12).

Bond Torsion

As in the case of the out-of-plane angle bend only the expressions for the planar case are required.





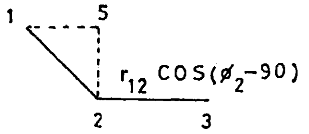
If the four atoms lie in the xy plane, for each atom the cartesian displacement required to change the angle between the plane defined by atoms 1,2,3 and that defined by atoms 4,3,2 by a small amount $d\tau$ is calculated.

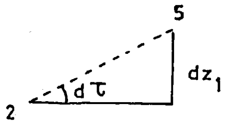
A. For atom 1.

If atom 1 is moved out of the plane of the molecule by small distance dz_1 the angle between the two planes $d\tau$ is given by

$$d\tau = \frac{dz_1}{r_{12}\cos(\phi_2-90)}$$

$$= \frac{dz_1}{r_{12}\sin\phi_2}$$





Therefore the B matrix element

$$\frac{r_{23}\,d\tau}{dz_1} = \frac{r_{23}}{r_{12}\sin\phi_2} \qquad 69$$

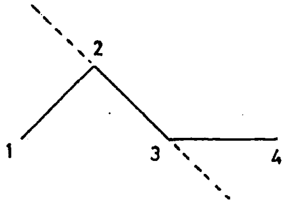
B. For atom 4.

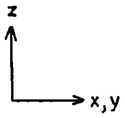
By similar reasoning to that used for atom 1, it can be shown that the B matrix element for atom 4 is

$$\frac{r_{23}\,d\tau}{dz_4} = \frac{r_{23}}{r_{34}\sin\phi_3} \qquad 70$$

C. For atom 2.

If atom 2 is displaced from the molecular plane by small distance dz_1 it can be returned to the plane by rigid rotation about atom 3 and in this case atoms 1 and 4 are displaced from the plane.





Atom 1 is displaced by dz_1 where, for small displacements

$$\frac{-dz_1}{r_{23}-r_{12}\cos\phi_2} = \frac{dz_2}{r_{23}},$$

Atom 4 is displaced by dz_4 where, for small displacements

$$\frac{dz_4}{-r_{34}\cos\phi_3} = \frac{dz_2}{r_{23}}$$

By substituting for dz_1 and dz_4 using equation 69 and 70 it can be shown that the change in angle for a simultaneous displacement of atoms 1 and 4 is

$$d\tau = \frac{-dz_2(r_{23}-r_{12}\cos\phi_2)}{r_{12}r_{23}\sin\phi_2} - dz_2\frac{\cos\phi_3}{r_{23}\sin\phi_3}$$

Therefore the B matrix element for atom 2 is

$$\frac{r_{23}d\tau}{dz_2} = -\frac{\cos\phi_3}{\sin\phi_3} - \frac{r_{23}-r_{12}\cos\phi_2}{r_{12}\sin\phi_2} \qquad 71$$

D. For atom 3.

By similar reasoning to that used for atom 2 it can be shown that the B matrix element for atom 3 is

$$\frac{r_{23}d\tau}{dz_3} = -\frac{\cos\phi_2}{\sin\phi_2} - \frac{r_{23}-r_{34}\cos\phi_3}{r_{34}\sin\phi_3} \qquad 72$$

For Benzene $\phi_2 = 240 \quad \sin\phi_2 = -3^{\frac{1}{2}}/2 \quad \cos\phi_2 = -\frac{1}{2}$

$\phi_3 = 120 \quad \sin\phi_3 = 3^{\frac{1}{2}}/2 \quad \cos\phi_3 = {}^{-1}/_2$

and $R = r_{12} = r_{23} = r_{34}$

Therefore

$$\frac{R.d\tau}{dz_1} = -\frac{2}{3^{\frac{1}{2}}}$$

$$\frac{R.d\tau}{dz_2} = +\frac{4}{3^{\frac{1}{2}}}$$

$$\frac{R.d\tau}{dz_3} = -\frac{4}{3^{\frac{1}{2}}}$$

$$\frac{R.d\tau}{dz_4} = +\frac{2}{3^{\frac{1}{2}}}$$

These values agree with those given by Whiffen (12).

Special Torsion

If $d\tau'$ is the Torsion coordinate for atoms 1,2,3,4

and $d\tau''$ is the Torsion coordinate for atoms 5,2,3,6

Then the B matrix elements for a Special Torsion are easily calculated from those for a Bond Torsion using the expression

$$R.d\phi = R.d\tau' + R.d\tau''$$

Alternatively they can be calculated using the expression given by Whiffen (12)

$$R.d\phi = 2R.d\tau' + 2/3^{\frac{1}{2}}.R(dy_5-dy_6)$$

SECTION 1.12 Symmetry Coordinates

All molecules have elements of symmetry and can therefore be assigned to a Symmetry Point Group. When a molecule containing n atoms is displaced the 3n cartesian coordinates describing the system change. These cartesian deformations transform as a Reducible Representation of the Symmetry Point Group. If any two sets of coordinates (a and b) are connected by a linear transformation (T)

i.e. $a = Tb$

then they transform as the same Reducible Representation.

Since $R = Bq$

and $R = LQ$

The changes in the Cartesian Coordinates q

Internal Coordinates R

and Normal Coordinates Q

all transform as the same Reducible Representation.

For singly degenerate Normal Coordinates each coordinate Q_i is transformed to $\pm Q_i$ under any symmetry operation. This follows from the fact that the Potential and Kinetic Energies are invariant under any symmetry operation. Equations 26 and 27 state that

$$2T = \sum_i \dot{Q}_i^2 \qquad 2V = \sum_i \lambda_i \, dQ_i^2$$

if in a particular vibrational state only Q_j is non-zero, then

$$2T = \dot{Q}_j^2 \qquad 2V = \lambda_j \, dQ_j^2$$

If under a symmetry operation 0

$$Q_j \xrightarrow{o} Q_k$$

$$2T \rightarrow \dot{Q}^2_k \qquad 2V \rightarrow \lambda_k \, dQ_k^2$$

The conditions of invariance are not satisfied, since if

$$2T = \dot{Q}_j^2 = \dot{Q}_k^2 \qquad 2V = \lambda_j \, dQ_j^2 \neq \lambda_k \, dQ_k^2$$

as $\lambda_j \neq \lambda_k$ for singly degenerate normal coordinates.

Therefore it can be stated that a singly degenerate normal coordinate transforms as an Irreducible Representation (or symmetry species) of the Symmetry Point Group.

A degeneracy occurs when a molecule possesses a threefold or higher proper axis of rotation. Two or more normal coordinates are degenerate when their associated vibrational frequencies are identical. The members of a degenerate set belong to the same symmetry species. When there are d equivalent normal coordinates it is called a d fold degeneracy. An example of degenerate Normal Coordinates is the bending modes of Carbon Dioxide. If the z axis passes through the atoms an angle bending mode can occur in either the x or y directions. These two vibrational modes have the same frequency but are orthogonal.

The conditions of invariance under any symmetry operation for degenerate coordinates are not so stringent. A symmetry operation of the molecule transforms a member of a degenerate set of Normal Coordinates into a linear combination of the members of the degenerate set.

Therefore $Q_i{}^a \xrightarrow{o} \sum_b c_{bi} \, Q_i{}^b$

where $Q_i{}^a$, $Q_i{}^b$ etc. are all members of a d fold degenerate set and the summation b is over all d members.

By definition each member of the set is orthogonal to all other members and the condition of invariance of Kinetic and Potential Energy is given by (8), p.107 and (10), p.49 as

$$\sum_b (C_{bi})^2 = 1$$

Therefore it can be stated that each set of d fold degenerate Normal Coordinates transforms as a d dimensional Irreducible Representation of the Symmetry Point Group.

It has already been shown that the Normal Coordinates form a Reducible Representation of the Symmetry Point Group of the molecule. The combination of Irreducible Representations (or Symmetry Species) of which this Reducible Representation consists is found using the equation, (8), p.99

$$a_i = \frac{1}{g} \sum X(RR)\ X_i\ (IR) \qquad 73$$

where a_i is the number of times the ith Irreducible Representation occurs in the Reducible Representation.

g is the order of the group, i.e. the number of symmetry operations in the group.

X(RR) is the trace of the Reducible Representation for the symmetry operation under consideration.

X_i(IR) is the trace of the ith Irreducible Representation for the symmetry operation under consideration.

and the summation is over all symmetry operations.

Provided the vibrations can be assigned to their particular symmetry species use can be made of these symmetry properties to reduce the size of the secular equation. To do this a new set of coordinates is introduced. They are Symmetry Coordinates and are linear combinations of the Internal Coordinates constructed so as to transform as the Irreducible Representations of the Symmetry Point Group, i.e. each Symmetry Coordinate belongs to a Symmetry Species of the molecule.

The transformation matrix is called the U matrix

i.e. $S = UR$ 74

and is constructed so that it is unitary

i.e. $UU^t = E$ 75

The Kinetic and Potential Energy expressions in matrix form are

$$2T = \dot{R}^tG^{-1}\dot{R} \qquad 31 \qquad\qquad 2V = R^tFR \qquad 17$$

Substituting for $\dot{R}$ and R

$$\dot{R} = U^t\dot{S} \qquad\qquad R = U^tS$$

$$2T = \dot{S}^tUG^{-1}U^t\dot{S} \qquad\qquad 2V = S^tUFU^tS$$

if $\mathfrak{G} = UGU^t$ and $\mathfrak{F} = UFU^t$

$$\mathfrak{G}^{-1} = UG^{-1}U^t$$

since $U^{-1} = U^t$

Therefore

$$2T = \dot{S}^t\mathfrak{G}^{-1}\dot{S} \qquad 76 \qquad\qquad 2V = S^t\mathfrak{F}S \qquad 77$$

where the Potential and Kinetic Energy expressions are now in Symmetry Coordinates.

In algebraic form

$$2T = \sum^2_{i,j} \dot{S}_i \dot{S}_j (\mathfrak{G}^{-1})_{i,j} \quad 78 \qquad 2V = \sum^2_{i,j} S_i S_j \mathfrak{F}_{i,j} \quad 79$$

where the summations i and j are over all Symmetry Coordinates.

If S_i and S_j belong to different symmetry species, there exists a symmetry operation O under which

$$S_i \xrightarrow{o} - S_i$$

$$S_j \xrightarrow{o} + S_j \qquad \text{or vice versa}$$

Therefore

$$\dot{S}_i\dot{S}_j(\mathfrak{G}^{-1})_{i.j} \xrightarrow{o} - \dot{S}_i\dot{S}_j(\mathfrak{G}^{-1})_{i.j} \qquad S_iS_j \mathfrak{F}_{i,j} \xrightarrow{o} - S_iS_j \mathfrak{F}_{i,j}$$

However since the Kinetic and Potential Energies must be invariant under all symmetry operations

$$(\mathfrak{G}^{-1})_{i,j} = 0 \qquad \mathfrak{F}_{i,j} = 0$$

This means that there can be no cross terms between different symmetry species and the Kinetic and Potential Energy expressions can be partioned.

$$2T = \sum_r(\dot{S}^r)^t (\dot{S}^r)(\mathfrak{G}^r)^{-1}$$

and

$$2V = \sum_r(S^r)^t(S^r)(\mathfrak{F}^r)$$

The summation r is over all symmetry species.

$\mathfrak{G}$ and $\mathfrak{F}$ are partioned into blocks, one block for each symmetry species and these blocks are treated independently.

Since by definition

$$R = LQ \qquad 25$$

and

$$S = UR$$

If $\mathcal{L}$ the eigen vector matrix in symmetry coordinates is defined as

$$\mathcal{L} = UL$$

Therefore $S = \mathcal{L}Q$ 80

Substituting for S and $\dot{S}$ in equations

$$2T = \dot{Q}^t\mathcal{L}^t\mathcal{G}^{-1}\mathcal{L}Q \qquad 2V = Q^t\mathcal{L}^t\mathcal{F}\mathcal{L}Q$$

and comparing with equations 28 and 29

$$\mathcal{G} = \mathcal{L}\mathcal{L}^t \quad 81 \qquad \mathcal{L}^t\mathcal{F}\mathcal{L} = \Lambda \quad 82$$

Therefore for a given symmetry species r, the secular equation is

$$\mathcal{G}^r\mathcal{F}^r\mathcal{L}^r = \mathcal{L}^r\Lambda^r \quad 83$$

and provided the U matrix can be evaluated the eigen vectors and eigen values are calculated for each symmetry species in turn.

Although the G, F and L matrices are now expressed in terms of symmetry coordinates it is still necessary to use internal coordinates for the force constants if they are to be transferable between similar molecules. Equation 36 relates the F, Z and Φ matrices.

$$F = \sum_j \phi_j Z^j \quad 36$$

Therefore $UFU^t = \sum_j \phi_j UZ^jU^t$

or $\mathcal{F} = \sum_j \phi_j \mathcal{Z}^j$ 84

F and Z are now expressed in symmetry coordinates but Φ is still in internal coordinates. The symmetry force constants, i.e. the elements of the matrix $\mathcal{F}$, are linear combinations of the internal force constants and the elements of $\mathcal{Z}$ are not restricted to being + or - 1.0.

The Jacobian is calculated using equation 54.

$$J_{i,j} = \frac{d\lambda_i}{d\phi_j} = L_i^t Z^j L_i \tag{54}$$

If $\mathcal{L}_i = UL_i$

where $\mathcal{L}_i$ is the ith column of the eigen vector matrix for a given symmetry species, then

$$L_i = U^t \mathcal{L}_i$$

also $Z^j = U^t \mathcal{Z}^j U$

since the transformation matrix U is unitary.

Substituting for L_i and Z^j in equation 54

$$\begin{aligned} J_{i,j} &= \mathcal{L}_i{}^t UU^t \mathcal{Z}^j UU^t \mathcal{L}_i \\ &= \mathcal{L}_i{}^t \mathcal{Z}^j \mathcal{L}_i \end{aligned} \tag{85}$$

Therefore, provided the force constants are always in terms of internal coordinates, the Jacobian can be calculated using either $\mathcal{L}$ and $\mathcal{Z}$ (i.e. symmetry coordinate expressions) or L and Z (i.e. internal coordinate expressions).

Construction of the Symmetry Coordinates

The symmetry coordinates are generated from the internal coordinates by considering how a representative internal coordinate transforms under the symmetry operations of the Symmetry Point Group. The representative internal coordinates are selected by considering sets of internal coordinates, which transform among themselves, and taking one from each set. The symmetry coordinates are then constructed using the equation, (8), P.119,

$$S^r = N \sum_o X_o^r \; OR_r \qquad 86$$

where S^r is a symmetry coordinate for the symmetry species r.

X_o^r is the trace of the symmetry operation O for the symmetry species r (taken from the Character Tables).

OR_r is the internal coordinate generated by operating on the representative coordinate R_r with symmetry operation O.

N is a normalising factor.

The summation is over all symmetry operations.

A symmetry coordinate is generated for each representative internal coordinate for each symmetry species. (A symmetry coordinate is not always generated since the internal coordinates may sum to zero).

Equation 86 if expressed in algebraic form relates the ith symmetry coordinate S_i to the change in the jth internal coordinate dR_j.

i.e. $$S_i = \sum_j U_{i,j} \, dR_j \qquad 87$$

$U_{i,j}$, the i,jth element of the U matrix, is evaluated by the above method.

i.e. If under symmetry operation O

$$R_r \xrightarrow{o} a \, R_j$$

For the symmetry species r

$$U_{i,j} = N \, X_o^r \, a$$

For non-degenerate coordinates $a = \pm 1$, and the normalising factor N arises since by definition U is unitary.

$$\text{i.e.} \qquad \sum_i U_{j,i} U_{k,i} = 1 \qquad j = k$$
$$= 0 \qquad j \neq k$$

For a d-fold degenerate symmetry species there exists d equivalent and orthogonal sets of symmetry coordinates. The symmetry coordinates are generated in the normal way but two further rules have to be observed.

1. For a given set of symmetry coordinates the representative internal coordinate must transform in the same manner under all symmetry operations.
2. The representative internal coordinates taken from the same set used to generate symmetry coordinates of different sets must be orthogonal.

These two rules mean that when selecting a representative internal coordinate it is sometimes necessary to use a linear combination of internal coordinates which transform in the required manner.

In Appendix II the method calculating symmetry coordinates is applied to 1,4 difluoro benzene.

Section 1.13 Separation of in and out-of-plane vibrations.

The introduction of the concept of symmetry leads immediately to the factorisation of the Secular Matrix L for planar molecules before the introduction of symmetry coordinates. A planar molecule possesses a σ_v symmetry plane, i.e. the molecular plane. If the x and y cartesian axes lie in this plane and the z axis is perpendicular to it consider what happens to these axes on reflection through this plane.

$$x \xrightarrow{\sigma\ xy} + x \qquad\qquad y \xrightarrow{\sigma\ xy} + y$$

$$z \xrightarrow{\sigma\ xy} - z$$

An in plane internal coordinate R_i (i.e. a bond strech, an angle bend, or an in plane angle bend) involves only motion in the x and y directions and on reflection at this plane

$$R_i \xrightarrow{\sigma\ xy} + R_i$$

An out of plane internal coordinate R_j (i.e. an out of plane angle bend, torsion or special torsion) involves only motion in the z direction and on reflection at this plane

$$R_j \xrightarrow{\sigma\ xy} - R_j$$

Therefore the terms in the Kinetic and Potential Energy expressions, given by equations 31 and 17 in algebraic form, involving R_i and R_j change sign on reflection.

$$g^{-1}_{i,j}\,\dot{R}_i\dot{R}_j \xrightarrow{\sigma\ xy} - g^{-1}_{i,j}\,\dot{R}_i\dot{R}_j \qquad f_{i,j}dR_idR_j \xrightarrow{\sigma\ xy} - f_{i,j}dR_idR_j$$

Since the Kinetic and Potential Energies must be invariant under all symmetry operations,

$$g^{-1}_{i,j} = 0 \qquad\qquad f_{i,j} = 0$$

It also follows that

$$g_{i,j} = o$$

since $g_{i,j}\ P_i P_j \xrightarrow{o\ xy} - g_{i,j}\ P_i P_j$

where P_i is the momentum conjugate with R_i (see Section 1.2).

Therefore the G and F matrices can each be factored into two blocks, G_{xy} and G_z, and F_{xy} and F_z.

Therefore $$\begin{vmatrix} G_{xy} & 0 \\ 0 & G_z \end{vmatrix} \begin{vmatrix} F_{xy} & 0 \\ 0 & F_z \end{vmatrix}$$

$$= \begin{vmatrix} G_{xy}\ F_{xy} & 0 \\ 0 & G_z F_z \end{vmatrix}$$

The G_z and F_z matrices alone need be constructed when considering only out of plane vibrations.

Section 1.14 Redundancies

In general to completely define the 3n-6 fundamental vibrations of an n atom molecule it is necessary to introduce more than 3n-6 internal coordinates. Obviously no internal coordinate can be arbitrarily excluded as the internal coordinates must form a complete set. If these are m internal coordinates the G, F, L and matrices are of dimension m so that when the secular equation is solved there will be m - (3n-6) zero eigen values. Their associated eigen vectors are also zero since a zero eigen value means no vibrational motion of the atoms.

In section 1.2 it was stated that

$$\sum_i (dV/dR_i)_e = o$$

This is only true if the set of internal coordinates used is an independent set i.e. it contains no redundancies. Then for each internal coordinate at the equilibrium point

$$dV/dR_i = 0$$

It is always possible to express the Potential Energy in terms of a set of coordinates which contain no redundancies but such a set is usually not convenient since the force constants are not transferable between molecules (11). Therefore it is necessary to examine the conditions under which dV/dR_i can be ignored.

If the redundancy condition is

$$\sum_i a_i R_i = 0$$

where a_i is a coefficient and the summation is over internal coordinates required to define the redundancy.

The condition for V to be a minimum is now, (8) p.172,

$$\sum_i \left[\frac{\partial V}{\partial R_i} - k \frac{\partial \sum_i a_i R_i}{\partial R_i} \right]_0 dR_i = 0$$

Therefore

$$\left| \frac{\partial V}{\partial R_i} \right|_0 - k\, a_i = 0$$

where k is an undetermined multiplier known as the Intermolecular Tension, (10) p.85. Although the Intermolecular Tension is a linear term it can be transformed to a quadratic term by expressing the redundancy condition to the second order. However even if this is done the intermolecular tension cannot be explicitly evaluated and is therefore usually ignored.

Crawford and Overend (11) pointed out that such a term can only occur in the fully symmetric symmetry species. If linear terms are included and the Potential Energy expressed in symmetry coordinates as

$$V = \sum_i \left| \frac{\partial V}{\partial S_i} \right|_o dS_i + \sum_{i,j}^{2} \left| \frac{\partial^2 V}{\partial S_i \partial S_j} \right|_o dS_i dS_j$$

only for the fully symmetric symmetry species does

$$S_i \xrightarrow{o} + S_i$$

for all symmetry operations.

If $$S_i \xrightarrow{o} - S_i$$

$$(\partial V / \partial S_i)_o = o$$

since the Potential Energy must be invariant under all symmetry operations.

Redundancies can also arise when expressing the Secular Equation in symmetry coordinates. A complete set of coordinates must be generated and this set can overdefine the Secular Matrix. if the redundant symmetry coordinates can be identified they are not included, e.g. in Benzene S_r

where $$S_r = \phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6$$

the sum over all the phicoordinates represents no overall vibrational motion and is excluded.

However the symmetry coordinates which give rise to zero eigen values are usually linear combinations of the original symmetry coordinates and are not always obvious on inspection. Whiffen (12) gives all the internal relationships which give rise to redundant symmetry coordinates in Benzene.

It is not normally necessary to remove the redundant coordinates. The secular equation can still be solved with the redundant coordinates giving rise to zero eigen values. However it must be realised that if redundancies are present G is singular

i.e. determinant $G = o$

and therefore cannot be inverted. This can give rise to problems when calculating the Cartesian Displacements of the atoms in a normal mode. Gussoni and Zerbi (13) have given a method of removing redundancies and this is reviewed later with other aspects of the programming of the vibrational problem.

Section 1.15 Band Shapes

In the gas phase the number of molecules with moments of inertia small enough to permit resolution and analysis of their individual rotational lines is limited (14). However useful information can be obtained from the overall band shapes. A molecule has three principal moments of inertia, labelled A, B and C such that $C > B > A$. Rotation about each of these axes is associated with a particular band shape.

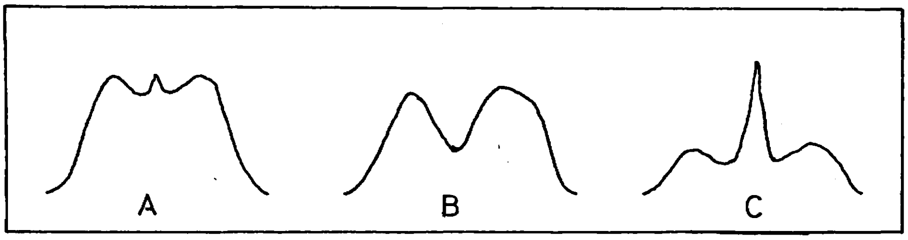
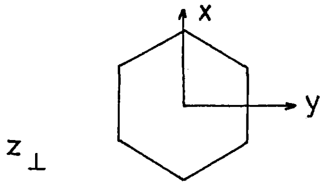


FIGURE 1.2

The problem is to determine the symmetry species to which an observed vibration with a particular band shape belongs.

The first step is to determine the magnitude of the moments of inertia and the orientation of the associated principal axes. Initially the geometry of the molecule is expressed in an arbitrarily orientated set of cartesian coordinates. For the planar Fluorine substituted Benzene molecules considered in this thesis the set used is given in Figure 1.3.

FIGURE 1.3



The coordinates of the centre of mass are calculated using these coordinates.

$$C_q = \frac{1}{M} \sum_i m_i q_i \qquad 88$$

where q is x, y or z.

Therefore C_q is the coordinate of the centre of mass and q_i the coordinate of the ith atom for the axis under consideration. m_i is the mass of the ith atom and

$$M = \sum_i m_i \qquad 89$$

In both equations 88 and 89 the summation i is over all atoms.

Also the elements of the moment of inertia tensor are calculated.

$$t_{qq} = \sum_i m_i \left[r_i^2 - (q_i - c_q)^2 \right] \qquad 90$$

where $$r_i^2 = \sum_q (q_i - c_q)^2$$

The summation is over the three cartesian axes and therefore r_i is the distance between the centre of mass and the ith atom.

Also $$t_{qq'} = -\sum_i m_i (q_i - c_q)(q'_i - c_q) \qquad 91$$

This gives the moment of inertia tensor T in three coordinate space, as designated by the cartesian coordinates x,y,z, in the form

$$T = \begin{vmatrix} t_{xx} & t_{xy} & t_{xz} \\ t_{xy} & t_{yy} & t_{yz} \\ t_{xz} & t_{yz} & t_{zz} \end{vmatrix}$$

This is diagonalized to find the principal axis transformation R (eigen vectors) and the principal moments of inertia I (eigen values).

Thus $$TR = RI$$

Both R and I are 3 by 3 matrices, I is diagonal.

The process is obviously comparable with the diagonalization of GF to give L and Λ. If q is the original set of coordinates used to express the moment of inertia tensor T, and Q is the new set of coordinates in which the tensor takes the diagonal form I, obviously

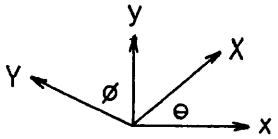
$$q = RQ \qquad (\text{cf. } R = LQ)$$

If the new axes are labelled X, Y, Z

and the old axes are labelled x, y, z

q is a column vector $\begin{matrix} x \\ y \\ z \end{matrix}$ and Q is a column vector $\begin{matrix} X \\ Y \\ Z \end{matrix}$

For the planar molecules under consideration z is always a principal axis and can immediately be relabelled Z. If the orientation of the axes X and Y with respect to the axes x and y is



$$\begin{aligned} \text{Then} \qquad x &= X \cos \theta - Y \sin \phi \\ y &= X \sin \theta + Y \cos \phi \\ z &= Z \end{aligned}$$

and $\quad q = RQ$ in full matrix form is

$$\begin{vmatrix} x \\ y \\ z \end{vmatrix} = \begin{vmatrix} \cos\theta & -\sin\phi & 0 \\ \sin\theta & \cos\phi & 0 \\ 0 & 0 & 1 \end{vmatrix} \begin{vmatrix} X \\ Y \\ Z \end{vmatrix}$$

R in this form is automatically orthogonal.

$$RR^t = E$$

The form of the rotation matrix R in the general case is the same as that relating a rotating to a nonrotating axis system using the so called Eulerian angles, (8) p.286.

The principal moment of inertia matrix I is of the form

$$\begin{vmatrix} I_x & o & o \\ o & I_y & o \\ o & o & I_z \end{vmatrix}$$

so with each principal axis Q is associated a principal moment I_Q.

These axes are now relabelled so that the one with the largest moment is C, the next B and the smallest A.

Therefore the magnitude and orientation of the principal moments of inertia have been determined and labelled A, B and C so that $A < B < C$.

The second step is to determine the symmetry species to which a particular axis belongs. It is not necessary to do this in full by examining how each axis transforms under a given symmetry operation, since the selection rule for a band to be infra red active is that its normal coordinate should transform with the same irreducible representation as a translation, and therefore each principal axis coincides with a translation axis. The translation axes are denoted T_x, T_y and T_z in the characters and their orientations are determined by one of two methods. Either from the irreducible representation of the symmetry species of which they are a member, e.g. consider a plane σ_v and a translation axis T_Q,

if $T_Q \xrightarrow{\sigma_v} + T_Q$ it lies in the plane

if $T_Q \xrightarrow{\sigma_v} - T_Q$ it is perpendicular to the plane.

OR, more usually, a set of axes is introduced, when determining the symmetry of the molecule, in a specific manner following Mulliken's Rules (15) and these axes will transform as T_x, T_y or T_z. These specific axes, labelled x, y, z must not be confused with the arbitary cartesian axes.

Having determined which symmetry axis coincides with which translation a band shape can be assigned to their appropriate symmetry species.

These remarks apply only to asymmetric top molecules i.e. $A \neq B \neq C$. Ueda and Shimanouchi (16) have calculated the band shapes for 40 such molecules.

In Appendix III the above calculations are performed on 1,2,3,5 Tetra fluoro Benzene.

CHAPTER TWO The Vibrational Assignments and other Input Data.

SECTION 2.1 Symmetry Point Groups

The method for the determination of force constants described in Chapter One is to be applied to the out-of-plane vibrations of some Fluorine substituted Benzenes. Since these molecules are all considered to be planar the vibrations are conveniently classed as either in plane or out of plane. Before the calculations on the force constants can be started the fundamental frequencies have to be determined and assigned to their symmetry species. Table 2.1 lists the molecules considered, their Symmetry Point Group classification, and the number and symmetry species of their out-of-plane vibrations. The Infra Red active vibrations are marked with an asterisk.

The labelling of the symmetry species and the orientation of the cartesian axes are in accordance with the Recommendations of Mulliken (15). They are:-

1. For planar C_{2v} molecules.

The z axis is the C_2 axis (the z axis is always the axis of highest symmetry).

The x axis is perpendicular to the molecular plane (Rec.5a).

2. For planar D_{2h} molecules.

The x axis is perpendicular to the molecular plane (Rec.5b).

The z axis passes through the maximum number of atoms (Rec.5b).

3. For planar D_{3h} molecules.

The z axis is the C_3 axis, and therefore perpendicular to the molecular plane.

The Symmetry Point Groups, and the Symmetry Species of the Out-of-Plane Vibrations of the Fluorine substituted Benzenes

MOLECULE	SYMMETRY	
	POINT GROUP	SPECIES
1. Benzene	D_{6h}	$2B_{2g} + E_{1g} + A_{2u}^* + 2E_{2u}$
2. Hexadeutero Benzene	D_{6h}	$2B_{2g} + E_{1g} + A_{2u}^* + 2E_{2u}$
3. Fluoro Benzene	C_{2v}	$3A_2 + 6B_1^*$
4. Fluoro Pentadeutero Benzene	C_{2v}	$3A_2 + 6B_1^*$
5. 1,2 difluoro Benzene	C_{2v}	$5A_2 + 4B_1^*$
6. 1,3 difluoro Benzene	C_{2v}	$3A_2 + 6B_1^*$
7. 1,4 difluoro Benzene	D_{2h}	$B_{1g} + 3B_{2g} + 2A_u + 3B_{3u}^*$
8. 1,4 difluoro Tetra-deutero Benzene	D_{2h}	$B_{1g} + 3B_{2g} + 2A_u + 3B_{3u}^*$
9. 1,2,3 trifluoro Benzene	C_{2v}	$3A_2 + 6B_1^*$
10. 1,2,4 trifluoro Benzene	C_s	$9A''^*$
11. 1,3,5 trifluoro Benzene	D_{3h}	$3A_2''^* + 3E''$
12. 1,3,5 trifluoro deutero Benzene	C_{2v}	$3A_2 + 6B_1^*$
13. 1,3,5 trifluoro dideutero Benzene	C_{2v}	$3A_2 + 6B_1^*$
14. 1,3,5 trifluoro trideutero Benzene	D_{3h}	$3A_2''^* + 3E''$
15. 1,2,3,4 tetrafluoro Benzene	C_{2v}	$5A_2 + 4B_1^*$
16. 1,2,3,5 tetrafluoro Benzene	C_{2v}	$3A_2 + 6B_1^*$
17. 1,2,4,5 tetrafluoro Benzene	D_{2h}	$B_{1g} + 3B_{2g} + 2A_u + 3B_{3u}^*$
18. Pentafluoro Benzene	C_{2v}	$3A_2 + 6B_1^*$
19. Pentafluoro Deutero Benzene	C_{2v}	$3A_2 + 6B_1^*$
20. Hexafluoro Benzene	D_{6h}	$2B_{2g} + E_{1g} + A_{2u}^* + 2E_{2u}$

Table 2.1

The x and y axes are degenerate and one of them must coincide with one of the C_2 axes.

4. For planar D_{6h} molecules.

The z axis is the C_6 axis and therefore perpendicular to the molecular plane.

The x and y axes are degenerate and one of them must coincide with one of the C_2' axes.

The C_2' axes and the σ_v planes pass through the greater number of atoms (Rec.5d).

5. For planar C_s molecules.

The xy plane is the σ_h plane and therefore the z axis is perpendicular to the molecular plane.

The Character Tables used are thoseof Wilson, Decius and Cross (8), Appendix X.

SECTION 2.2 Internal Coordinates and Symmetry Coordinates.

For all the molecules there are 12 internal coordinates, used to set up the G and F matrices initially. The force constants are evaluated in terms of the internal coordinates as only in this form are they transferable between similar molecules of different symmetry.

These twelve internal coordinates are designated

1. $r\,dy_i$ $i = 1,6$ the out-of-plane angle bends.
2. $R\,d\phi_i$ $i = 1,6$ the special (or Bell) torsions.

where R is the C-C bond length,

and r is the C-X bond length (X is the substituent).

In terms of the Benzene skeleton, where the carbon atoms are number 1 to 6, and the substituents 7 to 12, the internal coordinates are shown in Figure 2.1.

Using this scheme for the numbering of the atoms in the Benzene skeleton and the schemes for the numbering of the atoms in the internal coordinates given in Section 1.11, the atoms involved in the twelve internal coordinates are given in Tables 2.2 and 2.3.

Having set up the G and F matrices in internal coordinates they are now expressed in symmetry coordinates. There are nine different transformations from internal to symmetry coordinates depending on the symmetry and structure of the molecule. The U (or transformation) matrices are given in Appendix IV, Tables 2.4 - 2.12. Also shown are the symmetry elements for the molecules.

Appendix V lists the moments of inertia for the molecules and the symmetry species associated with a given band shape. This forms a useful aid to assignment of the observed frequencies of a molecule, provided the gas phase spectrum can be obtained.

SECTION 2.3 The Vibrational Assignments

Before commencing on the calculation of the force fields it is necessary to have a complete set (as far as possible) of

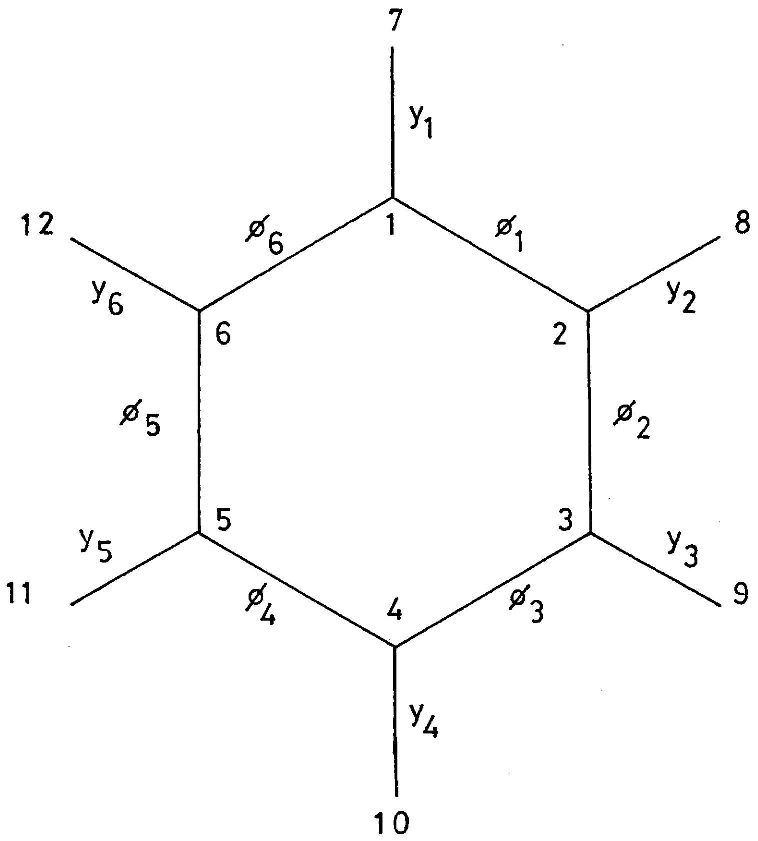


Figure 2.1 The Internal Coordinates

Atoms involved in an Out-of-Plane Angle Bend

INTERNAL COORDINATE	ATOM			
	1	2	3	4
rdy_1	7	6	2	1
rdy_2	8	1	3	2
rdy_3	9	2	4	3
rdy_4	10	3	5	4
rdy_5	11	4	6	5
rdy_6	12	5	7	6

Table 2.2

Atoms involved in a Special Torsion

INTERNAL COORDINATE	ATOM					
	1	2	3	4	5	6
$Rd\phi_1$	6	1	2	3	7	8
$Rd\phi_2$	1	2	3	4	8	9
$Rd\phi_3$	2	3	4	5	9	10
$Rd\phi_4$	3	4	5	6	10	11
$Rd\phi_5$	4	5	6	1	11	12
$Rd\phi_6$	5	6	1	2	12	7

Table 2.3

vibrational frequencies assigned to their symmetry species. Vibrational spectra and assignments for all the molecules considered (with the exception of 1,2,3 trifluoro Benzene) have been previously reported in the literature and form a good basis for this work. However very little data exists for the far Infra Red region. Therefore the vibrational spectra of the following compounds were recorded in the gas phase in the region 100 - 400 cm^{-1}.

1,2 difluoro Benzene
1,4 difluoro Benzene
1,2,4 trifluoro Benzene

1,3,5 trifluoro Benzene

1,2,3,5 tetrafluoro Benzene
1,2,4,5 tetrafluoro Benzene
Pentafluoro Benzene

Hexafluoro Benzene

The spectra are depicted in Figures 2.2 - 2.9.

They were measured in a 107 cm. gas cell using a Grubbs Parsons cube interferometer. The optical layout is shown in Figure 2.10. The output was in the form of a fourier transform of the spectrum recorded on punch tape. This was processed to give a conventional spectrum by the University of London Atlas Computer using an Autocode program.

The compounds were all commercial samples. They were degassed and dried and allowed to evaporate into the cell via a

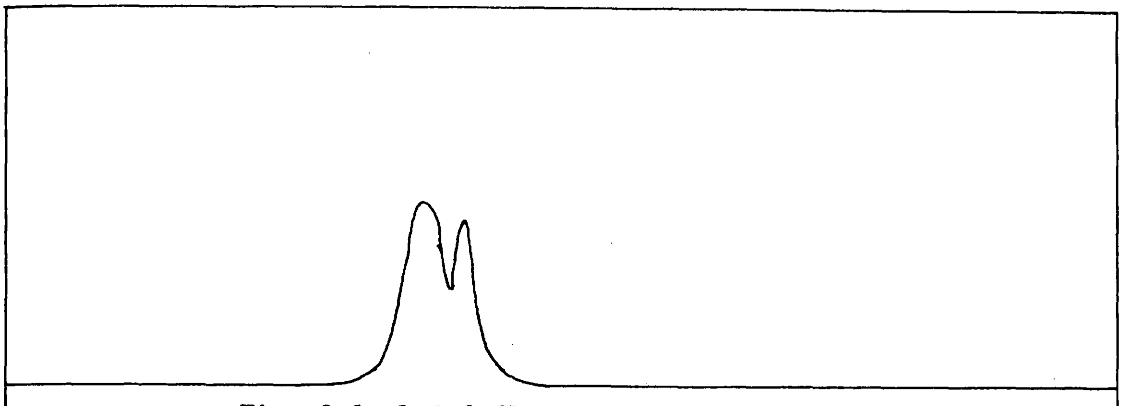


Fig. 2.2 1,2 difluoro Benzene

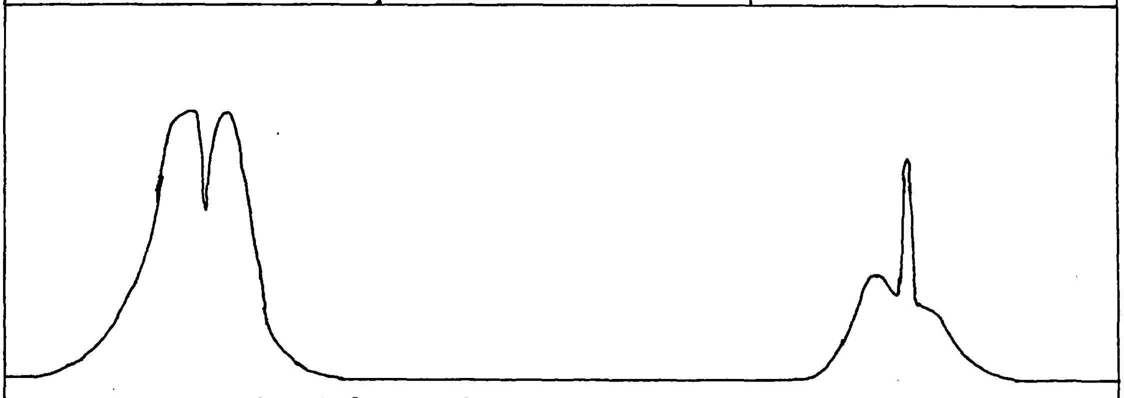


Fig. 2.3 1,4 difluoro Benzene

Fig. 2.4 1,2,4 trifluoro Benzene

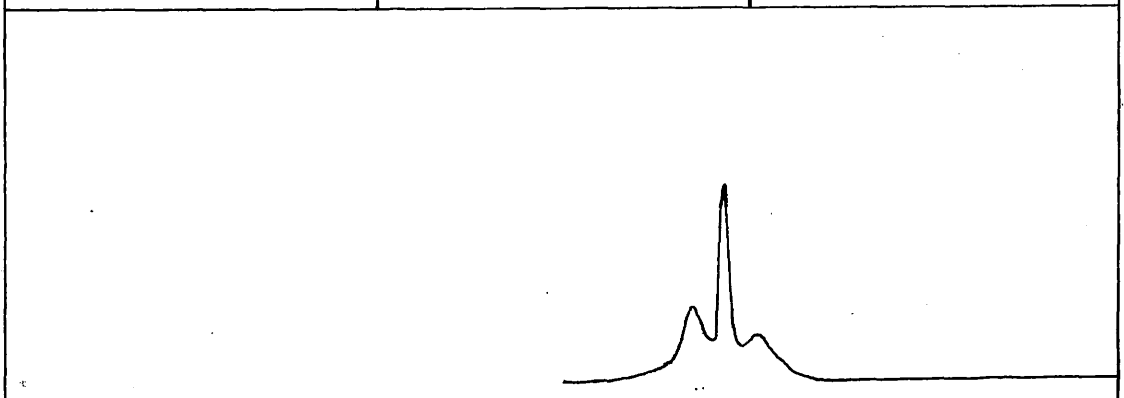


Fig. 2.5 1,3,5 trifluoro Benzene

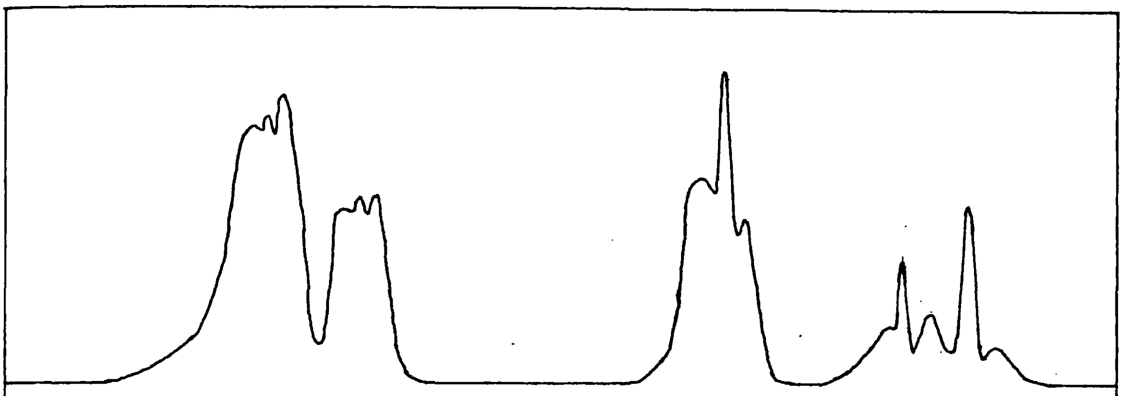


Fig. 2.6 1,2,3,5 tetrafluoro Benzene

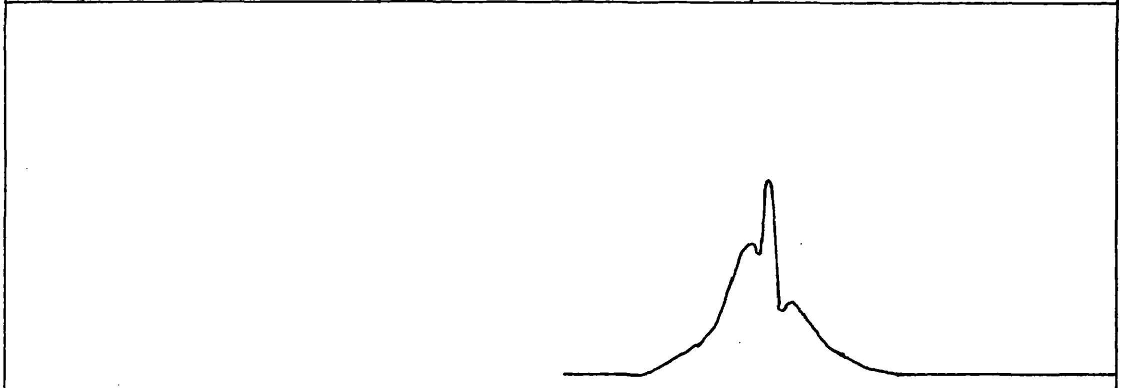


Fig. 2.7 1,2,4,5 tetrafluoro Benzene

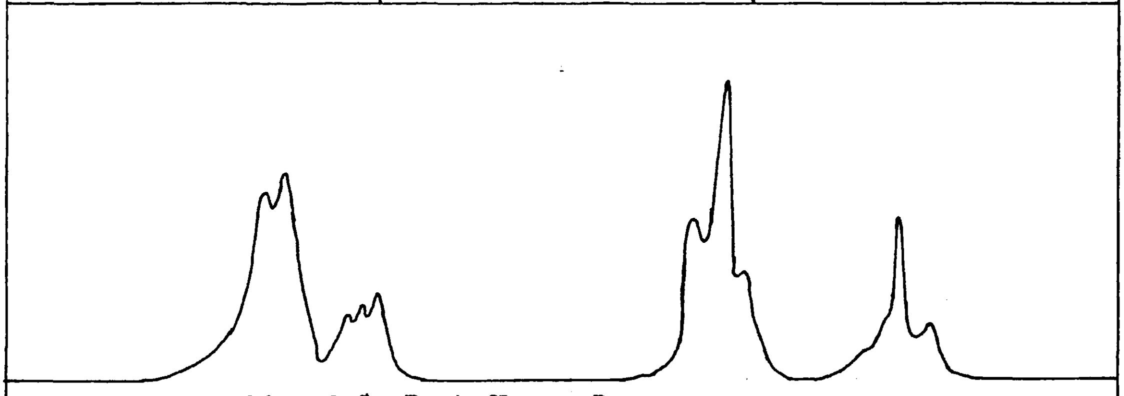


Fig. 2.8 Pentafluoro Benzene

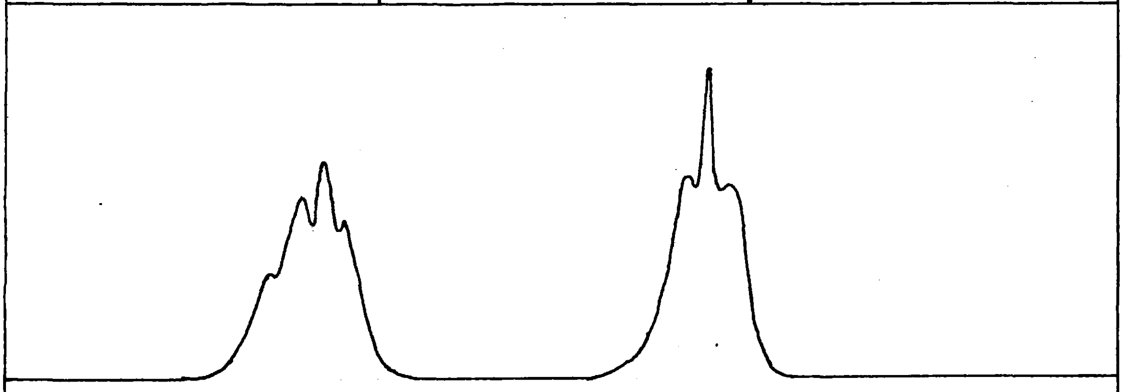


Fig. 2.9 Hexafluoro Benzene

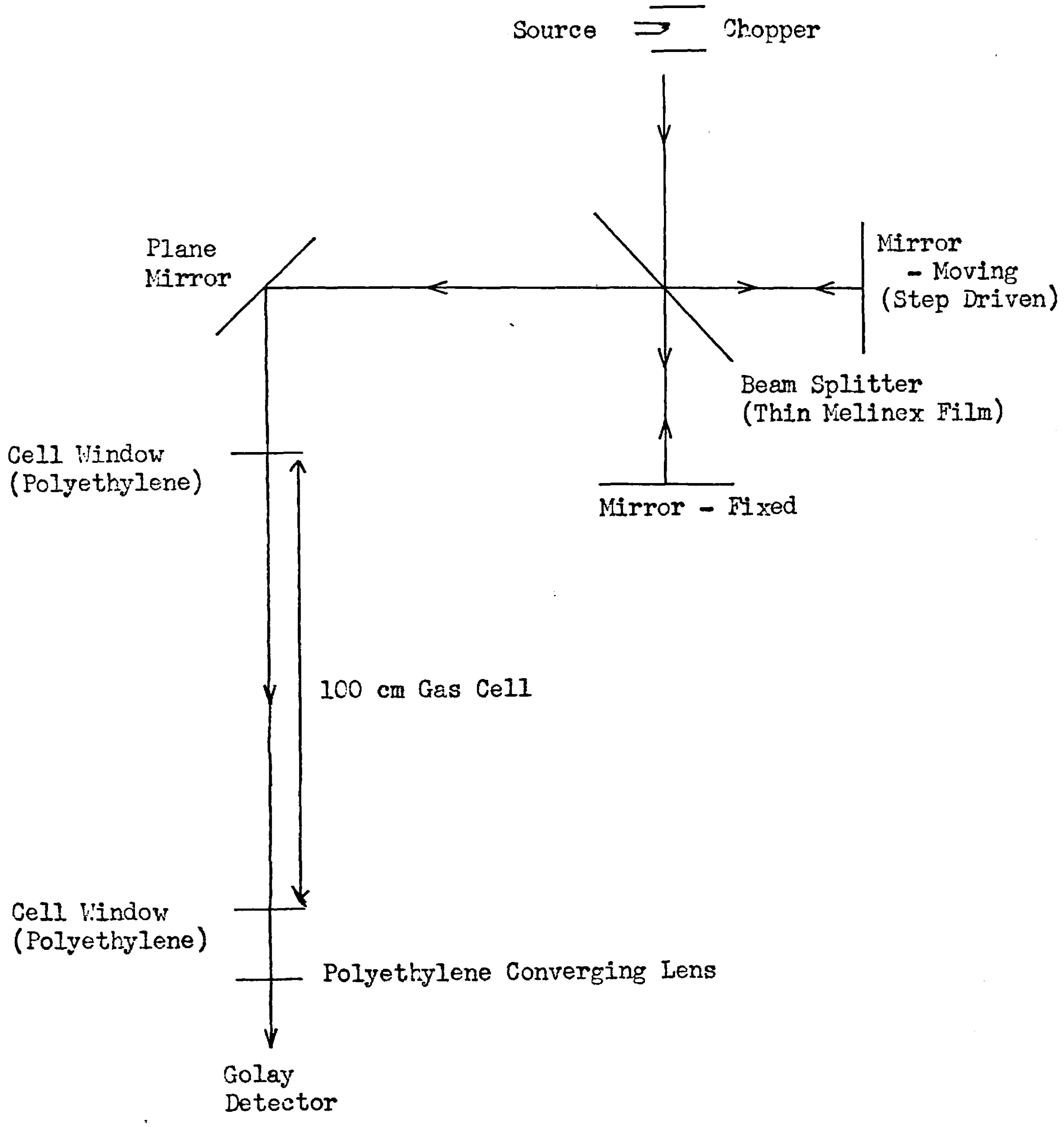


Figure 2.10 Optical Layout of Interferometer

vacuum line. The pressures, which were recorded using a Glycol manometer, were in the region of 5-30 cm. of Glycol (i.e. from $2.58.10^{-7}$ to $1.32.10^{-6}$ moles. cm^{-3}).

Also, wherever possible the spectra between 1000 and 400 cm^{-1} were remeasured in the gas phase in a 10 cm. cell using a Perkin Elmer 325 Infra Red Spectrometer.

The observed frequencies (obs.$\bar{v}$) and their weighting factors (w), which were used in the calculations, are given for each molecule in turn in tables 2.13 - 2.32. Also two sets of results (i.e. the calculated frequencies (calc.$\bar{v}$), the differences between the observed and calculated frequencies ($d\bar{v}$) and the standard deviation of the calculated frequencies (σ ($\bar{v}$))) are given,

A, for an 18 parameter force field

B, for a 23 parameter force field

Both fields were fitted to the data for the entire series of molecules. Also given are the weighted square error (WSQER), the weighted average frequency error ($\overline{|d\bar{v}|}$), and the weighted average standard deviation ($\overline{|\sigma|}$). All frequencies are given in units of cm^{-1}.

The assignments are based not only on the work reported in the literature and the present spectra but also on a number of sets of calculations. Radcliffe and Steele (24) fitted a 15 parameter force field (henceforth referred to as the field of RandS) to the out-of-plane vibrations of Benzene, Fluoro Benzene, 1,4 difluoro Benzene and their fully deuterated analogues (i.e. molecules 1,2,3,4,7 and 8 in Table 2.1) and the frequencies calculated for all molecules using this field form a good starting point for the assignments. Also three stages of perturbation analysis were performed and at each stage by making comparisons between the calculated frequencies and observed spectra it was possible to make further assignments.

Various techniques used in making the assignments include the inequality rule, the examination of the combination bands and the theoretical equivalence of the frequencies in certain cases and they are described in detail where their use occurs.

BENZENE

			18 Parameter Field			23 Parameter Field		
	obs. $\bar{v}$	w	calc. $\bar{v}$	$\overline{dv}$	$\sigma(\bar{v})$	calc. $\bar{v}$	$\overline{dv}$	$\sigma(\bar{v})$
B_{2g}	990	1.0	989.8	- 0.2	9.2	1002.8	+12.8	5.0
	707	1.0	727.7	+20.7	10.2	702.5	- 4.5	5.6
E_{1g}	846	1.0	820.0	-26.0	6.6	837.6	- 8.4	4.3
	846	0.0	820.0	-26.0	6.6	837.6	- 8.4.	4.3
A_{2u}	673	1.0	665.9	- 7.1	10.2	673.4	+ 0.4	5.4
E_{2u}	967	1.0	955.9	-11.1	7.1	981.3	+14.3	4.5
	967	0.0	955.9	-11.1	7.1	981.3	+14.3	4.5
	398	1.0	421.6	+23.6	6.8	411.1	+13.1	3.5
	398	0.0	421.6	+23.6	6.8	411.1	+13.1	3.5
$\overline{\lvert dv \rvert}$ and $\overline{\sigma(v)}$				14.8	8.3		8.9	4.7
WSQER			1.259×10^{-3}			0.618×10^{-3}		

Table 2.13

The fundamental frequencies of Benzene have been discussed in great detail by many authors. Brodersen and Langseth (17) have reviewed the subject as well as accurately measuring the frequencies in the gas and liquid phase. The fundamental frequencies they give are used here. Their assignments are based on those of Ingold and coworkers, who published a long series of papers entitled "The Structure of Benzene". Part XXI (18)summarizes the work.

Only one member of a set of degenerate frequencies is used in the calculations since the set represents only one observation.

HEXADEUTERO BENZENE

			18 Parameter Field			23 Parameter Field		
	obs. $\bar{v}$	w	calc. $\bar{v}$	$d\bar{v}$	$\sigma(\bar{v})$	calc. $\bar{v}$	$d\bar{v}$	$\sigma(\bar{v})$
B_{2g}	829	1.0	837.3	+ 8.3	11.6	832.4	+ 3.4	6.0
	599	1.0	608.9	+ 9.9	8.9	598.7	- .3	4.8
E_{1g}	660	1.0	637.8	-22.2	5.1	651.6	- 8.4	3.4
	660	0.0	637.8	-22.2	5.1	651.6	- 8.4	3.4
A_{2u}	496	1.0	489.1	- 6.9	7.5	494.4	- 1.6	3.9
E_{2u}	787	1.0	778.1	- 8.9	11.2	797.7	+10.7	5.9
	787	0.0	778.1	- 8.9	11.2	797.7	+10.7	5.9
	345	1.0	366.8	+21.8	5.9	357.7	+12.7	3.4
	345	0.0	366.8	+21.8	5.9	357.7	+12.7	3.4
$\overline{\lvert dv \rvert}$ and $\overline{\sigma\ (v)}$				13.0	8.4		6.2	4.6
WSQER				$.572.10^{-3}$			$.182.10^{-3}$	

Table 2.14

As for Benzene, the frequencies and assignments are those of Brodensen and Langseth (17).

FLUORO BENZENE

			18 Parameter Field			23 Parameter Field		
	obs. $\bar{v}$	w	calc.$\bar{v}$	d$\bar{v}$	$\sigma(\bar{v})$	calc.$\bar{v}$	d$\bar{v}$	$\sigma(\bar{v})$
A_2	970	1.0	952.2	-17.8	6.8	960.5	- 9.5	3.6
	826	1.0	811.2	-14.8	6.1	815.6	-10.4	3.2
	405	1.0	418.8	+13.8	6.6	4-8.5	+ 3.5	3.6
B_1	997	1.0	979.3	-17.7	6.5	992.5	- 4.5	3.5
	894	1.0	886.0	- 8.0	4.4	896.7	+ 2.7	2.4
	754	1.0	745.0	- 9.0	5.6	747.3	- 6.7	3.0
	685	1.0	687.4	2.4	5.9	681.6	- 3.4	3.5
	500	1.0	493.5	- 6.5	5.4	503.2	+ 3.2	3.3
	242	1.0	237.5	- 4.5	3.4	242.3	+ .3	2.1
$\overline{\lvert dv \rvert}$ and $\overline{\sigma\ (v)}$				10.5	5.6		4.9	3.1
WSQER			$1.232.10^{-3}$			$.304.10^{-3}$		

Table 2.15

The first complete assignment of Fluoro Benzene was that of Smith et.al.(19).` They observed type C bands in the gas phase infra red spectrum at 894, 754, 685 and 500 cm^{-1}, which were assigned to the B_1 species (B_2 in their notation). They also assigned the Raman band at 242 cm^{-1} as the lowest b_1 vibration. Their assignments for the A_2 species and the remaining b_1 vibration are incorrect and reassignments were made by Scott et.al.(20), which were based on the work of Kolhrausch and Wittig (21). They assigned the A_2 species as 970, 826 and 405 cm^{-1}, assuming that the 826 cm^{-1} band occurs in the liquid phase infra red spectrum in violation of the selection rules. Also they assigned the highest b_1 fundamental as 997 cm^{-1}. Whiffen (22) gives a value of 980 cm^{-1} for this band, but since it has not been observed as a type C band in the gas phase infra red it is impossible to make an accurate assignment.

FLUORO PENTADEUTERO BENZENE

	obs. $\bar{v}$	w	18 Parameter Field calc.$\bar{v}$	 d$\bar{v}$	 $\sigma(\bar{v})$	23 Parameter Field calc.$\bar{v}$	 d$\bar{v}$	 $\sigma(\bar{v})$
A_2	-	0.0	776.2	-	11.5	777.3	-	5.9
	639	1.0	631.2	- 7.8	4.7	634.5	- 4.5	2.5
	350	1.0	363.4	13.4	5.6	357.1	+ 7.1	3.0
B_1	825	1.0	817.2	- 7.8	8.2	817.0	- 8.0	4.3
	767	1.0	738.6	-28.4	6.5	761.5	- 5.5	3.8
	627	1.0	624.2	- 2.8	5.2	619.6	- 7.4	2.9
	556	1.0	545.6	-10.4	4.4	549.8	- 6.2	2.9
	427	1.0	428.3	+ 1.3	5.2	430.5	+ 3.5	2.9
	229	1.0	223.4	- 5.6	3.3	228.7	- .3	2.1
$\overline{\lvert dv \rvert}$ and $\overline{\sigma\ (v)}$				9.7	5.4		5.3	3.1
WSQER				$.812.10^{-3}$			$.154.10^{-3}$	

Table 2.16

The only reported spectra and assignments for Fluoro Pentadeutero Benzene are those of Steele et.al.(23). The strong type C bands at 627, 556 and 427 cm^{-1} were assigned immediately to the B_1 species. A Raman band at 229 cm^{-1} was assigned on the lowest b_1 fundamental. The two remaining b_1 fundamentals were assigned as 825 and 717 cm^{-1}. The 825 cm^{-1} assignment presumably was based on the combination bands and the 717 cm^{-1} assignment was based on an extremely weak type C contour. On the basis of the force field of R and S, which indicates a frequency of 757 cm^{-1}, it seems reasonable to reassign the second highest b_1 fundamental to the weak Raman band at 767 cm^{-1}. The lowest a_2 fundamental was assigned to the extremely weak Raman band at 350 cm^{-1}. The next a_2 fundamental was assigned to the liquid phase infra red band at 682 cm^{-1}, but this assignment is incorrect. It is calculated to be at 644 cm^{-1} using the field of R and S and is therefore reassigned as the medium strength Raman band at 639 cm^{-1}. A tentative assignment of 789 cm^{-1} for the highest a_2 fundamental was made on the basis of the combination bands but not used in the calculations reported here, which indicate however that it is correct.

1,2 DIFLUORO BENZENE

			18 Parameter Field			23 Parameter Field		
	obs. $\bar{v}$	w	calc.$\bar{v}$	d$\bar{v}$	$\sigma(\bar{v})$	calc.$\bar{v}$	d$\bar{v}$	$\sigma(\bar{v})$
A_2	982	0.8	975.3	- 6.7	5.8	984.8	+ 2.8	3.1
	840	0.8	838.5	- 1.5	5.1	847.1	+ 7.1	3.0
	703	1.0	715.7	+12.7	8.2	706.3	+ 3.3	4.9
	-	0.0	552.6	-	8.5	555.6	-	4.9
	198	1.0	178.3	-19.7	3.9	193.8	- 4.2	2.9
B_1	929	1.0	928.8	- 0.2	5.3	931.3	+ 2.3	2.8
	749.	1.0	742.2	- 6.8	5.9	744.5	- 4.5	3.2
	450	1.0	450.1	+ .1	5.2	446.8	- 3.2	3.5
	298	1.0	283.2	-14.8	4.9	279.4	-18.6	2.9
$\overline{\lvert dv \rvert}$ and $\overline{\sigma\ (v)}$				7.8	5.5		5.8	3.3
WSQER			$.242.10^{-3}$			$.122.10^{-3}$		

Table 2.17

Spectra and assignments for 1,2 difluoro Benzene have been reported by Nonnenmacher and Mecke (25),Scott et.al. (26), and Green et.al.(27). They all report type C bands at approximately 930, 750 and 450 cm^{-1}, which were assigned to the B_1 species. The actual values quoted above are those of Green. Using the force field of R and S the lowest b_1 fundamental was calculated to be at 298 cm^{-1} which agrees with the assignment of Green. This was based on a strong Raman line and re-examination of the Raman spectrum confirmed the presence of a strong band, depolarisation ratio 0.75 ± 0.05, at this frequency. The a_2 fundamentals were calculated to be at 978, 811, 743, 543 and 188 cm^{-1}. These values are in reasonable agreement with the assignments of Green with the exception of the band calculated to be at 543 cm^{-1}. Green assigned this fundamental as 596 cm^{-1} on the basis of a weak Raman line at this frequency and a weak liquid phase infra red band at 588 cm^{-1}, appearing in defiance of the selection rules. All calculations place this band in the region of 550 cm^{-1}. On re-examination of the Raman spectra no further bands in this region could be observed due to the presence of the strong b_2 fundamental at 551 cm^{-1} and the strong a_1 fundamental at 568 cm^{-1}. The alternative assignment of $2 \times 298 (b_1) = 596 (a_1)$ exists for the band at 596 cm^{-1}. The 982 and 840 cm^{-1} a_2 fundamentals are given weighting factors of 0.8 since they are assigned to liquid phase infra red bands (27) and are therefore appearing in defiance of selection rules. The 982 cm^{-1} band is very weak and the evidence for the 840 cm^{-1} band is based also on combination bands, which do not indicate an exact frequency. The lowest a_2 fundamental was remeasured and found to be at 198 cm^{-1} rather than 196 cm^{-1}.

Hatta and Kozima (28) from an investigation of the microwave spectra made the following assignments: the lowest a_2 fundamental at 208 ± 10 cm^{-1}; the lowest a_1 fundamental at 255 ± 10 cm^{-1}; the lowest b_1 fundamental at 300 ± 10 cm^{-1}. The a_2 and b_1 assignments agree with those used here but the a_1 causes some confusion. Scott assigned the lowest a_1 fundamental to a "very, very, very weak" Raman band at 240 cm^{-1} which was not detected on re-examination of the Raman spectrum. An examination of the gas phase infra red spectrum (Figure 2.2) showed a confused contour centered at 283 cm^{-1}. It cannot be a type B band as this would indicate a b_2 fundamental, the lowest of which is observed to be at 440 cm^{-1} (26) and calculated by Scherer (26) to be at 424 cm^{-1}. Also there is no strong Q branch and therefore it cannot be the b_1 fundamental observed in the Raman spectrum at 298 cm^{-1}. The liquid phase infra red spectrum shows only one band centred at 287 cm^{-1} too far removed from 298 cm^{-1} tobe the b_1 fundamental. Scherer calculated the lowest a_1 fundamental to be at 319 cm^{-1}. This suggests that the lowest a_1 fundamental is at 287 cm^{-1} and that the value given by Hatta and Kozima is low.

1,3 DIFLUORO BENZENE

			18 Parameter Field			23 Parameter Field		
	obs.$\bar{v}$	w	calc.$\bar{v}$	d$\bar{v}$	$\sigma(\bar{v})$	calc.$\bar{v}$	d$\bar{v}$	$\sigma(\bar{v})$
A_2	879	1.0	885.6	+ 6.6	5.0	887.8	+ 8.8	2.9
	599	1.0	563.4	-35.6	5.5	580.8	-18.2	3.7
	251	1.0	241.5	- 9.5	3.9	248.4	- 2.6	2.7
B_1	978	1.0	964.6	-13.4	4.9	967.0	-11.0	2.6
	853	1.0	867.2	+14.2	4.1	851.0	- 2.0	2.8
	769	1.0	775.8	+ 6.8	5.7	778.2	+ 9.2	3.2
	672	1.0	666.9	- 5.1	6.5	671.0	- 1.0	3.7
	458	1.0	447.6	-10.4	5.5	451.4	- 6.6	3.1
	235	1.0	227.9	- 7.1	3.3	231.0	- 4.0	1.9
$\lvert\overline{dv}\rvert$ and $\overline{\sigma (v)}$				12.1	4.9		7.1	3.0
WSQER			$1.181.10^{-3}$			$.492.10^{-3}$		

Table 2.18

Spectra and assignments for 1,3 difluoro Benzene have been reported by Ferguson et.al.(29) and Nonnenmacher and Mecke (25). Type C bands were observed in the gas phase infra red spectrum by both groups at 853 and 769 cm^{-1} and by Nonnenmacher and Mecke at 672 and 458 cm^{-1}. Ferguson and coworkers observed the corresponding bands in the liquid phase. However they assigned the 458 cm^{-1} band as a b_2 fundamental and one at 480 cm^{-1} as the b_1 fundamental. These assignments were reversed by Green et.al.(27), who revised many of Ferguson's assignments, and this is supported by calculations using the field of R and S which indicate that this b_1 fundamental is at 438 cm^{-1}. The lowest b_1 fundamental was assigned to a depolarised Raman line at 255 cm^{-1}. Green assigned the highest b_1 fundamental as 978 cm^{-1}. This is based on the infra red active C-H out-of-plane angle bend combination bands found in the region 1600 - 1900 cm^{-1}, which follow a highly characteristic pattern for substituted Benzenes (30). The following bands taken from Ferguson's paper indicate a fundamental in the region of 978 cm^{-1}.

		calc.	obs.
769 (b_1) + 978 (b_1)	=	1747	1751
879 (a_2) + 978 (b_1)	=	1857	1852
2 x 978 (b_1)	=	1956	1961

The assignments for the A_2 species made by Green (assuming that their value of 271 cm^{-1} for the lowest should read 251 cm^{-1}) are identical with those of Ferguson and are used in the calculations without modification.

1,4 DIFLUORO BENZENE

			18 Parameter Field			23 Parameter Field		
	obs.$\bar{v}$	w	calc.$\bar{v}$	$\bar{dv}$	$\sigma(\bar{v})$	calc.$\bar{v}$	$\bar{dv}$	$\sigma(\bar{v})$
B_{1g}	800	1.0	803.0	+ 3.0	6.4	799.9	- 0.1	3.7
B_{2g}	928	1.0	923.7	- 4.3	6.6	917.2	-10.8	4.4
	692	1.0	685.3	- 6.7	8.2	694.7	+ 2.7	4.4
	375	1.0	360.2	-14.8	5.3	380.7	+ 5.7	3.5
A_u	943	1.0	947.6	+ 4.6	6.8	933.2	- 9.8	4.5
	405	1.0	415.8	+10.8	6.4	406.0	+ 1.0	4.6
B_{3u}	836	1.0	824.9	-11.1	7.4	833.4	- 2.6	4.2
	508	1.0	515.8	+ 7.8	7.2	522.1	+14.1	4.1
	157	1.0	156.4	- 0.6	2.8	160.0	+ 3.0	1.7
$\overline{\vert dv \vert}$ and $\overline{\sigma}$ (v)				7.1	6.3		5.5	3.8
WSQER				$.295.10^{-3}$			$.347.10^{-3}$	

Table 2.19

Spectra and assignments have been reported for 1,4 difluoro Benzene by Ferguson et.al.(31). Stojiljkovic and Whiffen (32) made a number of reassignments based on a comparison with 1,4 dichloro, 1,4 dibromo and 1,4 diiodo Benzene. Steele et.al.(33) examined the liquid phase far infra red spectrum and assigned a band at 164 cm^{-1} as the lowest b_{3u} fundamental. An examination of the gas phase far infra red spectrum (Figure 2.3) confirmed this assignment by the observation of a band with a type C contour at 157 cm^{-1}. The two other b_{3u} fundamentals were also reexamined in the gas phase infra red and observed to be at 836 and 508 cm^{-1}. For the other symmetry species the assignments of Stojiljkovic and Whiffen were used in the calculations, except for the lower a_u fundamental for which they made no assignment. Gates et.al.(34) and Green et.al.(27) both give a value of 405 cm^{-1} for this fundamental but offer no explanation. Since vibrations of the A_u species are inactive in both the infra red and Raman the assignment is presumably made on the basis of the combination bands, of which the following support the value of 405 cm^{-1}.

	Calculated	Observed
405 (a_u) + 800 (b_{1g}) =	1205 (b_{1u})	1203
405 (a_u) + 1617 (b_{3g}) =	2022 (b_{3u})	2020

1,4 DIFLUORO TETRADEUTERO BENZENE

			18 Parameter Field			23 Parameter Field		
	obs.$\bar{v}$	w	calc.$\bar{v}$	d$\bar{v}$	$\sigma(\bar{v})$	calc.$\bar{v}$	d$\bar{v}$	$\sigma(\bar{v})$
B_{1g}	614	1.0	624.7	+10.7	4.9	622.3	+ 8.3	2.9
B_{2g}	780	1.0	768.2	-11.8	9.3	777.9	- 2.1	5.3
	600	1.0	609.2	+ 9.2	6.5	599.6	- 0.4	4.2
	366	1.0	347.7	-18.3	5.4	371.2	+ 5.2	3.6
A_u	-	0.0	774.2	-	11.9	751.9	-	7.5
	-	0.0	360.1	-	5.5	356.5	-	2.8
B_{3u}	732	1.0	719.3	-12.7	9.1	739.7	+ 7.7	4.8
	422	1.0	432.0	+10.0	6.6	427.8	+ 5.8	3.6
	163	1.0	154.1	- 8.9	2.8	158.4	- 4.6	1.8
$\overline{\lvert dv \rvert}$ and $\overline{\sigma (v)}$				11.6	6.4		4.9	3.7
WSQER			$.423.10^{-3}$			$.099.10^{-3}$		

Table 2.20

The only reported spectra and assignments for 1,4 difluoro Tetradeutero Benzene are those of Gates et.al.(34). Steele et.al. (33) examined the liquid phase far infra red spectrum and assigned the lowest b_{3u} fundamental to a band at 164 cm^{-1}. Tentative assignments of 780 and 367 cm^{-1} were made (34) for the two a_u

fundamentals on the basis of a comparison with 1,4 dichloro Tetradeutero Benzene but since they are inactive in both the Raman and infra red they were not observed. The calculations show that they are in the regions suggested.

1,2,3 TRIFLUORO BENZENE

			18 Parameter Field			23 Parameter Field		
	obs.$\bar{v}$	w	calc.$\bar{v}$	d$\bar{v}$	$\sigma(\bar{v})$	calc.$\bar{v}$	d$\bar{v}$	$\sigma(\bar{v})$
A_2			885.6		5.0	885.5		2.9
			562.6		5.5	556.7		4.6
			237.2		4.3	248.2		2.4
B_1			965.2		5.0	966.7		2.6
			769.9		4.5	774.6		2.9
			709.5		7.8	698.0		4.3
			543.6		8.6	537.4		4.6
			301.5		6.4	289.2		3.7
			139.5		3.9	155.6		3.3

Table 2.21

No spectra or assignments have been reported for 1,2,3 trifluoro Benzene. If and when they are obtained the out-of-plane fundamentals would be expected to be in close agreement with the calculated frequencies.

1,2,4 TRIFLUORO BENZENE

			18 Parameter Field			23 Parameter Field		
	obs.$\bar{v}$	w	calc.$\bar{v}$	d$\bar{v}$	$\sigma(\bar{v})$	calc.$\bar{v}$	d$\bar{v}$	$\sigma(\bar{v})$
A''	928	1.0	938.5	+10.5	4.0	925.5	- 2.5	3.4
	856	1.0	867.0	+11.0	3.9	848.2	- 7.8	2.8
	808	1.0	812.6	+ 4.6	4.2	815.4	+ 7.4	2.6
	688	0.8	690.1	+ 2.1	6.1	700.1	+12.1	4.5
	604	1.0	594.4	- 9.6	5.2	601.1	- 2.9	2.8
	455	1.0	449.9	- 5.1	5.3	449.1	- 5.9	3.4
	377	0.8	364.4	-12.4	4.3	377.0	0.0.0	2.8
	231	1.0	226.0	- 5.0	3.3	230.5	- 0.5	2.0
	151	1.0	143.8	- 7.2	3.2	153.1	+ 2.1	1.7
$\overline{\lvert dv \rvert}$ and $\overline{\sigma(v)}$				7.5	4.4		4.6	2.9
WSQER			.360.10^{-3}			.212.10^{-3}		

Table 2.22

The only reported spectra and assignments for 1,2,4 trifluoro Benzene are by Ferguson et.al.(35). As they only reported liquid phase infra red spectra it was desirable to check their assignments by examining the gas phase spectra. Type C bands were found at 928, 856, 808, 604, 455, 230 and 151 cm^{-1}. The far infra red spectrum is shown in Figure 2.4. These assignments agree with those of Ferguson who also assigned the two remaining a'' fundamentals as 688 and 377 cm^{-1}. Since the infra red bands at these frequencies were observed to be of medium strength in the liquid phase and depolarized in the Raman, these assignments were accepted but since no gas phase frequencies are known they are given weighting factors of 0.8.

Further confirmation for the positions of these two fundamentals is afforded by a comparison with 1,2 difluoro Benzene, which is converted to 1,2,4 trifluoro Benzene by replacement of a Hydrogen atom by a Fluorine atom in the 4 position. According to the inequality rule of Steele and Whiffen (37) the ith highest frequency of 1,2,4 trifluoro Benzene lies between the ith and i+1 th highest frequencies of 1,2 difluoro Benzene, provided that:-

1. There is no change in the force field of the $C_6H_3F_2$ - skeleton.
2. The interaction force constants between this skeleton and the substituent (either Hydrogen or Fluorine) are negligible.

Introduction of a Fluorine atom in the 4 position of 1,2 difluoro Benzene removes the C_2 axis and the A_2 and B_1 symmetry species coalesce to become the A'' species of 1,2,4 trifluoro Benzene. The σ_h plane is retained so when comparing the frequencies only the out-of-plane vibrations are considered. The observed frequencies and the calculated frequencies, using the field of R and S, of the two molecules are compared below.

observed		calculated	
1,2 $C_6H_4F_2$	1,2,4 $C_6H_3F_3$	1,2 $C_6H_4F_2$	1,2,4 $C_6H_3F_3$
982		978	
	928		952
929		941	
	856		903
840		871	
	808		840
750		753	
	688		731
703		743	
	604		594
585		543	
	455		437
451		440	
	377		383
289		298	
	231		240
197		188	
	151		151

As expected, the 377 cm^{-1} fundamental of 1,2,4 trifluoro Benzene lies between the 451 and 289 cm^{-1} fundamentals of 1,2 difluoro Benzene. The 688 cm^{-1} fundamental does not lie between the 750 and 703 cm^{-1} fundamentals but the inequality rule does show that the remaining fundamental of 1,2,4 trifluoro Benzene has to be assigned as the fourth highest. Ferguson et.al.(35) report a weak infra red band at 717 cm^{-1} but to assign this as an a'' fundamental in preference to the medium strength band at 688 cm^{-1} seems dubious. Comparison with the calculated frequencies shows that again the fourth highest fundamental of

1,2,4 trifluoro Benzene (calculated to be at 731 cm^{-1}) does not lie between the fourth (753 cm^{-1}) and the fifth (743 cm^{-1}) highest fundamentals of 1,2 difluoro Benzene. This is because the second condition is not upheld, there are interaction force constants between the substituent and the ring and furthermore they change on altering the substituent. Since the calculated and observed frequencies deviate from the predictions of the inequality rule in the same manner the assignment of the 688 cm^{-1} band as an a'' fundamental is justified.

Green et.al.(36) suggested that the assignments of the lowest a' fundamental at 288 cm^{-1} and the second lowest a'' fundamental at 230 cm^{-1} should be reversed. However the gas phase infra red spectrum shows clearly a type C band at 230 cm^{-1} and a type A band at 284 cm^{-1}.

1,3,5 TRIFLUORO BENZENE

			18 Parameter Field			23 Parameter Field		
	obs.$\bar{v}$	w	calc.$\bar{v}$	d$\bar{v}$	$\sigma(\bar{v})$	calc.$\bar{v}$	d$\bar{v}$	$\sigma(\bar{v})$
A_2''	847	1.0	857.8	+10.8	8.7	847.7	+ 0.7	4.6
	664	1.0	648.7	-15.3	9.5	665.0	+ 1.0	5.1
	206	1.0	212.5	+ 6.5	4.5	217.0	+11.0	2.8
E''	858	0.5	874.6	+16.6	5.4	853.5	- 4.5	4.1
	858	0.0	874.6	+16.6	5.4	853.5	- 4.5	4.1
	595	1.0	559.4	-35.6	5.4	581.3	-13.7	3.6
	595	0.0	559.4	-35.6	5.4	581.3	-13.7	3.6
	253	1.0	240.6	-12.4	4.0	246.6	- 6.4	2.6
	253	0.0	240.6	-12.4	4.0	246.6	- 6.4	2.6
$\overline{\lvert dv \rvert}$ and $\overline{\sigma\ (v)}$				16.2	6.3		6.2	3.8
WSQER			$1.003.10^{-3}$			$.113.10^{-3}$		

Table 2.23

Spectra and assignments for 1,3,5 trifluoro Benzene have been reported by Nielsen et.al.(38) and by Scherer et.al.(40). Nielsen's assignments were revised by Ferguson (39). The gas phase far infra red spectrum (Figure 2.5) shows a previously unobserved type C band at 206 cm^{-1}. This confirms the previous assignment (38) which was based on combination bands. The positions of the two other a_2'' fundamentals were also checked by reexamining the gas phase infra red spectra and type C bands were observed at 847 and 664 cm^{-1}. The assignments of Nielsen for two of the e'' fundamentals are followed but the assignment of 1191 cm^{-1} for the highest is incorrect. Ferguson reassigns a weak Raman band at 847 cm^{-1} to this fundamental (it could also be the a_2'' fundamental appearing in defiance of the selection rules) but an assignment of approximately 858 cm^{-1}, on the basis of a medium strength combination band at 1695 cm^{-1} (847 (a_2'') + 858 (e'')) is preferred. It is given a weighting factor of 0.5.

This conclusion is supported by a comparison with the b_1 fundamentals of 1,3 difluoro Benzene. Replacement of a Fluorine atom by a Hydrogen in the 5 position lowers the symmetry from D_{2h} to C_{2v}. The A_2'' symmetry species and one set of the doubly degenerate E'' species of the point group D_{3h} coalesce to become the B_2 species in the point group C_{2v}. Thus the b_1 fundamentals of 1,3 difluoro Benzene are compared with the combined a_2'' + e'' fundamentals of 1,3,5 trifluoro Benzene.

1,3 $C_6H_4F_2(b_1)$	1,3,5 $C_6H_3F_3(a_2'' + e'')$
978	858
853	847
769	664
672	595
458	253
235	206

The other set of the E'' species becomes the A_2 species. These fundamentals are discussed in the section on 1,2,3,5 tetrafluoro Benzene.

1,3,5 TRIFLUORO MONODEUTERO BENZENE

			18 Parameter Field			23 Parameter Field		
	obs.$\overline{v}$	w	calc.$\overline{v}$	d$\overline{v}$	$\sigma(\overline{v})$	calc.$\overline{v}$	d$\overline{v}$	$\sigma(\overline{v})$
	-		874.6	-	5.4	853.5	-	4.1
A_2	595		559.4	-35.6	5.4	581.3	-13.7	3.6
	253		240.6	-12.4	4.0	246.6	- 6.4	2.6
	840		863.3	+23.3	5.4	849.3	+ 9.3	3.3
	743		743.6	+ 9.6	5.5	747.6	+13.6	3.5
B_1	628		610.5	-17.5	7.2	622.5	- 5.5	3.7
	537		527.2	- 9.8	4.6	532.4	- 4.6	2.9
	240		227.8	-12.2	4.1	235.3	- 4.7	2.8
	-		212.2	-	4.5	217.0	-	2.8
$\overline{\lvert dv \rvert}$ and $\sigma\,\overline{(v)}$				17.2	5.2		8.2	3.2
WSQER								

Table 2.24

The assignments and frequencies for 1,3,5 trifluoro Monodeutero Benzene were taken from the paper of Scherer et.al.(40). They were not weighted to avoid over emphasis on the frequencies of the 1,3,5 trifluoro Benzenes in the calculations. The average frequency erros and average dispersions given are the unweighted results instead of the weighted.

1,3,5 TRIFLUORO DIDEUTERO BENZENE

			18 Parameter Field			23 Parameter Field		
	obs.$\bar{v}$	w	calc.$\bar{v}$	d$\bar{v}$	$\sigma(\bar{v})$	calc.$\bar{v}$	d$\bar{v}$	$\sigma(\bar{v})$
A_2	-		721.1	-	8.3	712.2	-	5.7
	537		528.0	- 9.0	5.4	536.0	- 1.0	3.5
	236		222.2	-13.8	4.2	230.4	- 5.6	2.9
B_1	837		868.9	+31.9	3.9	851.2	+14.2	2.9
	754		756.0	+ 2.0	8.1	766.2	+12.2	4.0
	606		582.4	-23.6	5.5	598.1	- 7.9	3.2
	527		525.6	- 1.4	4.2	526.6	- 0.4	2.8
	250		233.8	-16.2	4.1	240.7	- 9.3	2.7
	-		212.1	-	4.5	217.0	-	2.8
$\overline{\lvert dv \rvert}$ and $\overline{\sigma(v)}$				14.0	5.1		7.2	3.1
WSQER								

Table 2.25

The assignments and frequencies for 1,3,5 trifluoro Dideutero Benzene were taken from the paper of Scherer et.al.(40). They were given weighting factors of 0.0 to avoid over emphasis on the frequencies for the 1,3,5 trifluoro Benzenes in the calculations. The average frequency errors and average dispersions given are the unweighted results instead of the weighted.

1,3,5 TRIFLUORO TRIDEUTERO BENZENE

			18 Parameter Field			23 Parameter Field		
	obs.$\overline{v}$	w	calc.$\overline{v}$	d$\overline{v}$	$\sigma(\overline{v})$	calc.$\overline{v}$	d$\overline{v}$	$\sigma(\overline{v})$
A''_2	771	1.0	764.3	- 6.7	11.1	779.4	+ 8.4	5.5
	520	1.0	522.0	+ 2.0	7.8	517.5	- 2.5	4.1
	214	0.5	212.0	- 2.0	4.5	217.0	+ 3.0	2.8
E''	-	0.0	721.1	-	8.3	712.2	-	5.7
	-	0.0	721.1	-	8.3	712.2	-	5.7
	537	1.0	528.0	- 9.0	5.4	536.0	- 1.0	3.5
	537	0.0	528.0	- 9.0	5.4	536.0	- 1.0	3.5
	236	1.0	222.2	-13.8	4.2	230.4	- 5.6	2.9
	236	0.0	222.2	-13.8	4.2	230.4	- 5.6	2.9
$\lvert\overline{dv}\rvert$ and $\overline{\sigma(v)}$				6.7	6.6		4.1	3.8
WSQER			.084.10^{-3}			.065.10^{-3}		

Table 2.26

The assignments and frequencies for 1,3,5 trifluoro Trideutero Benzene were taken from the paper of Scherer et.al.(40) and were used without modification.

1,2,3,4 TETRAFLUORO BENZENE

			18 Parameter Field			23 Parameter Field		
	obs.$\bar{v}$	w	calc.$\bar{v}$	d$\bar{v}$	$\sigma(\bar{v})$	calc.$\bar{v}$	d$\bar{v}$	$\sigma(\bar{v})$
A_2	922	0.5	938.4	+16.4	4.1	924.6	+ 2.6	3.4
	717	0.5	708.5	- 8.5	8.1	707.1	- 9.9	4.7
	537	0.8	545.1	+ 8.1	5.7	527.7	- 9.3	4.2
	374	1.0	363.4	-10.6	4.4	373.0	- 1.0	2.6
	169	1.0	137.9	-31.1	4.3	155.9	-13.1	3.9
B_1	802	1.0	812.5	+10.5	4.6	813.1	+11.1	2.9
	596	1.0	620.0	+24.0	8.5	597.8	+ 1.8	4.7
	286	0.8	292.5	+ 6.5	6.6	278.5	- 7.5	3.8
	154	1.0	141.8	-12.2	3.5	152.4	- 1.6	2.0
$\overline{\lvert dv \rvert}$ and $\overline{\sigma(v)}$				14.2	5.5		6.2	3.6
WSQER				$.665.10^{-3}$			$.189.10^{-3}$	

Table 2.27

The only reported spectra and assignments for 1,2,3,4 tetrafluoro Benzene are by Steele (41). A reexamination of the gas phase infra red spectrum confirmed the presence of type C bands at 802 and 596 cm^{-1}. A type C band was observed at 154 cm^{-1} in the far infra red spectrum. No other type C band was observed which would correspond to Steele's assignment of the Raman band at 292 cm^{-1} as the remaining b_1 fundamental. However there is a shoulder at 286 cm^{-1} on the type B band centred at 279 cm^{-1} and this was assigned as the remaining b_1 fundamental and given a weighting factor of 0.8. To assist in the assignments of the A_2 species the Raman spectrum was also reexamined. The only assignment Steele makes for this species is the highest at 929 cm^{-1}. This was remeasured to be at 922 cm^{-1}. Using the force field of R and S the a_2 fundamentals were calculated to be at 952, 792, 538, 383 and 150 cm^{-1}. On this basis the Raman bands at 537, 374 and 169 cm^{-1} were assigned as a_2 fundamentals. The bands at 374 and 169 cm^{-1} were previously assigned as b_1 fundamentals (41). The weak bands in the liquid phase infra red spectrum at 540 and 376 cm^{-1} are the a_2 fundamentals appearing in defiance of the selection rules.

These assignments were used in a first set of calculations to help to establish the position of the remaining a_2 fundamental. They indicated that it was in the region of 707 cm^{-1}. An examination of the combination bands provided four bands which suggest a fundamental at approximately 717 cm^{-1}.

		Calculated	Observed
$922(a_2) + 717(a_2)$	=	1639 (a_1)	1638 m.
$596(b_1) + 717(a_2)$	=	1313 (b_2)	1314 vw.
$374(a_2) + 717(a_2)$	=	1091 (a_1)	1089 w.
$286(b_1) + 717(a_2)$	=	1003 (b_2)	1003 w.

Therefore the final a_2 fundamental was assigned as 717 cm^{-1} and given a weighting factor of 0.5.

1,2,3,5 TETRAFLUORO BENZENE

			18 Parameter Field			23 Parameter Field		
	obs.$\bar{v}$	w	calc.$\bar{v}$	d$\bar{v}$	$\sigma(\bar{v})$	calc.$\bar{v}$	d$\bar{v}$	$\sigma(\bar{v})$
A_2	838	0.8	874.5	+36.5	5.4	851.0	+13.0	4.1
	-	0.0	558.5	-	5.5	557.2	-	4.5
	258	1.0	236.3	-21.7	4.5	246.5	-11.5	2.3
B_1	843	1.0	863.3	+20.3	4.7	845.4	+ 2.4	3.1
	706	1.0	700.5	- 5.5	7.0	701.5	- 4.5	4.0
	610	1.0	595.9	-14.1	4.7	611.8	+ 1.8	3.2
	368	0.8	372.5	+ 4.5	4.4	369.5	+ 1.5	2.6
	205	0.8	211.2	+ 6.2	4.2	211.1	+ 6.1	2.4
	139	1.0	124.4	-14.6	4.0	138.6	- 0.4	2.7
$\overline{\|dv\|}$ and $\overline{\sigma(v)}$				15.4	4.9		5.1	3.1
WSQER				$1.672.10^{-3}$			$.168.10^{-3}$	

Table 2.28

The only reported spectra and assignments for 1,2,3,5 tetrafluoro Benzene are by Steele (41). On reexamining the gas phase infra red spectra the sample used was found to be contaminated with Pentrafluoro Benzene. However type C bands belonging to 1,2,3,5 tetrafluoro Benzene could be observed at 843,708 and 610 cm^{-1}, which agreed with the assignments of Steele, and at 139 cm^{-1} (Figure 2.6) in the far infra red, which was previously unobserved. Using the field of R and S the two remaining b_1 fundamentals were calculated to be 388 and 222 cm^{-1}. No absorption was observed in the region of 388 cm^{-1} so Steele's assignment of 368 cm^{-1}, based on the liquid phase infra red spectrum, was accepted and given a weighting factor of 0.8. The strong absorption in the region of 205 cm^{-1} is partly due to the Pentafluoro Benzene impurity but the band due to this molecule is obviously overlaid by something on the high frequency side (compare Figures 2.6 and 2.8). This was assigned as the b_1 fundamental of 1,2,3,5 tetrafluoro Benzene, given a value of 205 cm^{-1} and a weighting factor of 0.8.

For the C_{2v} point group the a_2 vibrations are antisymmetrical to both the $\sigma_v(yz)$ and $\sigma_v(xz)$ planes. This means that if the C_2 axis and $\sigma_v(xz)$ plane coincide with four of the atoms (e.g. for 1,2,3,5 tetrafluoro Benzene they coincide with atoms 2 and 8, and 5 and 11) no a_2 vibration can involve motion of these atoms. This follows since an out-of-plane vibration of these atoms must be in the $\sigma_v(xz)$ plane and therefore can only be symmetrical with respect to this plane. Thus the G matrices for the A_2 species is the same for all substituted Benzenes whose only differences are the substituents coincident with the C_2 axis.

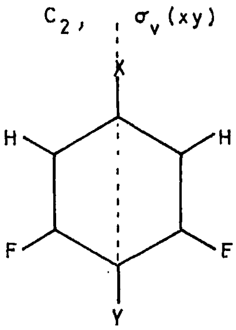


Figure 2.11

From Figure 2.11 can be seen that one such series is formed by the molecules

1,3 difluoro Benzene (X and Y = H)
1,2,3 trifluoro Benzene (X = H, Y = F)
1,3,5 trifluoro Benzene (X = F, Y = H)
1,2,3,5 tetrafluoro Benzene (X and Y = F)

Therefore unless there is force field change, the a_2 frequencies, going through the series, will be identical. A comparison of the fundamental frequencies shows that there are some changes but the theory still forms a considerable aid in making assignments.

1,3 $C_6H_4F_2$	1,3,5 $C_6H_3F_3$	1,2,3,5 $C_6H_2F_4$
879	858	838
599	595	561
251	253	258

Steele (41) incorrectly compared the a_2 vibrations of 1,2,3,5 tetrafluoro Benzene with the a_2'' vibrations of 1,3,5 trifluoro Benzene. On making the correct comparison with the e'' vibrations (see the section on 1,3,5 trifluoro Benzene) the lowest

a_2 fundamental was assigned to the Raman band at 258 cm^{-1}. The highest a_2 fundamental was obtained from the C-H summation bands. According to Whiffen (30) three such bands are expected: the highest b_1 + the highest a_2 fundamental; 2 x the highest b_1 ; and 2 x the highest a_2. The medium strength liquid phase infra red band at 1681 cm^{-1} was assigned as the $a_2 + b_1$ summation band, giving a frequency of approximately 838 cm^{-1} for the a_2 fundamental. It was given a weighting factor of 0.8.

The assignment of the remaining fundamental is made on the basis of the calculations, which indicate a value in the region of 557 cm^{-1}. Steele reported a medium strength combination band at 1267 cm^{-1} in the liquid phase infra red which was assigned as 997 (a_1) + 258 (b_2) = 1255 (b_2). The reassignment of the 258 cm^{-1} Raman band as an a_2 fundamental means that the combination band would also be an a_2 vibration and therefore inactive in the infra red. A preferable assignment of 706 (b_1) + 561 (a_2) = 1267 (b_2) indicates a value of 561 cm^{-1} for the a_2 fundamental, which is in good agreement with the calculations.

1,2,4,5 TETRAFLUORO BENZENE

			18 Parameter Field			23 Parameter Field		
	obs.$\bar{v}$	w	calc.$\bar{v}$	$d\bar{v}$	$\sigma(\bar{v})$	calc.$\bar{v}$	$d\bar{v}$	$\sigma(\bar{v})$
B_{1g}	417	1.0	410.6	- 6.4	6.6	410.9	- 6.1	4.6
B_{2g}	835	0.8	851.2	+16.2	6.6	838.3	+ 3.3	4.4
	-	0.0	669.5	-	9.9	696.1	-	7.3
	295	1.0	279.0	-16.0	6.8	303.5	+ 8.5	4.1
A_u	-	0.0	682.0	-	15.7	676.4	-	9.1
	-	0.0	115.2	-	4.0	128.7	-	2.7
B_{3u}	868	1.0	884.9	+16.9	5.9	852.6	-16.0	4.2
	457	1.0	450.8	- 6.2	7.4	453.4	- 3.6	5.1
	194	1.0	191.0	- 3.0	4.4	185.3	- 8.7	2.8
$\overline{\lvert dv \rvert}$ and $\overline{\sigma\ (v)}$				10.8	6.3		7.7	4.2
WSQER			$.562.10^{-3}$			$.296.10^{-3}$		

Table 2.29

The only reported spectra and assignments for 1,2,4,5 tetrafluoro Benzene are by Ferguson et.al.(42). Steele and Whiffen have reported force fields for the infra red active vibrations (the

B_{1u}, B_{2u} and B_{3u} species) (43) and made some reassignments on the basis of a comparison with Pentafluoro Benzene (44). Type C bands were observed in the gas phase infra red spectrum at 868 and 457 cm^{-1}, which agreed with the previous assignments, and at 197 cm^{-1} in the far infra red spectrum (figure 2.7), which was previously unobserved. The assignment of 417 cm^{-1} for the b_{1g} fundamental was accepted. The value of 871 cm^{-1} for the highest b_{3g} fundamental appeared to be too high. On examination of the C-H summation band region no band was observed which would support this assignment but a medium strength band was observed at 1703 cm^{-1}. This indicates a value of approximately 835 cm^{-1} (835 (b_{2g})+ 868 (b_{3u}) = 1703 (b_{3u})) for the highest b_{2g} fundamental. There is a weak Raman band at 832 cm^{-1}, which Ferguson assigned as an a_g fundamental. Steele suggested that this fundamental should be in the region of 280 cm^{-1} and provided the alternative assignment of 2 x 417 (b_{1g}) = 834 (a_g) for the 832 cm^{-1} band. Alternatively it could be the highest b_{2g} fundamental which is Raman active. The positions of all the b_{2g} fundamentals are supported by a comparison with the b_1 fundamentals of Pentafluoro Benzene, which are well known, and application of the inequality rule. In going from point group D_{2h} to C_{2v} the B_{2g} and B_{3u} symmetry species coalesce to become the B_1 species.

1,2,4,5 $C_6H_2F_4$ (b_{2g} + b_{3u})	C_6HF_5 (b_1)
868	837
835	697
669	555
457	323
295	206
194	158

All the 1,2,4,5 tetrafluoro Benzene fundamentals occupy the predicted positions. The two other b_{2g} assignments of 669 and 295 cm^{-1} are those of Ferguson (42). The 669 cm^{-1} value, though not used in the calculations, is probably correct.

The two a_u fundamentals are inactive in both the infra red and Raman and no values were used in the calculations. Ferguson gave a value of 140 cm^{-1} for the lower a_u fundamental based on combination bands. The calculations indicate a slightly lower value. For the higher a_u fundamental Ferguson suggested that one of four weak bands in the liquid phase infra red in the region of 600 cm^{-1} is possibly this fundamental appearing in defiance of the selection rules. The highest one at 677 cm^{-1} agrees well with the calculations.

PENTAFLUORO BENZENE

			18 Parameter Field			23 Parameter Field		
	obs.$\bar{v}$	w	calc.$\bar{v}$	d$\bar{v}$	$\sigma(\bar{v})$	calc.$\bar{v}$	d$\bar{v}$	$\sigma(\bar{v})$
A_2	-	0.0	681.9	-	15.7	651.4	-	8.7
	391	1.0	407.3	+16.3	6.6	397.0	+ 6.0	3.8
	-	0.0	113.6	-	4.3	128.8	-	3.2
B_1	837	1.0	869.6	+32.6	4.1	845.1	+ 8.1	3.0
	697	1.0	693.4	- 3.6	9.9	700.0	+ 3.0	5.9
	556	1.0	571.8	+15.8	4.7	554.8	- 1.2	4.1
	323	1.0	319.8	- 3.2	4.1	321.5	- 1.5	2.9
	206	1.0	210.6	+ 4.6	4.3	206.0	0.0	2.8
	158	1.0	137.8	-20.2	4.4	154.6	- 3.4	3.4
$\overline{\lvert dv \rvert}$ and $\overline{\sigma(v)}$				13.8	5.4		3.3	3.7
WSQER			$1.269.10^{-3}$			$.080.10^{-3}$		

Table 2.30

The only reported spectra and assignments for Pentafluoro Benzene are by Steele and Whiffen (44). On reexamination of the gas phase infra red spectrum type C bands were observed at 837,697 and 556 cm^{-1}, which confirmed the previous assignments, and at 206 and 158 cm^{-1} in the far infra red (Figure 2.8). The remaining b_1

fundamental was calculated to be at 334 cm^{-1} using the field of R and S. No clearly identifiable type C band was observed in this region but the sharp shoulder at 323 cm^{-1} on the low frequency side of the type B band centred at 329 cm^{-1} was assigned as the b_1 fundamental. Steele and Whiffen assigned the Raman band at 391 cm^{-1} as an a_2 fundamental and this assignment was accepted. They also assigned the Raman band at 171 cm^{-1} as the lowest a_2 fundamental but all the calculations indicate that this is too high. The band was remeasured as 164 cm^{-1}, only 6 cm^{-1} above the gas phase infra red value of 158 cm^{-1} for the lowest b_1 fundamental so it is probably due to this fundamental displaced in the liquid phase Raman spectra. No assignment could be made for the a_2 fundamental. A value of 673 cm^{-1} for the high a_2 fundamental was obtained from a consideration of the combination bands.

		Calculated	Observed (gas phase)
$837(b_1) + 673(a_2)$	=	1510 (b_2)	1504
$556(b_1) + 673(a_2)$	=	1229 (b_2)	1228 A
$206(b_1) + 673(a_2)$	=	879 (b_2)	879

The value was not used in the calculations which show that it is probably correct. It is supported by the assignment of the higher a_u fundamental of 1,2,4,5 tetrafluoro Benzene as 677 cm^{-1}. These assignments are discussed further in the section on Hexafluoro Benzene.

PENTAFLUORO DEUTERO BENZENE

			18 Parameter Field			23 Parameter Field		
	obs.$\bar{v}$	w	calc.$\bar{v}$	d$\bar{v}$	$\sigma(\bar{v})$	calc.$\bar{v}$	d$\bar{v}$	$\sigma(\bar{v})$
A_2	-	0.0	681.9	-	15.7	651.4	-	8.7
	-	0.0	407.3	-	6.6	397.0	-	3.8
	-	0.0	113.6	-	4.3	128.8	-	3.2
B_1	738	1.0	727.4	-10.6	6.1	731.2	-6.8	4.9
	674	1.0	692.0	+18.0	9.5	669.2	-4.8	5.4
	494	1.0	524.9	+30.9	4.8	507.4	+13.4	3.1
	-	0.0	303.2	-	4.0	307.0	-	2.7
	-	0.0	209.5	-	4.1	205.9	-	2.7
	-	0.0	136.9	-	4.4	153.6	-	3.3
$\overline{\lvert dv \rvert}$ and $\overline{\sigma(v)}$				19.8	6.8		8.3	4.4
WSQER				$.638.10^{-3}$			$.110.10^{-3}$	

Table 2.31

In their paper on Pentafluoro Benzene Steele and Whiffen (44) also reported some assignments for Pentafluoro Deutero Benzene. The only assignments they made for the out of plane vibrations were for the three highest b_1 fundamentals based on the band shapes. They were used in the calculations without modification.

HEXAFLUORO BENZENE

			18 Parameter Field			23 Parameter Field		
	obs.$\overline{v}$	w	calc.$\overline{v}$	d$\overline{v}$	$\sigma(\overline{v})$	calc.$\overline{v}$	d$\overline{v}$	$\sigma(\overline{v})$
B_{2g}	-	0.0	682.1	-	17.5	696.2	-	10.6
	-	0.0	170.7	-	6.1	195.3	-	4.8
E_{1g}	370.0	1.0	403.9	+33.9	6.6	385.9	+15.9	4.8
	370.0	0.0	403.9	+33.9	6.6	385.9	+15.9	4.8
A_{2u}	210.0	1.0	226.0	+16.0	8.4	203.9	- 6.1	5.3
E_{2u}	-	0.0	681.9	-	15.7	623.2	-	11.9
	-	0.0	681.9	-	15.7	623.2	-	11.9
	-	0.0	112.0	-	4.7	128.8	-	3.8
	-	0.0	112.0	-	4.7	128.8	-	3.8
$\overline{\lvert dv \rvert}$ and $\overline{\sigma(v)}$				25.0	7.5		11.0	5.0
WSQER			.255.10^{-3}			.053.10^{-3}		

Table 2.32

Spectra and assignments have been reported for Hexafluoro Benzene by Delbouille (45 and 46) and by Steele and Whiffen (37), who have also calculated a force field based on their assignments (47).

Hexafluoro Benzene is a member of the D_{6h} point group and therefore has many inactive fundamentals. Of the out-of-plane vibrations the a_{2u} fundamental is infra red active and the degenerate e_{1g} fundamentals are Raman active, the b_{2u} and e_{2u} fundamentals are inactive in both. The assignment by Steele and Whiffen (37) of a medium strength depolarized Raman band at 370 cm^{-1} as the e_{1g} fundamentals was accepted. This assignment is supported by a comparison of the b_{1g} and a_u fundamentals of 1,2,4,5 tetrafluoro Benzene, the a_2 fundamentals of Pentafluoro Benzene, and one set of the e_{1g} and one set of the e_{2u} fundamentals of Hexafluoro Benzene, which all become the a_2 fundamentals when their respective molecules are considered as members of the C_{2v} point group and all then have identical G matrices for this species. Therefore any changes in the frequencies in this series are due to force constant changes.

1,2,4,5 $C_6H_2F_4$ (b_{1g} + a_u)	$C_6HF_5(a_2)$	$C_6F_6(e_{1g}$ + $e_{2u})$
(677)	(673)	(647)
417	391	370
(140)	-	(123)

Although the assignments of the two e_{2u} fundamentals are not known accurately the calculations show that they lie above and below the e_{1g} fundamental. By comparison with the two similar fundamentals of the other two molecules, which are known accurately the value of 370 cm^{-1} for the e_{1g} fundamental of Hexafluoro Benzene is seen to be preferable to Delbouille's value of 435 cm^{-1} (45 and 46).

The assignment of the a_{2u} fundamental has been the subject of much discussion. The far infra red spectra contains two bands of similar intensities in the region of 315 and 215 cm^{-1}. In the gas phase spectrum (figure 2.9) they were observed to have similar band shapes and the measured frequencies were 313 and 210 cm^{-1}. One of these bands is the a_{2u} fundamental and the other the lowest fundamental of the inplane, infra red active E_{1u} species. Delbouille (45) originally assigned the 313 cm^{-1} band as the e_{1u} fundamental and the 210 cm^{-1} band as the a_{2u} fundamental but later (45) reversed these assignments. Steele and Whiffen (37) agreed with his original assignments. Person et.al.(48) from a study of the band shapes concluded that the 210 cm^{-1} band was a parallel band of Hexafluoro Benzene, an oblate symmetric top, and therefore due to the a_{2u} fundamental and that the 313 cm^{-1} band was a perpendicular band and therefore due to the e_{1u} fundamental. However they also pointed out that the band at 313 cm^{-1} showed no splitting in the infra red spectrum of the crystal whilst the other e_{1u} fundamentals at 1531 and 1020/1002 cm^{-1} both showed this characteristic splitting observed for the e_{1u} fundamentals of Benzene (49). They tentatively suggested that the low intensity of the 313 cm^{-1} was the reason that the splitting was not observed.

However the conclusions of Person and coworkers were based on a comparison of observed and calculated values for the speration of the P and R branch maxima, which are not in agreement with other results. Their values were a separation of 6 cm^{-1} for the 313 cm^{-1} band, 13.5 cm^{-1} for the 210 cm^{-1} band and a calculated separation of 16 cm^{-1} for a parallel band of Hexafluoro Benzene. Wheatley (50) observed separations of 10.7 cm^{-1} for the 313 cm^{-1} band, 10.3 cm^{-1} for the 210 cm^{-1} band and calculated a value of 11.4 cm^{-1} at 298.15°K (25°C). The values observed in the present work were 11.3 cm^{-1} and 10.5 cm^{-1}. The value of Person and coworkers for the 313 cm^{-1} band is much lower than the two other values but the spectrum shown in their paper only agrees with the present one if it is assumed that the abscissa scale is incorrectly marked in units of 5 cm^{-1} instead of 10 cm^{-1}. This would make the separation of the P and R band maxima 12 cm^{-1} in much better agreement with the other two observations. However the evidence from these separation values is inconclusive since the observed separations for the two bands are approximately the same.

The overall band shapes are more helpful, the stronger Q branch of the 210 cm^{-1} band suggests that it is a parallel band. Also the calculations of Nonnenmacher and Mecke (25) gave a value of 199 cm^{-1} for the a_{2u} fundamental and those using the field of R and S a value of 229 cm^{-1}.

A comparison with Pentafluoro Benzene (37) and application of the inequality rule yields no useful information on the a_{2u} fundamental which should lie between the b_1 fundamentals at 323 and 206 cm^{-1} and could therefore be either the 313 cm^{-1} or the 210 cm^{-1} band. However it shows that the lowest e_{1u} fundamental should lie between the a_1 fundamentals at 325 and 272 cm^{-1} which supports the assignment of 313 cm^{-1} as this fundamental.

The only support for the later assignment of Delbouille (46) comes from Fujiyama and Crawford (51) in a somewhat novel approach based on time correlation functions. The theory was developed for vibrational transitions by Gordon (52) from a consideration of the time development (or Heisenberg) approach to spectral absorption as opposed to the conventional static (or Schrodinger) approach, which is concerned with changes between states of different energy levels. To quote Gordon:

> The Heisenberg picture of spectroscopy leads naturally to the consideration of a spectrum as the Fourier transform of an appropriate time correlation function.

For infra red spectroscopy the time correlation function C(t) is defined as

$$C(t) = \overline{\langle \mu(0) \cdot \mu(t) \rangle}$$

where $\mu(t)$ is the vectorial projection of the dipole moment along the original direction of the transition dipole moment at time t. The bar indicates that the function is an ensemble average.

Consider a system irradiated over the entire frequency range of the band. At $t = o$ by definition all the dipoles are aligned along the original direction of the transition dipole and the time correlation function is normalised so that $c(o) = 1$. Then as the system relaxes, the dipoles rotate and $c(t)$ drops in value but at a short time it still has some dependance on the original orientation of the dipoles. At long time the dipoles will be orientated randomly with respect to their original directions and $c(t)$ will be zero.

If $I(w)$ is the intensity of the band (normalised so that $\int_{band} I(w)\,dw = 1$, and hence $c(o) = 1$) at frequency w (where w is the circular frequency measured from the band centre and expressed in units of reciprocal time) it can be shown that (52),

$$I(w) = 1/2 \int_{-\infty}^{+\infty} e^{-iwt} \left\langle \overline{\mu(o).\mu(t)} \right\rangle dt$$

Again quoting Gordon:

> This equation expresses the Heisenberg-type description of an infra red band shape: The distribution of absorption frequencies about the vibration frequency is the Fourier transform of the average motion of the transition dipole moment.

Provided the observed spectrum extends over the entire range of rotation - vibration frequencies of the band then the real part of the inverse Fourier integral allows the average motion of the transition dipole moment to be reconstructed. Therefore

$$c(t) = \int_{band} I(w) \cos(wt)\,dw$$

This is evaluated using a summation of the form given by Fujiyama and Crawford (53). The time correlation function of the band is calculated for a series of time intervals (the time scale involved is of the order of picoseconds, i.e. 10^{-12} sec.) and a graph of c(t) versus t plotted.

Fujiyama and Crawford (51) showed that in solution the e_{1u} fundamentals at 1531 and 1020/1002 cm^{-1} had similar curves but that the band at 313 cm^{-1} was considerably different. They therefore concluded that the 313 cm^{-1} band could not be an e_{1u} fundamental and therefore must be the a_{2u} fundamental and the band at 210 cm^{-1} the e_{1u} fundamental. However they did not investigate the 210 cm^{-1} band so this was undertaken in the course of the present work. The time correlation functions of the 313 and 210 cm^{-1} bands of Hexafluoro Benzene measured in Cyclohexane solution together with that for the 1531 cm^{-1} band calculated using the data given by Fujiyama and Crawford (51) are shown in figure 2.12. As can be seen, the 313 cm^{-1} band does not decay at the same rate as the 1531 cm^{-1} band but neither does the 210 cm^{-1} band. In fact the similarity is between the 313 and 210 cm^{-1} bands. These cannot be members of the same symmetry species and therefore the assignment of the 313 cm^{-1} band as the a_{2u} fundamental on the basis of time correlation functions is rejected.

The time correlation functions for the 313 and 210 cm^{-1}

Figure 2.12 Time Correlation Functions for the 1527, 315 and 215cm^{-1} Bands of Hexafluoro Benzene in Solution

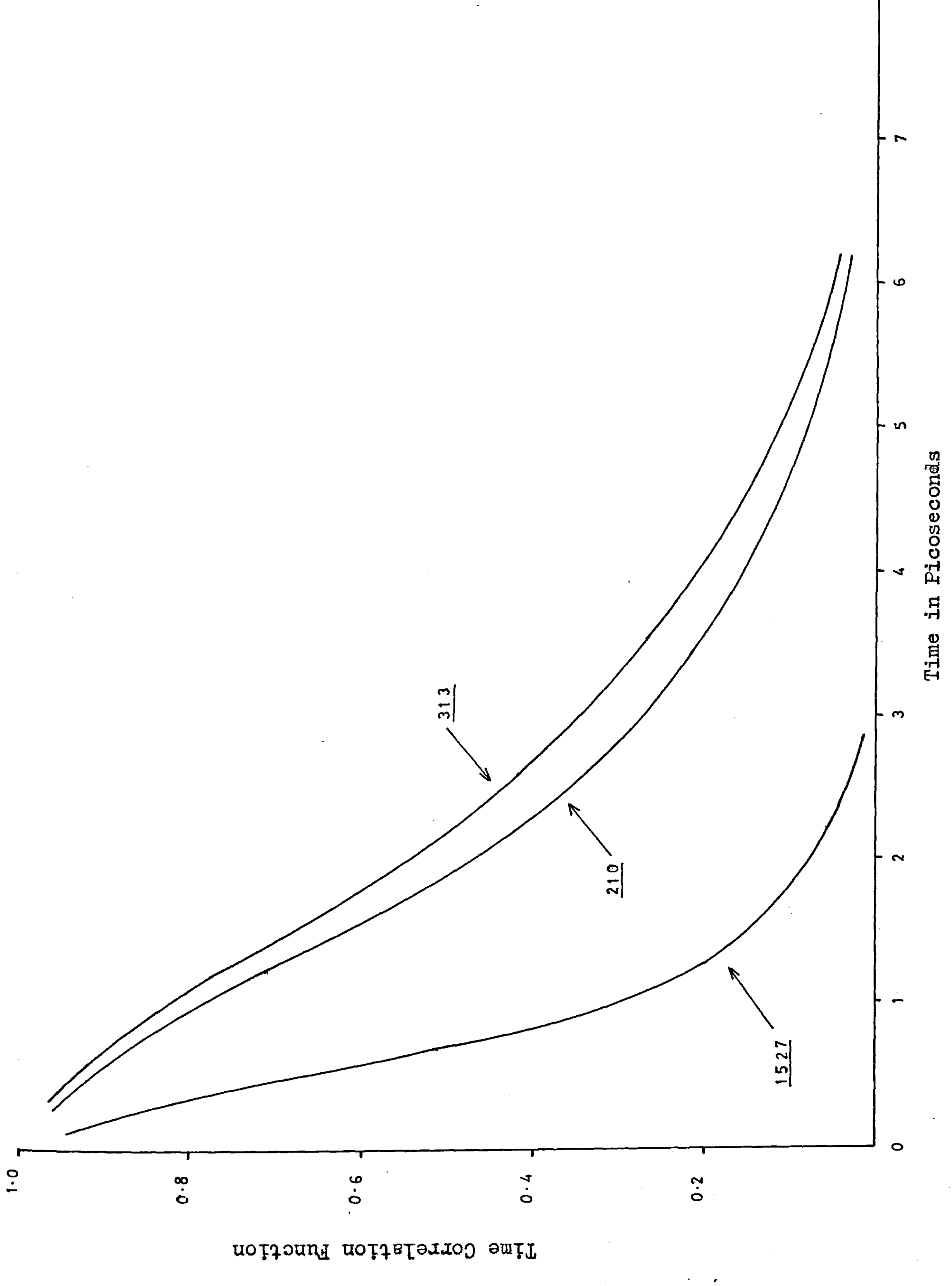
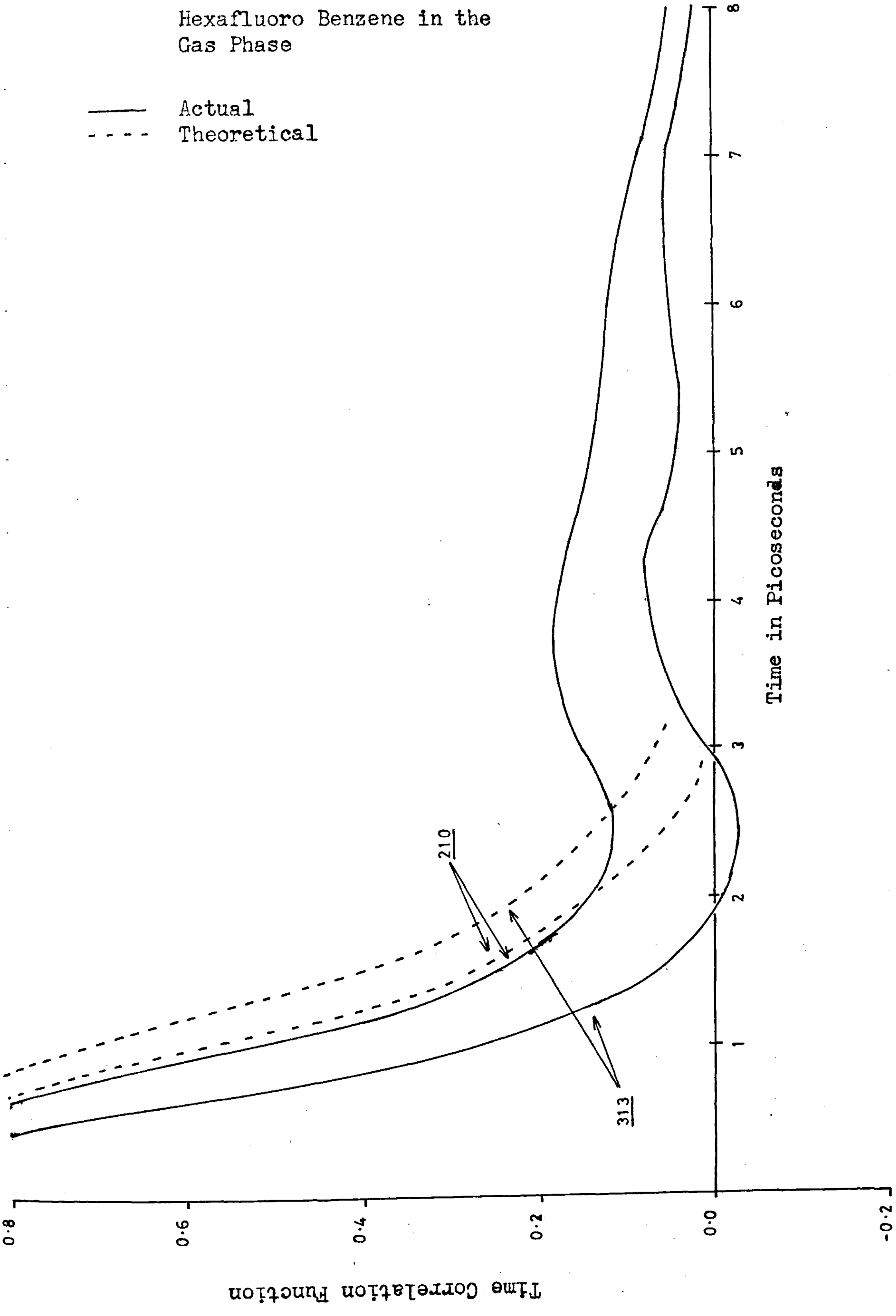


Figure 2.13 Time Correlation Functions for the 315 and 215 cm^{-1} Bands of Hexafluoro Benzene in the Gas Phase



bands measured in the gas phase are shown in figure 2.13. Also shown are the functions expected for Hexafluoro Benzene freely rotating about either the perpendicular or one of the parallel axes. These are calculated using the equations given by Rothschild (54),

$$c(t)(\text{freely rot } 11) \sim \exp / - (kT/I_{\perp}\ )\ t^2\ /$$

$$c(t)(\text{freely rot } \perp) \sim \exp / - \tfrac{1}{2}\ kT\ (1/I_{\perp} + 1/I_{\parallel}\ )t^2/$$

where $I_{\perp}$ and $I_{\parallel}$ are the moments of interia perpendicular and parallel to the unique axis.

The curves for the 210 cm^{-1} band and the parallel free rotator are almost identical for 2 psec. indicating the the band is a parallel band (and therefore the a_{2u} fundamental) and that the molecules behave as free rotators about this axis for 2 psec. before the rotations become hindered by interactions between the molecules. The curves for the 313 cm^{-1} band and the perpendicular free rotator are vastly different. It is possible that this is due to the fact that the band is broadened by Coriolis interactions between the doubly degenerate fundamentals (50), which is not taken into account in the free rotator theory.

It was thus concluded that the only positive evidence indicates that the 210 cm^{-1} is the a_{2u} fundamental and the 313 cm^{-1} band the lowest e_{1u} fundamental.

The assignments of the inactive fundamentals of the B_{2g} and e_{2u} species has to be based on the combination bands. Steele and

Whiffen (37) gave values of 714 and 249 cm^{-1} for the b_{2g} fundamentals and 595 and 175 cm^{-1} for the e_{2u} fundamentals. Of these assignments only the higher b_{2g} fundamental is supported by the calculations. The alternative assignments of 714 and 190 cm^{-1} for the b_{2g} fundamentals and 647 and 123 cm^{-1} for the e_{2u} fundamentals, which are in agreement with the calculations, are proposed. They are based on the infra red active combination bands. Table 2.33 lists the fundamentals and the observed and calculated combination bands which give rise to these assignments. The observed frequencies and the summation rules are taken from Steele and Whiffen (37). The summation rules are based on those given by Bailey et.al.(55) for Benzene, which show that b_{2g} + $b_{1u} = o_{2u}$ (not e_{1u} as given by Steele and Whiffen) and $b_{2g} + e_{2u} = e_{1u}$ (not a_{2u}).

These assignments are in good agreement with the b_1 fundamentals of Pentafluoro Benzene.

C_6HF_5 (b_1)	C_6F_6 ($b_{2g} + e_{1g} + a_{2u} + e_{2u}$)
837	714
697	647
555	370
323	210
206	190
158	123

As can be seen the inequality rule holds throughout with these assignments whereas with Steele and Whiffen's assignments it does not.

THE COMBINATION BANDS OF HEXAFLUORO BENZENE

FUNDAMENTALS			COMBINATION BANDS	
			CALCULATED	OBSERVED
B_{2g}		B_{1u}	A_{2u}	
714	+	1323	2037	2040 l
714	+	640	1354	1348 l
190	+	1323	1513	1513 g
190	+	640	830	841 l
E_{2u}		E_{2g}	A_{2u}	
647	+	1655	2302	
647	+	1157	1804	1802 g
647	+	443	1090	1092 g
647	+	264	911	
123	+	1655	1778	
123	+	1157	1280	1277 l
123	+	443	566	569 l
123	+	265	387	
E_{2u}		E_{1g}	E_{1u}	
647	+	370	1017	
123	+	370	493	489 g
E_{2u}		B_{2g}	E_{1u}	
647	+	714	1361	
647	+	190	837	841 l
123	+	714	837	841 l
123	+	190	313	

l - band observed in liquid phase

g - band observed in gas phase

Table 2.33

The equivalence of the b_{1g} and a_u fundamentals of 1,2,4,5 Tetrafluoro Benzene, the a_2 fundamentals of Pentafluoro Benzene and the e_{1g} and e_{2u} fundamentals of Hexafluoro Benzene was previously discussed in conjunction with the assignment of the e_{1g} fundamental. It is also a useful comparison for the e_{2u} fundamentals. The value of 647 cm^{-1} for the higher e_{2u} fundamental of Hexafluoro Benzene is in reasonable agreement with the postulated values of 677 cm^{-1} for the higher a_u fundamental of 1,2,4,5 Tetrafluoro Benzene and 673 cm^{-1} for the highest a_2 fundamental of Pentafluoro Benzene and lends support to the series as a whole. Likewise the value of 123 cm^{-1} for the lower e_{2u} fundamental of Hexafluoro Benzene and 140 cm^{-1} for the lower a_u fundamental of 1,2,4,5 Tetrafluoro Benzene are in good agreement.

The value of 123 cm^{-1} for the lower e_{2u} fundamentals is supported also by the calculations of Counsell et.al.(56), who found it necessary to postulate a fundamental at 125 cm^{-1} in order to get agreement between the observed and calculated molar entropies. However they assumed that the other assignments of Steele and Whiffen (37) were correct so subsequent reassignments might affect this value.

It must be remembered that while these postulated fundamental assignments agree reasonably with the available date for confirmation a complete assignment of Hexafluoro Benzene is required including calculations of the in plane fundamentals. This is necessary since the reassignments of the combination bands made here leave some bands, previously explained by Steele and Whiffen (37), without explanation and make multiple assignments for others.

SECTION 2.4 Masses and Geometry

The atomic weights used in all the calculations were (in atomic mass units):

Hydrogen	1.00797
Deuterium	2.01410
Carbon	12.01115
Fluorine	18.99840

The values were taken from Kaye and Laby (1), p.118.

The bond lengths used were (in Angstroms):

C - C	1.397
C - F	1.3
C - H	1.084

The values for the C - C and C - H bonds, which are those calculated for Benzene, were also taken from Kaye and Laby (1), p.159. The value for the C - F bond was that used by Radcliffe and Steele (24) in their calculations.

Planarity was assumed for all the molecules.

All the bond angles (i.e. the $\angle$C-C-C, $\angle$C-C-H and the $\angle$C-C-F) were assumed to be 120°.

It was necessary to assume that all the molecules have the same bond lengths and angles since in the Harmonic Oscillator Approximation

$$2V = \sum_{i,j} f_{i,j} \, dR_i \, dR_j \qquad 16$$

If the internal coordinates are scaled by appropriate bond lengths to be unitless, all the force constants have to be similarly scaled (and their values are then quoted in millidynes per Angstrom). This scaling of the force constants was implicit in all the calculations and for such force constants to be transferable between molecules the internal coordinates to which they referred had to contain bonds of constant length.

The complete molecular structure of Fluoro Benzene was determined by Nygaard et.al.(57) from their microwave spectra of four mono (^{13}C) substituted Fluoro Benzenes and earlier data on various Deuterium substituted Fluoro Benzenes. Their results show a slight shortening of the two C - C bonds nearest the Fluorine atom while the rest of the molecule is practically like Benzene and a C - F bond length of 1.35 Å. However since their geometry has different lengths for C - C and C - H bonds at different positions comparative frequencies were not calculated. McCulloh and Pollnow (58) concluded that Fluoro Benzene is planar from measurements of the moments of inertia. Critas et.al.(59) determined a ground state geometry for Fluoro Benzene as a starting point for the interpretation of the rotational constants of the first singlet excited state in terms of the molecular geometry. Their bond parameters are

C - C	1.397 A	$\angle C_6C_1C_2$	121°
C - F	1.319 A	$\angle C_3C_4C_5$	120°
C - H	1.084 A	$\angle C_1C_2H_2$	120°
		$\angle C_4C_3H_3$	120°

The carbons are numbered according to the scheme shown in Figure 2.1. The substituents are numbered according to which carbon atom they are attached, with the Fluorine atom attached to C_1. Critas and coworkers used a number of assumptions in determining this geometry. Using this geometry and an appropriately rescaled 23 parameter force field the fundamental frequencies of Fluoro Benzene were recalculated and compared with the frequencies calculated using the standard geometry.

	Standard Geometry	Critas's Geometry
A_2	960	961
	816	815
	408	403
B_1	994	994
	899	898
	745	745
	683	687
	502	507
	242	238

The greatest discrepancy between the two sets of calculated frequencies is 5 cm^{-1} and the average is 2.5 cm^{-1}, indicating that for work of high accuracy it would be necessary to know the accurate geometry but for the type of calculations considered here the standard geometry used for Fluoro Benzene is adequate.

The effect of changing the geometry is nullified to some extent by the fact that the force field has to be rescaled so that $f_{i,j}\ dR_i\ dR_j$ is a constant independent of geometry. Therefore if

f_{cf} is a diagonal force constant referring to a C - F bond length of 1.3 A

$(1.5/1.3)^2\ f_{cf}$ is a diagonal force constant referring to a C - F bond length of 1.5 A.

Nygaard et.al.(60) also examined the microwave spectrum of 1,2 difluoro Benzene and 1,3 difluoro Benzene. They concluded from the small values of the inertial defect that both molecules are planar. Assuming an undistorted C_6H_4 skeleton with 120^o angles, a C - C bond length of 1.397 A and a C - H bond length of 1.084 A, they calculated C - F bond lengths of 1.318 A in 1,2 difluoro Benzene and 1.308 A in 1,3 difluoro Benzene. They also concluded that the CCF angles differ by less than 0.5^o from 120^o.

Almenningen et.al.(61) determined the geometry of Hexafluoro Benzene from electron diffraction measurements in the gas phase. Their bond lengths are for the C - C bond 1.394 ± .007 A and for the C - F bond 1.327 ± .007 A. They also concluded that there is no significant deviation from planarity. Using this geometry and a rescaled 23 parameter force field the fundamentals were recalculated and compared with those calculated using the standard geometry.

	Standard Geometry	Almenningen's Geometry
B_{2g}	694	690
	197	194
E_{1g}	385	381
A_{2u}	204	200
E_{2u}	636	631
	130	128

The frequencies are systematically lowered by an average of 4 cm^{-1} due to the increased C - F bond lengths. The standard geometry is still adequate but the results do indicate that the value used for the C - F bond length is slightly low.

CHAPTER THREE The Force Fields and their Calculation.

SECTION 3.1 The Calculation of Force Constants.

The most direct way of obtaining the individual elements of the F matrix in the secular equation

$$HL = L\Lambda$$

where $GF = H$

is by expansion of the secular determinant

$$|H - \lambda E| = 0$$

If there are n vibrational frequencies a polynomial equation of the form

$$\lambda^n + C_1 \lambda^{n-1} \ldots . + C_n \lambda + C_n = 0$$

is obtained.

The coefficients c are related to the roots (or eigen vectors) $\lambda_1, \lambda_2 \ldots . \lambda_n$ and also to the individual elements of the matrix H and thus n elements of F can be calculated. The forms of these relationships are given in Wilson, Decius and Cross (8), p.214. In practice this method is time consuming and impracticable for n greater than five.

Methods of starting with a set of trial force constants which are gradually refined until a set is obtained which most nearly reproduces the observed frequencies are preferable since they involve only linear algebra and are therefore amenable to machine computation. These methods all depend on the calculation of the Jacobian which relates changes in the eigen values (or sometimes frequencies) to those in the force constants.

Mann et.al.(62) obtained the Jacobian by making an increment of .01 mdyn.A^{-1} in one of the force constants and solving the secular equation for the new F matrix. The resulting changes in the eigen values gave the d $\lambda_i/d\phi_j$ for all λ_i and one ϕ_j, i.e. the jth row of the Jacobian. This process was repeated for each force constant in turn and the Jacobian constructed. The new set of force constants was then obtained by the method of least squares (as outlined in section 1.7). Such a method is tedious and in view of this Mann and coworkers used only one Jacobian, calculated at the start of the iteration cycle, instead of recalculating a new one at each stage of refinement. The method of calculating the Jacobian from the eigen vectors (as outlined in section 1.8) is therefore preferable. This method, which appears to have been first applied to the vibrational problem by King (63), though it is given in essence by Wilson et.al.(8), p.273, was developed by Overend and Scherer (64). Although their method of deriving the expression for the Jacobian gives the correct result it contained some unnecessary assumptions as pointed out by Long et.al.(6a). Mills (65) derived the same expression using a slightly different treatment, which was still based however, as were the other methods (6a and 64), on first-order perturbation theory. The term perturbation is therefore more correctly applied to the derivation of the Jacobian rather than the entire process of force constant evaluation.

There are a number of difficulties which can be encountered in this type of calculation and these can be listed in three main groups.

1. Multiple Solutions

The function X was introduced in Section 1.7 as a measure of the lack of agreement between the observed and calculated eigen values.

i.e. $$X = \sum_i w_i \left(\lambda_i^{obs} - \lambda_i \right)^2$$

Since each λ_i is a function of the force constants $\phi_1 \ldots \phi_m$ it follows that X is also a function of the force constants.

i.e. $$X = X\left(\phi_1 \ldots \phi_m\right)$$

Therefore X can be represented as a series of hypersurfaces in m + 1 dimensional space.

Thus a set of m force constants can be postulated and a set of n eigen values calculated. The question now arises of how these calculated eigen values are to be compared with the n observed eigen values. If the observed eigen values are listed in decreasing order the n calculated eigen values can be ordered and compared in n! different ways (67) and hence n! values of X calculated. With each eigen value λ_i there is associated an eigen vector Li (the ith column of L), which describes the ith normal coordinate in terms of the internal coordinates and which can be applied to each observed eigen value in turn. So these n! arrangements correspond to the n! possible eigen vector descriptions of the observed eigen values. Although the arrangement which gives rise to the lowest X value might be thought of as the "correct" set, in fact by starting at each of these n! different points in turn and provided that the eigen vector description of the observed eigen values is retained, by refining the force constants convergence can be achieved to n! different minima. If n = m an exact set of solutions is found each time, i.e. X = 0 for all n! minima. In the more normal case $n \neq m$ and generally X is not equal to zero.

If the problem is factored into symmetry blocks there are $\prod_i n_i!$ minima where n_i is the number of eigen values for the ith symmetry block and multiplication is over all symmetry blocks. This still applies when more than one molecule is considered (i.e. the overlay procedure is used), since X cannot distinguish between molecules.

Needham and Scherer (66) considered the two a_1 stretching vibrations of HCN, which are observed at 2089 and 3312 cm^{-1}. From the two frequencies, two sets of force constants were obtained. The first set (f_{CH} = 5.88, f_{CN} = 17.88 $md.A^{-1}$) gave 3312 cm^{-1} as the CH stretching frequency and the 2089 cm^{-1} as the CN stretching frequency whereas the second set (f_{CH} = 2.57, f_{CN} = 40.48 $md.A^{-1}$) gave the reverse assignment, which is incorrect.

When calculating the force constants the solution obtained depends on the refinement method and the initial force field. Needham and Scherer (66) describe a method whereby a set of assignments can be introduced into the calculations so that even if the initial field is the second set of force constants, the calculated 2089 cm^{-1} frequency can be compared with the observed CH stretching frequency at 3312 cm^{-1} and likewise the calculated 3312 cm^{-1} frequency with the observed CN stretching frequency at 2089 cm^{-1}. Therefore the convergence will be to the first (and correct) set of force constants. However, if the observed and calculated frequencies are listed in descending order and compared the final set of force constants obtained depends on the initial set and using this method the first set could never be obtained from the second.

The method used in comparing the frequencies in the calculations reported here is this second method of listing the calculated frequencies in descending order and the observed frequencies in a predetermined order. There is one hypersurface X with n! minima in this case. (In the method of Needham and Overend (66) there are n! hypersurfaces with one minima each). A maxima between two minima is a "cross-over" point between the two possible eigen vector descriptions of two frequencies. In the HCN example (66) starting from the maxima between the two minima convergence could be to either of the two sets of solutions.

This method requires that the initial and final force fields are in the same region of hyperspace, which is assumed to be the region which yields the correct solutions.

Radcliffe and Steele (24) found two alternative force fields for a series of Bromine substituted Benzenes. The two sets of force constants had similar values and corresponded to a permutation of the mode descriptions of the 681 and 736 cm^{-1} b_1 vibrations of Bromo Benzene. Long and Gravenor (6b) considered a hypothetical two frequency, two solution problem and how the solution obtained depended on the method of refinement.

Toman and Pliva (68) suggested a method whereby all possible solutions might be obtained but its numerical complexity makes it impracticable (69). Spirko and Moravek (69) suggested an alternative method based on a statistical simulation (or Monte Carlo) technique. Random sets of initial force constants were generated (limited to ± 20 mdyn/A) and then convergence was achieved by the standard perturbation method. This method is also limited in that it requires an infinite number of sets to be generated to achieve all possible solutions. It does however introduce some measure of physical reality by excluding all force constants larger than ± 20 mdyn/A (which would rule out the second set of solutions to the HCN problem).

2. Singularity

If matrices C and D are as defined by equation 61 (section 1.10), equation 47 (section 1.7) becomes

$$\Delta \Phi = C^{-1}D$$

and this is the equation to be solved to obtain the changes which have to be made in the force constants.

The matrix C is singular if its determinant is equal to zero and in this case it cannot be inverted. This equality to zero can be exact or accidental (psuedo-singularity) where the determinant is so small that it has large computer rounding errors.

Exact singularity is due to the existence of one or more linear relationships between the force constants.

i.e. $$\sum_i a_i \phi_i = 0$$

$$\sum_i b_i \phi_i = 0$$

etc. depending on the number of relationships,

where a_i, b_i..... are constants and the summation i is over all m force constants.

The form of these linear relationships can be obtained from the matrix C by examining its eigen vectors V and eigen values Λ.

$$CV = V\Lambda$$

and if $\lambda_j = 0$, matrix C is singular.

Then $$\sum_i \phi_i v_{ij} = 0$$

This is known as singularity due to exact linear dependence and these linear relationships must be recognised and removed before the problem can be solved. An example is considered later in connection with the force constants of Benzene.

A small determinant is due usually to one or more near linear relationships amongst the force constants.

i.e.
$$\sum_i a_i \phi_i = ua(\phi_1 \ldots \phi_m)$$
$$\sum_i b_i \phi_i = ub(\phi_1 \ldots \phi_m)$$
etc.

where ua, ub .... although functions of the force constants change very little as the force constants change. Lees (70) and Bruton and Woodward (71) have given geometrical interpretations of near linear dependance, which can also be recognised by looking for small eigen values of C. Near linear dependence is due to insufficient data and can be distinguished from exact linear dependence by the introduction of artificial data (70) into the calculation. This would take the form of introducing calculated frequencies as though they were observed frequencies. Provided the new set of data is large enough any near linear dependencies will be removed whereas any exact linear dependencies will be unaffected.

Assuming C can be inverted another test for near linear dependence is to examine the statistical errors in the force constants and the degree of coupling between them (70,72).

The rms error σ (ϕ_i) in the ith force constant is obtained from

$$\sigma^2(\phi_i) = \sigma_c^2 \, (C^{-1})_{i,i} \qquad 1$$

where $$\sigma_c^2 = \sum_i w_i \, (\lambda_i^{obs} - \lambda_i^{calc})^2 \, / \, (n-m) \qquad 2$$

where n is the number of observables (frequencies) and m is the number of unknowns (force constants). Summation i is over all n observables.

The correlation coefficient $t_{i,j}$ which is a measure of the degree of coupling between the ith and jth force constants is given by

$$t_{i,j} = \frac{(C^{-1})_{i,j}}{\left[(C^{-1})_{i,i}(C^{-1})_{j,j}\right]^{\frac{1}{2}}} \qquad 3$$

If a near linear dependancy exists in a set of force constants then the associated correlation coefficients will approach ± 1, (70).

Aldous and Mills (72) suggested that a simple test for singularity was to compare the determinant of C with the product of its diagonal elements. If C is a diagonal matrix

$$|C| = \prod_i c_{i,i}$$

$$(C^{-1})_{i,i} = 1 / c_{i,i}$$

and all correlation coefficients are zero.

With the introduction of off-diagonal elements the determinant gets smaller but provided they are small the product and the determinant are of the same order of magnitude and the correlation coefficients remain unimportant. But as the off diagonal elements get larger the product becomes much greater than the determinant, C approaches singularity and some of the correlation coefficients start to approach unity. In this case usually one of the diagonal elements of C^{-1} will be large, giving rise to a high uncertainty in the associated force constant (72).

To overcome any near linear dependencies it is necessary either to introduce more data and thereby remove them or, if this is not possible, to constrain one of each set of force constants giving rise to a near linear dependency of a fixed value. The most effective force constants to constrain are those which have large rms errors but unlike exact linear dependencies these constraints are made on physical rather than mathematical grounds (72).

Papousek et.al.(73) suggested that the method of damped least squares (74) could be applied to force constant calculations. The psuedo-singularity is removed by the addition of a weighting factor to the diagonal elements of C. This factor is chosen with care (68,73) and has the effect of bringing the ratio of the determinant of C to the product of its diagonal elements closer to unity.

3. Non-linearity

In Section 1.7, equation 38 is the linear approximation of equation 37 and is obtained by assuming that the changes in the force constants are small so that terms of the type $d\phi_i\ d\phi_j$ can be neglected. If the initial force field is not close to the final force field this condition does not necessarily hold and second and higher order terms become important. In this case equation 38 is no longer valid so by ignoring these terms the fit may get worse.

The test for non-linearity as given by Duinker (3), p.32 and Aldous and Mills (72) is to compare the residuals at the nth stage of refinement with the errors at the (n + 1)th stage.

The residual $t_i^n = (\lambda_i^{obs} - \lambda_i^n) - \sum_j J_{i,j}^{\;n} \, d\phi_j$ 4

and the error as

$$e_i^{n+1} = \lambda_i^{obs} - \lambda_i^{n+1}$$

The condition of linearity is that

$$\sum_i w_i \, (t_i^n)^2 \sim \sum_i w_i \, (e_i^{n+1})^2$$

This follows from substituting for λ_i^n in the residual using equation 39, Section 1.7.

$$r_i^n = \lambda_i^{obs} - (\lambda_i^{n+1} - \sum_j J_{i,j}^{\;n} \, d\phi_j) - \sum_j J_{i,j}^{\;n} \, d\phi_j$$

$$= \lambda_i^{obs} - \lambda_i^{n+1} = e_i^{n+1}$$

Thus if the problem were truly linear the residual at the nth stage would exactly equal the error at the (n+1)th stage. The discrepancy between the two measures the deviation from linearity.

If the condition of linearity is not upheld and the changes in the force constants are large the usual technique to overcome this problem is to take only a fractional quantity of the calculated changes (6b)(72) (Section 1.9) so that second and higher order terms can again be neglected. Long and Gravenor (6b) examined the effect different scaling parameters had on the rates of convergence for a hypothetical two frequency, two force constant problem. Some of the results were surprising, for instance they found that adding on only half the calculated force constant changes gave more rapid convergence than adding the entire change. They also examined the second order terms for this problem and found that their complexity ruled out the extension of their use to problems of greater size.

One of the most interesting improvements to the perturbation process has been described by Schachtschneider (7,75). This is the inclusion of statistical tests at each stage of the refinement to determine which force constants are to be varied. It is particularly useful when dealing with large numbers of force constants. It can represent a considerable improvement over the method described in Section 1.9 whereby the force constant weight matrix is introduced by hand.

If R^n is a column matrix of the residuals (as previously defined) at the nth stage of refinement

and $\Delta\Lambda^n$ is a column matrix of errors, also at the nth stage of refinement, equation 4 can be expressed in matrix form as

$$R^n = \Delta\Lambda^n - J^n\,\Delta\Phi \qquad 5$$

The weighted square residual is

$$R^tWR = (\Delta\Lambda - J\Delta\Phi)^t\,W\,(\Delta\Lambda - J\,\Delta\Phi) \qquad 6$$

where the superscript n has been dropped as all matrices are defined at the nth stage of refinement.

If matrices C and D are as defined by equation 61, Section 1.10,

i.e. $C = J^tWJ$ and $D = J^tW\Delta\Lambda$

and $\Delta\Phi = C^{-1}D$

By expanding and substituting equation 6 becomes

$$R^tWR = \Delta\Lambda^tW\,\Delta\Lambda - D^tC^{-1}D$$

By definition $X = \Delta\Lambda^tW\Delta\Lambda$ - the weighted square error at the nth stage.

If $\Delta X = X - R^tWR = D^tC^{-1}D$

the reduction in error obtained by adjusting the jth force constant only is given by

$$\Delta X_j = (C^{-1})_{j,j}\,D_j^2 \qquad 7$$

From equation 1 the statistical error in the jth force constant is given by

$$\sigma^2(\phi_j) = \sigma_c^2\,(C^{-1})_{j,j}$$

Schachtschneider defined two conditions for the inclusion of force constants in the refinement process.

Condition A is

$$X/(n-m) > \Delta X_j /(n-m+1) > e_1$$

It compares the reduction of the weighted square error in the computed eigen values due to adjustment of ϕ_j with the standard error obtained if this force constant is not adjusted. e_1 is an arbitarily fixed small number representing the smallest reduction in the error worth considering.

Condition B is

$$\sigma (\phi_j) - \phi_j < e_2$$

It compares the statistical error in the jth force constant with the force constant itself.

If both conditions hold the force constant ϕ_j is refined at the nth stage of refinement.

If condition B does not hold, i.e. the error exceeds the force constant by more than e_2, an abitrarily fixed number, the frequencies are probably not dependent on the force constant ϕ_j and it is therefore dropped from the calculations, i.e. put equal to zero.

Finally if condition B is upheld but not condition A, force constant ϕ_j is retained in the calculations but not adjusted at the nth stage of refinement.

Use of this method ensures that only the significant force constants are refined and avoids problems due to singularity.

However it must be realised that the force constants in a problem are not independent and therefore holding some constant or putting them equal to zero affects the final values of those allowed to vary.

Many methods of calculating the F matrix directly have been proposed and these are discussed in Section 3.2 in connection with the general harmonic force field.

Finally, an entirely different approach to the calculation of force constants is by direct differentiation of the potential energy V to obtain the terms of the type $(\partial^2 V/\partial R_i \partial R_j)_e$. Initially V is calculated as a function of a set of coordinates. This requires a wave-mechanical approach to the problem. Then the point where all $dV/dR_i = 0$ is found. (This also gives the coordinate parameters for the equilibrium geometry of the molecule under consideration). Finally the second derivatives $\partial^2 V/\partial R_i \partial R_j$ at this point are calculated. Pulay described such a method (76) and applied it successfully to calculating the four force constants of H_2O (77). Gerratt and Mills (78) described another method which they applied to some simple diatomics. Calculating force constants from something other than experimental data is an intriguing prospect especially when the results from the two types of calculation are in agreement but again the complexity of the methods and the large amount of time, both human and computer, required (79) appears to rule out their extension to larger molecules in the near future.

SECTION 3.2 Force Constants and Force Fields

The most explicit quadratic force field for any molecule is the general quadratic force field (GQFF). This is composed of all the entries in the F matrix. If this is set up in terms of the internal coordinates and there are n frequencies there are $n(n+1)/2$ force constants in the F matrix (not n^2 as it is symmetric). If the molecule contains no elements of symmetry (i.e. is a member of the C_1 point group) they are all different. If it is necessary to include r redundancies in the internal coordinates there are $(n+r)(n+r+1)/2$ force constants. However these force constants are not independent. If the redundancies are eliminated they are regrouped into $n(n+1)/2$ independent sets (80) so that even in the most favourable cases only $n(n+1)/2$ force constants can be evaluated. These $n(n+1)/2$ force constants cannot be evaluated from the n frequencies alone, only n force constants can. Therefore the problem is underdetermined by degree $d = n(n-1)/2$. Only for $n=1$ does $d=0$, i.e. a diatomic molecule.

If the molecule possesses any elements of symmetry not all the $n(n+1)/2$ force constants are different. However by transforming to a non-redundant set of symmetry coordinates if there are n_i frequencies belonging to the ith symmetry species, there are $n_i(n_i+1)/2$ different symmetry force constants in this species. Again, only if $n_i = 1$ can all the symmetry force constants be calculated from the vibrational frequencies alone.

Summing over all the symmetry blocks of the molecule under consideration there are $\sum_i n_i(n_i+1)/2$ different symmetry force constants and assuming that they all can be evaluated only the same number of internal (normally called valence) force constants can be evaluated.

Referring back to the case where $n_i = 1$ and there is one symmetry force constant, this is found at least once in a large number of highly symmetrical molecules but for only a small number of molecules do all the $n_i = 1$. Besides the trivial example of the diatomic molecule it occurs in symmetric linear triatomic molecules of the type AB_2 which belong to the $D_{\infty h}$ point group. In this example there are four vibrations, one a_{1g}, one a_{2u} and a pair of degenerate e_{1g}'s (which constitute only one piece of data as the symmetry force constants are the same). Therefore the three valence force constants can be determined, the AB stretch, the stretch/stretch interaction and the angle bend. There is no interaction force constant between the stretch and the angle bend due to symmetry restrictions. Also the P_4 molecule, which is tetrahedral in shape and therefore belongs to the T_d point group, has one a_{1g}, a pair of degenerate e vibrations and a triplet of degenerate f vibrations. Therefore three symmetry force constants can be calculated and from them three valence force constants. These can be in two sets,

i. the bond stretch and two types of stretch/stretch interaction.

ii. the angle bend and two types of angle-bend/angle-bend interaction.

These two sets are equivalent (81,82), one can be obtained from the other using simple relationships.

Many methods of obtaining the complete F matrix from the frequencies alone for cases in which $d>0$ have been proposed, most using some form of extra constraint on the system. All suffer from the basic problem that there are more unknowns than data and any attempt to set up the Jacobian and proceed from there would fail as the matrix C would be singular. Averbukh et.al.(83) have critically reviewed a number of these methods and found fallacies in all of them. Freeman (84) has described a method and reviewed some of the literature concerned with force constant calculations.

For the case where $d = 1$, i.e. a two frequency, three force constant problem, Torkington (85) has described a method whereby each diagonal force constant is plotted as an elliptical function of the off-diagonal force constant. This method, now known as the force constant display method, gives a range of possible solutions to the force constants and has been applied to many problems by many workers, e.g. Sawodny (86) and Duncan and Mills (87,88). A technique to find the ranges of possible solutions of higher order problems, utilising an analogue computer, has been described by Lehmann et.al.(80).

The only method of obtaining the correct GQFF is to calculate the n(n+1)/2 unknowns from n(n+1)/2 or more observations. This means using more data than the n vibrational frequencies. Other experimentally determined quantities which can be used in calculating force constants are:-

Coriolis coupling constants (89),
Centrifugal distortion constants (90, 91),
Mean square amplitudes (92),
l-type doubling (93),
Inertia defects (94),
Raman intensity data (95).

By applying first order perturbation theory to the appropriate equations Mills (65) has obtained the Jacobians which relate changes in the Coriolis coupling constants and in the centrifugal distortion constants to changes in the force constants so that they can be incorporated with the vibrational frequencies in an iterative force constant refinement calculation. Unfortunately such quantities can usually only be determined for small highly symmetrical molecules, e.g. the Methyl Halides (96), so for larger molecules an alternative approach has to be used.

The necessary additional information can be vibrational frequencies. One force field can be applied to a number of molecules which are chemically equivalent but differ in the particular isotope present of one or more atoms. Since the force field is a function of the electronic structure of the molecule substituting one isotope of an atom for another of the same atom does not effect the force field according to the Born-Oppenheimer approximation (97). The masses are changed however and therefore the G matrices and so the vibrational frequencies and the normal coordinates are changed. If this change in mass is small the changes in the vibrational frequencies are also small and as normal frequency data these new frequencies provide no useful extra data. However, as shown by Chalmers and McKean (98), provided the frequencies can be measured accurately the changes in frequency in isotopic substitution can prove to be highly significant in fixing the values of the off-diagonal force constants. Substitution of Deuterium for Hydrogen causes a large relative change in mass and as can be seen from the appropriate sections in Chapter Two the changes in frequency are usually large enough to provide useful extra information.

It might therefore appear that if x isotopically substituted molecules are available the number of pieces of data available to determine the force field is xn and if $x \geqslant (n+1)/2$ the GQFF can be completely solved. However there are a number of rules which relate the frequencies of a series of isotopic molecules to each other, independently of the force field and therefore limit the amount of independent data available. The first of these is the Redlich-Teller product rule (see, for instance, Wilson, Decius and Cross (8), p.183) which states that the product of the vibrational frequencies of a molecule bears a constant ratio to the same product of an isotopic derivative.

i.e. $\prod_i w_i / \prod_i w_i' = \text{constant}$

The constant, which is derivable, is a function of the masses of the atoms and sometimes the moments of inertia and the masses of the molecules as a whole. The rule can be applied to two molecules as a whole or to a symmetry species which is common to both. Therefore in a symmetry block, dimension n_i, common to two molecules the number of independent frequencies is $2n_i-1$.

For instance, in the A_1 species of H_2O, and D_2O, $n_i = 2$ and therefore there are three force constants and three independent frequencies. Also the inclusion of T_2O adds no extra information, since

$$\frac{(w_1w_2)_{H_2O}}{(w_1w_2)_{D_2O}} = c_1 \qquad \frac{(w_1w_2)_{H_2O}}{(w_1w_2)_{T_2O}} = c_2 \qquad \frac{(w_1w_2)_{D_2O}}{(w_1w_2)_{T_2O}} = c_3$$

There are three equations relating six frequencies so still only three are independent.

For the B_1 species of H_2O, D_2O and T_2O, $n_i = 1$ so only one of the three frequencies is independent.

A sum rule, which is applied to the frequencies of three or more isotopic molecules, has been given by Decius and Wilson (98). Again it can either be applied to the molecules as a whole or to common symmetry blocks.

As applied to H_2O, D_2O and HDO it is

$$2\sum w^2_{HDO} = \sum w^2_{H_2O} + \sum w^2_{D_2O}$$

In this case the sum rule must be applied to all three vibrations of each molecule as introduction of one D into H_2O, which is a member of the C_{2v} symmetry point group, destroys the C_2 axis and $\sigma_v(yz)$ plane and the two a_1 and one b_1 vibrations coalesce to become the three a' vibrations of the HDO molecule, which is a member of the C_s symmetry point group. Using the product rule two further relationships between the frequencies of these molecules can be formed so that HDO can supply no additional information to the force field. This also applies to HTO and DTO, so of the 18 vibrational frequencies of six molecules only 4 are independent and determine uniquely the 4 force constants.

The existence of higher order isotope rules has also been recognised (99,100,101) which further limits the amount of independent data available from larger molecules.

It must be stressed that these relationships only hold strictly for harmonic frequencies (for this reason the symbol w is used for the frequencies). Frequencies corrected for anharmonicity should be used in the calculation of harmonic force fields. The use of uncorrected, anharmonic frequencies, which do not obey the rules, does not increase the amount of useful data, it only increases the errors in the calculation.

The next stage is to extend the data set of vibrational frequencies to include molecules, which although not isotopically related, are similar and this can be considered as the point of introduction of classical chemistry into force constant calculations. This extension is based on the assumption that bonds which are alike in the set of molecules have similar electronic environments and therefore the force field is transferable between the molecules. It is important to realise that it is the force field which is transferable between molecules and not individual force constants since a force constant is defined only in terms of the force field of which it is a member, (8) p.176. The fact that the force field is being transferred between molecules means that it will probably not reproduce the GQFF of each molecule exactly but the difference between this "theoretical" GQFF and the actual QFF will be slight unless the concept of transferability has broken down. Careful choice of the set of molecules to be considered should avoid this.

One of the best examples of the overlay technique is due to Schachtschneider and Snyder (102) who fitted a 35 parameter force field to 270 vibrational frequencies of 20 n-alkanes (or n-paraffins).

This field has formed the basis of many calculations on similar molecules.

So far the calculation of force fields has been discussed in terms of the General Quadratic Force Field. However when the data set is not large enough to calculate the GQFF or such a detailed field is not required a simpler field can be used in which certain interaction force constants are ignored. Such a field is only an approximation but provided that the force constants to be ignored are chosen on a correct basis it should satisfactorily reproduce the observed vibrational frequencies. Usually in a simplified field the number of force constants is less than the number of frequencies and the additional frequencies provide a check on the force field. Since in these cases any data, additional to frequencies, is not usually known additional checks of this nature do not exist.

The simplest approximation is the Valence Force Field (VFF) which consists only of the diagonal elements of the F matrix when it is expressed in terms of the internal coordinates. All the interaction terms are assumed to be zero so that the bending or stretching of one coordinate affects none of the others. For CO_2 the Potential Energy expression in terms of the VFF is

$$V = f_r\ (dr_1)^2 + f_r\ (dr_2)^2 + f_a\ (rda)^2$$

where f_r is the stretching force constant and dr_1 and dr_2 are the stretching coordinates, and f_a is the angle bending force constant and da is the angle bending coordinate.

Even for this molecule and other linear symmetric triatomic molecules the approximation is not a good one, (10) p.72. For CO_2 the predicted ratio of the asymmetric to the symmetric stretching frequencies is 1.915 as compared to the actual value of 1.749 and it follows that the stretch/stretch interaction cannot be ignored. That there is an interaction between the two stretches has been shown using quantum mechanical resonance theory (103). CO_2 is represented as a hybrid of three forms

$$\begin{array}{cl} O = C = O & \text{i} \\ O - C \equiv O & \text{ii} \\ O \equiv C - O & \text{iii} \end{array}$$

If the left hand bond is stretched the structure tends towards ii which implies a shortening of the right hand bond. Therefore the vibration is not confined to one bond, there is an interaction. According to section 1.2 the interaction force constant is predicted to be positive as it is found to be in practice.

Since the VFF is not adequate it is necessary to introduce some interaction force constants. The force fields obtained can be divided into two general types depending on the method of selecting the interaction force constants to be included.

Force fields of the fast group, known generally as Modified

Valence Force Fields (MVFF), are simply the VFFs of the molecules under consideration plus certain additional interaction force constants which might be expected to be significant. The additions are often ad hoc empirical modifications often without any theoretical basis and care has to be taken that any assumptions made are sound. Califano (104) has pointed out the fallacies in two common assumptions. The first and more serious is that the force constants for the interaction of a C - H stretch with any other coordinates can be neglected. This is based on the fact that since the C - H stretching frequencies are usually much greater than the others it is possible to factorise the secular equation and calculate the C - H stretching frequencies separately, (8) p.174. This is a mathematical procedure without any chemical basis and cannot be applied to C - D stretches since these frequencies are much closer to the others and the interaction force constants cannot be neglected. But the force constants for C - H stretches should be transferable to C - D stretches and vice versa and the above assumption is not valid. The second assumption often made is that interactions between coordinates become less important the further apart they are in the molecule. This is a reasonable approximation for some large molecules but not for systems containing conjugated bonds, like Benzene, where resonance structures become important.

Califano (104) also suggests that the method of inspecting the elements of the Jacobian for selecting interaction force constants. Only those force constants for which at least one element is greater than a factor, which determines if they are important, are included in the force field. The method of Schachtschneider outlined in section 3.1 can also be used but this has the disadvantage that the matrix C ($= J^tWJ$) must be invertable and therefore the number of force constants used initially must be less than the number of frequencies. Using Califano's method the initial trial force field can be of any size provided sufficient force constants are discarded before the matrix C is inverted.

The second group of force fields are those in which the interaction force constants are selected on a theoretical basis. The most well known of such fields is the Urey-Bradley Force Field (UBFF) (105), which besides the diagonal valence force constants includes forces arising from interactions between non-bonded atoms, which will also be diagonal entries in the F matrix. For instance in a linear triatomic molecule ABC there are four internal coordinates, the AB stretch, the BC stretch, the ABC angle bend and the AC non-bonded repulsion, and therefore four diagonal harmonic force constants. Since there are only three vibrational degrees of freedom for this systemthere exists a redundancy condition between the four internal coordinates. (Obviously stretching either of the bonds or altering the angle affects the AC non-bonded distance). For this reason it is necessary to include linear terms in the potential energy expression (see Section 1.2) but provided the redundancy condition is known these linear terms can be equated to zero. However the mathematics involved for even this simple ABC system are tedious (rather than complex), (10) p.83.

The UBFF in its strict form cannot always reproduce the observed vibrational frequencies and it has been necessary to introduce interaction force constants in certain cases. Thus Scherer and Overend (106) introduced the so called Kekule constant into the force field of Benzene so as to calculate correctly the B_{2u} ring vibration. But as Califano (104) points out this is in reality not a Urey-Bradley force constant but a modified valence force constant. It is in view of this and other ad hoc attempts to "save" the Urey-Bradley Force Field that Steele (10), p.83 states "Few people today would uphold the view that the UBFF is a generally valid field". Further limitations of the field have been pointed out by Duncan (107).

Linnett's Orbital Valence Force Field (OVFF) introduced further terms into the VFF to account for changes in the overlap of atomic orbitals during bending vibrations. Thus in CH_4 if a Hydrogen atom moves in a direction at right angles to the C - H bond a force acts tending to restore it to its original position. This is a valence force constant. In certain vibrations however, it is possible to rotate the orbitals of the carbon atom as a whole to improve the overlap of the carbon bonding orbitals and those on the displaced Hydrogen atoms (108). It is in introducing extra terms to allow for this orbital following that the OVFF differs from the VFF. The OVFF was applied originally to planar XY_3 molecules (109) and the same force constant was used for both in and out-of-plane bonding vibrations as opposed to the VFF which requires the introduction of an additional force constant to allow for out-of-plane vibrations.

The idea that interaction force constants are related to electronic charge movements has already been mentioned in connection with the stretch/stretch interaction force constants of CO_2. Similar reasoning can be applied to stretch/angle bend interactions. It is generally accepted that in s-p hybride orbitals an increase in p content results in a longer bond and an increase in s content results in a shorter bond (110). Thus if an increase in a particular bond angle results in the increase of s content for a particular bond the energy can be minimised by shortening the bond and according to Section 1.2 this implies a positive interaction force constant. These ideas have been put on a qualitative basis by Mills (110) so that not only can the signs of the interaction force constants be predicted but also the ratio they bear to the stretch force constants. Mills calls a force field derived this way as a Hybrid Orbital Force Field (HOFF).

These three "theoretical" fields so far mentioned all are widely applicable but the UBFF is the only one which has been widely used. A number of other "theoretical" fields have been suggested but these have been generally related to particular problems. Thus Jones has proposed both the resonance interaction valence force field (111, 112) applied to octahedral $X(YZ)_6$ type complexes and the π-electron interaction valence force field (113) applied to tetrahedral $X(YZ)_4$ type complexes. Also Burdett (114) has applied the valence shell force field to $M(CO)_6$ and $M(CN)_6^{n-}$ type complexes.

SECTION 3.3 The Force Fields for the Fluorine substituted Benzenes.

So far in this chapter force fields and their calculation have been considered in general terms. It is now necessary to consider the out-of-plane vibrations of the fluorine substituted Benzenes. The Potential Energy expression for all these molecules is

$$
\begin{aligned}
2V = \; & \textstyle\sum_i f(rdy_i)^2 \\
+2 \; & \textstyle\sum_i ff^o(rdy_i . rdy_{i+1}) \;\; +2 \; \sum_i ff^m(rdy_i . rdy_{i+2}) \\
+2 \; & \textstyle\sum_i ff^p(rdy_i . rdy_{i+3}) \\
+ \; & \textstyle\sum_i f(Rd\phi_i)^2 \\
+2 \; & \textstyle\sum_i ff^o(Rd\phi_i . Rd\phi_{i+1}) \;\; +2 \; \sum_i ff^m(Rd\phi_i . Rd\phi_{i+2}) \\
+2 \; & \textstyle\sum_i ff^p(Rd\phi_i . Rd\phi_{i+3}) \\
+2 \; & \textstyle\sum_i ff^o \; rdy_i(Rd\phi_{i-1} - Rd\phi_i) \\
+2 \; & \textstyle\sum_i ff^m \; rdy_i(Rd\phi_{i-2} - Rd\phi_{i+1}) \\
+2 \; & \textstyle\sum_i ff^p \; rdy_i(Rd\phi_{i-3} - Rd\phi_{i+2})
\end{aligned}
$$

where summation i is from 1 to 6 in a cyclic manner, so that if $i = 6$, $i + 2 = 2$.

Both out-of-plane angle bends rdy_i

and special torsions $Rd\phi_i$ are numbered 1 to 6 as given in Figure 2.1.

The factor 2 occurs in connection with the interaction terms since for each force constant $f_{i,j}$ there should be another $f_{j,i}$ which is equivalent.

The negative term occurs in the $y\phi$ interactions since the bracketed ϕ terms although equivalent have opposite signs. This is clearly illustrated in Figure 3.1 which shows the motions involved in a $y\phi$ meta interaction.

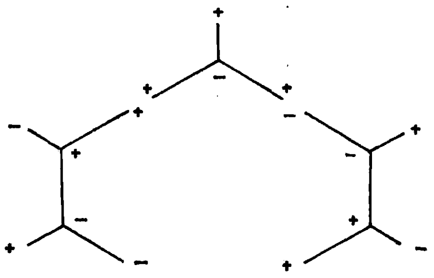


Figure 3.1

The choice of which interaction is defined as the positive one is abitary.

The Potential Energy expression is completely general but does not differentiate between the different substituents on different molecules and can therefore show the force constants only in the most general terms. The GVFF's for all the molecules can be constructed from the force field given in Table 3.1. (The notation A,B ... etc. is used for convenience only). It contains 50 different force constants and includes all possible types of interaction between the five types of internal coordinate but excludes any effects from atoms which are not involved in the internal coordinates defining a particular force constant. Thus there is only one interaction force constant between two meta Y_{CH} coordinates and this force constant is assumed to be independent of the substituent on the Carbon atom which is between the two meta Carbon atoms. This is illustrated in Figure 3.2.

50 Parameter Force Field

	y_H	ϕ_{HH}
y_H	A,a^o,a^m,a^p	ac^o,ac^m,ac^p
ϕ_{HH}		C,c^o,c^m,c^p

	y_F	ϕ_{FF}
y_F	B,b^o,b^m,b^p	bc^o,bc^m,bc^p
ϕ_{HH}		E,e^o,e^m,e^p

	y_F
y_H	ab^o,ab^m,ab^p

	ϕ_{HF}	ϕ_{FF}
y_H	ad^o,ad^m,ad^p	ae^o,ae^m,ae^p

	ϕ_{HH}	ϕ_{HF}
y_F	bc^o,bc^m,bc^p	$be^o,be^m be^p$

	ϕ_{HF}
ϕ_{HF}	D,d^o,d^m,d^p

	ϕ_{HF}	ϕ_{FF}
ϕ_{HH}	cd^o,cd^m,cd^p	ce^o,ce^m,ce^p

	ϕ_{HF}	
ϕ_{FF}	de^o,de^m,de^p	

Table 3.1

19 Parameter Force Field

	y_H	ϕ_{HH}
y_H	A, a^o, a^m, a^p	ac^o, ac^m
ϕ_{HH}		C_1, c^o

	y_F	ϕ_{FF}
y_F	B, b^o, b^m, b^p	bc^o, bc^m
ϕ_{FF}		C_3, c^o

	y_F
y_H	ab^o, ab^m, ab^p

	ϕ_{HF}	ϕ_{FF}
y_H	ac^o, ac^m	ac^o, ac^m

	ϕ_{HH}	ϕ_{HF}
y_F	bc^o, bc^m	bc^o, bc^m

	ϕ_{HF}
ϕ_{HF}	C_2, c^o

	ϕ_{HF}	ϕ_{FF}
ϕ_{HH}	c^o	c^o

	ϕ_{HF}
ϕ_{FF}	c^o

$$\left.\begin{array}{l} C_1 = C \\ C_2 = D \\ C_3 = E \end{array}\right| \text{ in the 50 Parameter Force Field}$$

Table 3.2

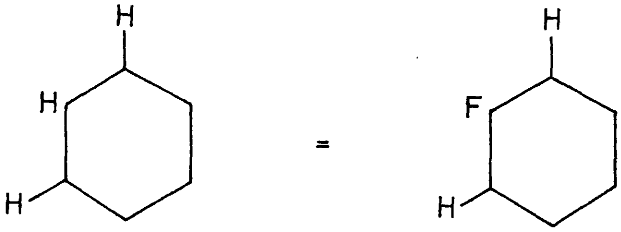


Figure 3.2

If the 50 parameter force field defined in Table 3.1 were to be calculated it would not necessarily reproduce the GVFF of each molecule since it would assume that terms labelled the same in different molecules have the same values. Therefore it would be an overlay force field for all the molecules. In fact this 50 parameter force field is not used since it is too large and complex and would not be a good test of the transferability of the force constants between molecules. Therefore a smaller field is required.

The VFF is obviously too small as it contains only the five diagonal force constants and the choice is between a MVFF and a "theoretical" field. The field used is a MVFF but before it is described the reasons why all the "theoretical" fields are inadequate are given.

The UBFF would contain only the five diagonal force constants plus the five corresponding linear terms since for the very small amplitudes of motion involved the distances between non-bonded atoms do not change during an out-of-plane vibration.. That it is not applicable to all molecules is one of the general drawbacks of the UBFF.

The OVFF uses the same force constants for both in and out-of-plane angle bends. These motions are different however, as will be shown in Part II where this point is discussed in connection with dipole moment derivatives.

The HOFF is really just a method of calculating stretch/angle bend interaction force constants from the diagonal stretch force constants and is therefore not applicable to out-of-plane vibrations.

Therefore the force field has to be a MVFF and the problem is to decide which interaction force constants are to be included. Radcliffe and Steele (24) in their work on the out-of-plane vibrations of the Fluoro Benzenes and Scherer (115) in his work on the out-of-plane vibrations of the Chloro Benzenes both used force fields similar to the 19 parameter force field given in Table 3.2. Radcliffe and Steele used a 15 paramter field the differences being that:-

i b^o and b^m were not applicable to the molecules they studied ;

ii $C_2 = \frac{1}{2}(C_1 + C_3)$;

iii $ac^m = 0$, this being its Benzene value.

Scherer used a 23 parameter force field in which the diagonal out-of-plane bending force constants A and B were each replaced by three force constants A_1, A_2, A_3 and B_1, B_2, B_3. These terms will be explained later. He also used τ torsion coordinates (actually δ coordinates in his notation) which means that although the force constant descriptions are very similar direct numerical comparisons cannot be made. Neither Radcliffe and Steele (24) nor Scherer (115) explained their choice of force field so the following arguments are proposed to justify the 19 parameter force field.

One of the tests for transferability is that those force constants in the MVFF applied to all the Fluoro Benzenes which occur in Benzene, are in reasonable agreement with the values calculated separately for Benzene. Both Miller and Crawford (115) and Whiffen (12) have made thorough studies on the out-of-plane force field of Benzene. The two sets of results are basically the same but since Miller and Crawford used δ coordinates and expressed their results in symmetry force constants, the force field used to test transferability was Whiffen's, who used ϕ coordinates and internal coordinate force constants.

In the GVFF for the out-of-plane vibrations of Benzene there are 11 internal coordinate force constants (ifc's),

$A \quad a^o \quad a^m \quad a^p \quad C \quad c^o \quad c^m \quad c^p \quad ac^o \quad ac^m \quad ac^p$

There are 9 vibrations, $2B_{2g} + E_{1g} + A_{2u} + 2\ E_{2u}$ and using the U matrix given in Table 2.12 11 symmetry coordinates, $2B_{2g} + 2\ E_{1g} + A_{2u} + 2\ E_{2u}$. Thus there are two redundancies in the

E_{1g} symmetry group. According to Whiffen (12) the redundancy conditions are

$$S_{1a}/r = 3^{\frac{1}{2}}/2. \; S_{2a}/R$$

$$S_{1b}/r = 3^{\frac{1}{2}}/2. \; S_{2b}/R$$

The symmetry coordinates are as given in Table 2.12. R is the C - C bond length and r the C - H bond length.

Using the transformation matrix

$$N\begin{vmatrix} 1 & -x \\ x & 1 \end{vmatrix}$$

where $x = 3^{\frac{1}{2}}/2.\ r/R$ and N is a normalising factor so that the transformation is orthogonal, a new set of symmetry coordinates is formed. Thus if S_{ra} and S_a are the new symmetry coordinates such that

$$\begin{vmatrix} S_{ra} \\ S_a \end{vmatrix} = N \begin{vmatrix} 1 & -x \\ x & 1 \end{vmatrix} \begin{vmatrix} S_{1a} \\ S_{2a} \end{vmatrix}$$

then
$$S_{ra} = N\ (S_{1a} - x\ S_{2a}) = 0$$

$$S_a = N\ (x\ S_{1a} + S_{2a})$$

and the redundant coordinate S_{ra} can be dropped.

Using the same transformation the equivalent redundant coordinate S_{rb} can also be dropped.

With the redundant coordinates removed from the symmetry coordinates the 11 internal coordinate force constants can be grouped into 8 different symmetry coordinate force constants (including only one set from each pair of degenerate blocks). These 8 symmetry coordinate force constants can be calculated using frequency data from Benzene and Hexadeutero Benzene but from them 11 different internal coordinate force constants cannot be calculated. However using the two redundancy conditions previously given plus a third

$$d\phi_1 + d\phi_2 + d\phi_3 + d\phi_4 + d\phi_5 + d\phi_6 = 0$$

(which is not included in the symmetry coordinates since it is the sole member of the A_{1u} symmetry class) Whiffen (12) substituted for certain terms in the Potential Energy expression to remove explicit reference to the force constants c^m, c^p and ac^p. Thus in the

$$c^m\ (Rd\phi_i \cdot Rd\phi_{i+2})$$
$$c^p\ (Rd\phi_i \cdot Rd\phi_{i+3})$$
$$ac^p\ rdy_i(Rd\phi_{i-3} - Rd\phi_{i+2})$$

interaction terms the ϕ coordinates are rewritten in other terms so as to exclude reference to these types of interaction. The Potential Energy expression is regrouped according to the internal coordinates and the force constants expressed in tilde form.

The Potential Energy expression is:-

$$\begin{aligned} 2V = \; & \tilde{A} \sum_i (rdy_i)^2 \\ & +2\tilde{a}^o \sum_i rdy_i . rdy_{i+1} \quad +2\tilde{a}^m \sum_i rdy_i . rdy_{i+2} \\ & +2\tilde{a}^p \sum_i rdy_i . rdy_{i+3} \\ & + \tilde{C} \sum_i (Rd\phi_i)^2 \quad +2\tilde{c}^o \sum_i Rd\phi_i . Rd\phi_{i+1} \\ & +2\widetilde{ac}^o \sum_i rdy_i (Rd\phi_{i-1} - Rd\phi_i) \\ & +2\widetilde{ac}^m \sum_i rdy_i (Rd\phi_{i-2} - Rd\phi_{i+1}) \end{aligned}$$

and the tilde force constants are

$$\begin{aligned} \tilde{A} &= A + 2y(c^m - c^p) - 2z.ac^p & \tilde{c} &= c - 4c^m + 3c^p \\ \tilde{a}^o &= a^o + y(c^m - c^p) - z.ac^p & \tilde{c}^o &= c^o - 3c^m + 2c^p \\ \tilde{a}^m &= a^m - y(c^m - c^p) + z.ac^p & \widetilde{ac}^o &= ac^o - ac^p \\ \tilde{a}^p &= a^p - 2y(c^m - c^p) + 2z.ac^p & \widetilde{ac}^m &= ac^m - 2ac^p \end{aligned}$$

where $y = 4/3. (R/r)^2$ and $z = 4/3^{\frac{1}{2}}. R/r$

Using the Potential Expression the 8 tilde force constants can be calculated. This is not the same as putting c^m, c^p and ac^p equal to zero, these force constants are implicit in Whiffen's tilde force constants. However these force constants were presumably chosen for this treatment since their values might be expected to be small in comparison with the other force constants. Therefore in the MVFF they are put equal to zero and then the calculated values of A a^o a^m a^p C_1 c^o ac^o ac^m in this MVFF can be compared directly with Whiffen's tilde force constants for

Benzene in the test for transferability.

O'Reilly (117) has attempted to calculate all 11 internal coordinate force constants of Benzene by introducing the three extra constraints that the value of a symmetry force constant associated with a redundant coordinate (i.e. zero vibrational frequency) is zero. However he incorrectly gives S_{2a} and S_{2b} as the redundant symmetry coordinates in the E_{1g} symmetry group instead of the linear combinations previously discussed. Kydd (118) points out further deficiencies in O'Reilly's symmetry coordinates and also that since the redundant coordinates cannot be displaced it is not possible to measure their resistance to any displacement and therefore the values of the associated force constants are indeterminate. Kydd goes on to give an alternative method of calculating the diagonal torsion force constant in Benzene following Anno (119), who suggested that the value of a torsional force constant about a C - C bond is proportional to the product of the associated π - bond order and the overlap integral. However Kydd (118) states that Whiffen (12) put c^m, c^p and ac^p equal to zero, directly compares his C torsional force constant with Whiffen's $\tilde{C}$ and concludes that Whiffen's value is incorrect. Kydd's value for C should be substituted into Whiffen's value for $\tilde{C}$ to evaluate $4c^m - 3c^p$.

A similar set of tilde force constants could be constructed for Hexafluoro Benzene from B b^o b^m b^p E e^o e^m e^p be^o be^m be^p but they could not be calculated since isotopic frequency data is not available. However for consistency it is reasonable that e^m, e^p and be^p are excluded from the MVFF.

So far the 50 parameter force field has been reduced by only 6 terms. The next step, which immediately reduces it to the 19 parameter MVFF, is that in all the interaction terms involving a ϕ coordinate no distinction is made between the three types ϕ_{HH}, ϕ_{HF} and ϕ_{FF}. Thus it is assumed that there are no electronic differences between these coordinates, the mass differences are taken care of in the G matrix. The differences are retained in the diagonal terms, thus C, D and E become C_1, C_2 and C_3 respectively. As will be seen later in any true force field the differences between these terms are slight thus providing a self justification of the force field. Under this condition the force constant associated with all $\phi\phi^o$ terms is c^o, the $\phi\phi^m$ and $\phi\phi^p$ terms are excluded in accordance with the Benzene and Hexafluoro Benzene conditions, the force constants associated with the $y\phi^o$ and $y\phi^m$ terms are ac^o, bc^o and ac^m, bc^m depending on whether the y coordinate is CH or CF and the $y\phi^p$ terms are excluded again in accordance with the Benzene and Hexafluoro Benzene conditions.

Thus the Potential Energy expression for all the Fluorine substituted Benzenes becomes:-

$$\begin{aligned} 2V = \; & \sum_i (A,B)\ (rdy_i)^2 \\ & + 2\sum_i (a^o, ab^o, b^o)\ rdy_i . rdy_{i+1} \\ & + 2\ \sum_i (a^m, ab^m, b^m)\ rdy_i . rdy_{i+2} \\ & + 2\ \sum_i (a^p, ab^p, b^p)\ rdy_i . rdy_{i+3} \\ & + \ \sum_i (C_1, C_2, C_3)\ (Rd\phi_i)^2 \ + 2\ \sum_i c^o\ Rd\phi_i . Rd\phi_{i+1} \\ & + 2\ \sum_i (ac^o, bc^o)\ \ rdy_i (Rd\phi_{i-1} - Rd\phi_i) \\ & + 2\ \sum_i (ac^m, bc^m)\ rdy_i (Rd\phi_{i-2} - Rd\phi_{i+1}) \end{aligned}$$

Thus a small overlay modified valence force field has been postulated for the out-of-plane vibrations of the Fluorine substituted Benzenes, the force constants have been selected on a logical basis and it is easily comparable with the known force field of Benzene to check that the solutions are in the correct minimum in force constant space.

Actually the MVFF was never calculated on this 19 parameter form but in two very similar forms as 18 and 23 parameter force fields.

A. The 18 Parameter Force Field

In this field $C_2 = \frac{1}{2}(C_1 + C_3)$, i.e. the value of the diagonal HF torsional force constant lies midway between the HH and FF values. This assumption brings the force field in line with that of Radcliffe and Steele (24) which is the starting point to all the calculations and is also an additional check on the solutions.

B. The 23 Parameter Force Field

This field is very similar in description to Scherer's field for the Chloro Benzenes (115), except that Scherer used τ torsion coordinates. It introduces a neighbouring substituent dependence into the diagonal y coordinates. Thus the two diagonal out-of-plane bending force constants A and B are each replaced by three force constants A_1, A_2, A_3 and B_1, B_2, B_3. A_1, A_2 and A_3 are diagonal y_{CH} force constants with HH, HF and FF respectively as the neighbouring substituents and B_1, B_2 and B_3 are diagonal y_{CF} force constants with HH, HF and FF respectively as the neighbouring substituents. They are illustrated in figures 3.3 and 3.4.

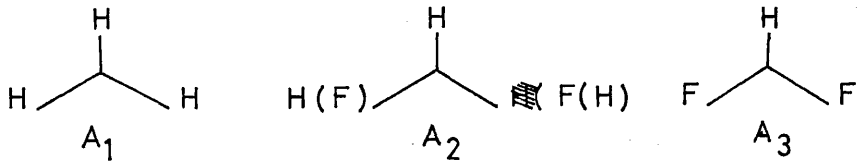


Figure 3.3

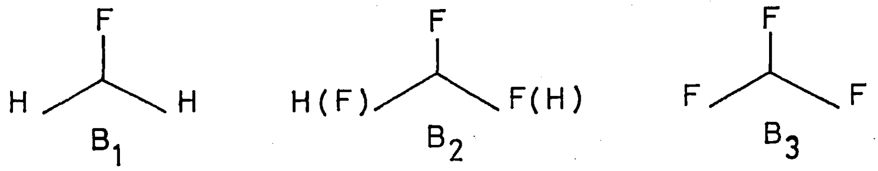


Figure 3.4

Scherer (115) found that introducing this substituent dependence considerably reduced the weighted square-error sum (WSQER) in the molecules he studied. His results were:-

for a 23 parameter force field, WSQER = 0.5×10^{-3},

for a 21 parameter force field (substituent dependence removed from the diagonal τ force constants), WSQER = 0.6×10^{-3}.

for a 17 parameter force field (substituent dependence removed also from the diagonal y force constants), WSQER = 2.2×10^{-3}.

Attempts were also made to introduce substituent dependence in only the off-diagonal force constants but no weighted square-error sums approached the 0.5×10^{-3} for the 23 parameter force field, so the conclusion is that by far the most significant reductions in error were achieved by introducing this substituent dependance into the diagonal y force constants.

An interesting consequence of substituent dependence is in connection with the equivalence of the A_2 symmetry blocks of the G matrices of certain molecules as discussed in the part of section 2.3 dealing with 1,2,3,5 Tetrafluoro Benzene. Without these extra force constants the F matrices of these molecules are equivalent too and therefore the calculated frequencies are the same. However since the observed frequencies are usually different, the F matrices must also be different and now allowance can be made for this. This point can be clarified by studying Figures 2.11, 3.3 and 3.4.

As has been frequently mentioned, Scherer (115) has published a similar study on the Chloro Benzenes to that on the

Fluoro Benzenes being reported here. It would therefore be useful to compare his results for the Chloro Benzenes with those for the Fluoro Benzenes. There is a drawback in that Scherer used τ torsion coordinates as opposed to the ϕ coordinates used here and therefore the two sets of results cannot be directly compared. However the two types of coordinate are related according to the equation given by Whiffen (12),

$$Rd\phi_i = 2Rd\tau_i + 2.3^{\frac{1}{2}} R (dy_i - dy_{i+1})$$

and a force field in terms of y,ϕ coordinates can readily be converted into one in terms of y,τ coordinates and vice versa. Firstly, using the above equation, the $Rd\phi_i$ terms are substituted for in the Potential Energy expression, then like internal coordinate terms are collected, i.e. all the $(rdy_i)^2$, $(Rd\tau_i)^2$, $rdy_i\ R(d\tau_{i-1} - d\tau_i)$ terms, etc. The force constant coefficients of these terms are the y,τ force constants expressed in terms of the y,ϕ force constants.

For the MVFF the expressions for the Benzene force constants are

$$\underline{A} = A - 2z.ac^{o} + 2y(C_1 - c^{o})$$
$$\underline{a^{o}} = a^{o} - y(C_1 - 2c^{o}) + z(ac^{o} - ac^{m})$$
$$\underline{a^{m}} = a^{m} - y.c^{o} + z.ac^{m}$$
$$\underline{a^{p}} = a^{p}$$
$$\underline{C_1} = 4C_1$$
$$\underline{c^{o}} = 4c^{o}$$
$$\underline{ac^{o}} = 2ac^{o} - y(C_1 - c^{o})$$
$$\underline{ac^{m}} = 2ac^{m} - y.c^{o}$$

where the y,τ force constants are those underlined and $y = 4/3.(R/r)^2$ $z = 4/3^{\frac{1}{2}}.R/r$

A similar substitution for Hexafluoro Benzene gives:

$$\underline{B} = B - 2z.bc^{o} + 2y(C_3 - c^{o})$$
$$\underline{b^{o}} = b^{o} - y(C_3 - 2c^{o}) + z(bc^{o} - bc^{m})$$
$$\underline{b^{m}} = b^{m} - y.c^{o} + z.bc^{m}$$
$$\underline{b^{p}} = b^{p}$$
$$\underline{C_3} = 4C_3$$
$$\underline{c^{o}} = 4c^{o}$$
$$\underline{bc^{o}} = 2bc^{o} - y(C_3 - c^{o})$$
$$\underline{bc^{m}} = 2bc^{m} - y.c^{o}$$

The remaining expressions are taken to be:

$$\underline{ab^o} = ab^o - y(C_2 - 2c^o) + z/2.(ac^o + bc^o - ac^m - bc^m)$$

$$\underline{ab^m} = ab^m - y.c^o + z/2.(ac^m + bc^m)$$

$$\underline{ab^p} = ab^p$$

$$\underline{C_2} = 4C_2$$

The expressions for $\underline{A_1}$, $\underline{A_2}$, $\underline{A_3}$ are calculated by substituting A_1, A_2, A_3 as appropriate for A and likewise for $\underline{B_1}$, $\underline{B_2}$, $\underline{B_3}$.

SECTION 3.4 Calculation of the Force Fields

The force field to be used having been decided, the Z matrices for each molecule were set up, first in internal coordinates, then using the U matrices given in section 2.2 in symmetry coordinates. And with the G matrices and the observed frequencies the force fields could now be calculated. The force fields could be fitted to the frequency data for all twenty molecules at once and this was done but also the force fields were fitted to only some of the molecules. The molecules were divided into three sets:-

A, The Nil (i.e. Benzene), Mono and Di Fluoro Benzenes,

B, The Di, Tri and Tetra Fluoro Benzenes,

C, The Tetra, Penta and Hexa Fluoro Benzenes,

(plus set Z, all the molecules).

The idea is to investigate how the force constants change on going from one set to another.

The order of calculation is described below.

18 Parameter Force Field

1. Using the field of Radcliffe and Steele (24) as the initial field the force field for set Z was calculated allowing all the force constants to vary.

2. Using the field for set Z as the initial field the force field for set B was calculated, firstly allowing only the 4 diagonal force constants to vary, then using this field as the initial field allowing all force constants to vary.

3. Using the field for set B as the initial field the force field for set A was calculated, firstly allowing only the 4 diagonal force constants to vary then using this field as the initial field allowing 15 force constants to vary, but no b^o, b^m and b^p. These force constants were excluded since they occur only in the Difluoro Benzenes. Therefore no new frequency data to influence their values is introduced but some is removed (i.e. that for the Tri and Tetrafluoro Benzenes.). Allowing them to vary when they are dependent on very little data might result in highly individual non-transferable values.

4. Using the field for set B as the initial field the force field for set C was calculated, firstly allowing only the 4 diagonal force constants to vary then using this field as the initial field

allowing 15 force constants to vary, but not a^o, a^m and a^p. These force constants were excluded since they occur only in the Tetrafluoro Benzenes, and for similar reasons to those discussed above.

5. Using the field for set Z as the initial field the force fields for first set A and then set C were calculated varying only the diagonal force constants.

23 Parameter Force Field

1. Using the 18 parameter force field for set Z as the initial force field the 23 parameter force field for set Z was calculated, first allowing the 9 diagonal force constants to vary, then using this field as the initial field allowing all force constants to vary.

2. Using the field for set Z as the initial field the force field for set B was calculated first allowing the 9 diagonal force constants to vary and then using this field as the initial field allowing all the force constants to vary.

3. Using the field for set B as the initial field the force field for set A was calculated first allowing 5 diagonal force constants (A_1, A_2, B_1, C_1, C_2) to vary. A_3, B_2 and C_3 were not allowed to vary since they occur only in the Difluoro Benzenes and B_3 does not occur at all in set A (it requires three adjacent Fluorine substituents). Then using this field as the initial

field the force field was calculated allowing 16 force constants to vary. Those force constants not included were the 4 diagonals A_3, B_2, B_3 and C_3 and the 3 off-diagonals b^o, b^m and b^p.

4. Using the field for set B as the initial field the force field for set C was calculated first allowing 5 diagonal force constants (A_3, B_2, B_3, C_2, C_3) to vary. A_2, B_1 and C_1 were not allowed to vary since they occur only in the Tetrafluoro Benzenes and A_1 does not occur at all in set C. Then using this field as the initial field the force field was calculated allowing 16 Force constants to vary. Those force constants not included were the 4 diagonals A_1, A_2, B_1 and C_1 and the three off-diagonals a^o, a^m and a^p.

The frequencies were not corrected for anharmonicity. Gayles et.al.(75) made such corrections to the observed frequencies of Propane and its deutero derivatives using a method requiring a knowledge of all the binary combination and first overtone frequencies. They concluded that:

> "very accurate data is needed to obtain anharmonicity corrected frequencies to determine molecular potential functions that represent any significant improvement on the zeroth approximation of just using the observed fundamental frequencies in the calculation. "

Brodersen and Langseth (17) found that in Benzene the errors due to anharmonicity were small. This should apply to the Fluoro Benzene as the replacement of light Hydrogen atoms with much heavier Fluorine atoms would be expected to cause a reduction in the anharmonicity of vibration. This follows from the fact that the anharmonicity of a vibration is correlated strongly with the amplitude of motion in that vibration, (3) p.23.

Where no correction is made for anharmonicity Aldous and Mills (72) argued that since the differences between observed and calculated frequencies are not due to experimental error but to anharmonicity then these errors will be larger for higher frequencies and percentage weighting should be used. Overend and Scherer (119) considered that anharmonicity effects are not random and therefore cannot be dealt with in this manner and therefore the weighting should be absolute since theerrors, for which the correction is being made (i.e. experimental error) are evenly distributed.

The Weighting factor used here was absolute, not for any theoretical reasons but for the more mundane fact that it gave a better fit. It was found in a series of comparative tests that the two weighting factors gave similar fits to the lower frequencies but at the higher frequencies the fit was much worse when using percentage weighting.

All the force fields were calculated using a perturbation program which gives four refinement cycles. This was sufficient in all cases to achieve a convergence which could be described as complete. In the case of the 18 parameter force field for set Z continuation of the perturbation for another four cycles reduced the WSQER from 0.0125384 to 0.0125004. This is not a significant change and in fact the weighted average frequency error was increased from 11.753 to 11.766 cm^{-1}. (This apparent anomaly is due to the fact that the WSQER considers the square of the errors, and this is the quantity reduced in the perturbation cycle, as opposed to the weighted average frequency error, which does not involve any squared quantities). In no case were the initial and final solutions in different minima. This can be deduced from the fact that the convergence was always smooth, i.e. there were no sudden changes in the WSQER. In the majority of cases the scaling factor a was unity.

The calculated force fields are given in Tables 3.3 to 3.12. The value given in brackets after a force constant is its dispersion or r.m.s. error calculated using equation 1 given in section 3.1 (singularity). If a force constant is not varied in a particular calculation it cannot have a dispersion value and therefore none is shown. In some tables no dispersion values are given and those force constants which are not varied are starred thus *. The number of force constants in a particular field is shown above the field with the number of force constants varied in calculating that field shown in brackets. The following values are given below each field.

1. The weighted square - error sum (WSQER)

where $\mathrm{WSQER} = \sum_i w_i (d\lambda_i)^2$ 8

and $d\lambda_i = \lambda_i^{calc} - \lambda_i^{obs}$

2. The weighted average frequency error ($\overline{|dv|}$)

where $dv = \sum_i w_i (|dv_i|) / n$ 9

and $|dv_i|$ is the absolute value of

$dv_i = v_i^{calc} - v_i^{obs}$

3. The weighted average standard deviation ($\overline{\sigma (v)}$)

where $\overline{\sigma (v)} = \sum_i w_i (\sigma (v_i)) / n$ 10

and $\sigma (v_i)$ is the standard deviation or calculated error in the ith calculated frequency.

In the above equations the summation i is over all observed frequencies and w_i is the weighting factor for the ith frequency as given in the tables in Chapter Two. The weighting factors are not scaled to be either absolute or percentage.

4. The ratio of the determinant of matrix C to the product of its diagonal elements ($|C| / \prod_i c_{i,i}$). This is a test for singularity as discussed in section 3.1. (It is given the symbol C/c in the tables).

The units of the force constants and force constant dispersions are mdyn.A^{-1}, those of the WSQER's are frequency squared, and those of $\overline{|dv|}$ and $\overline{\sigma (v)}$ are cm^{-1}. $|C|/\prod_i c_{i,i}$ is unitless. An arrow thus, X → Y, indicates that field Y is calculated from field X.

The Tables are as follows:

Comparison of 18 and 23 Parameter Force Fields for set Z

FORCE FIELD	23(23) ←	18(18)	→ 23(9)
FORCE CONSTANT			
A_1	0.2664 (.0096)		0.2720 (.0027)
A_2	.2361 (.0109)	0.2662 (.0185)	.2628 (.0025)
A_3	.2128 (.0116)		.2505 (.0030)
B_1	.2479 (.0055)		.2336 (.0041)
B_2	.2247 (.0064)	.2147 (.0083)	.2154 (.0049)
B_3	.1922 (.0062)		.2011 (.0043)
a^o	.0114 (.0022)	.0085 (.0041)	.0085
a^m	-.0147 (.0050)	-.0121 (.0096)	-.0121
a^p	-.0114 (.0034)	-.0119 (.0064)	-.0119
ab^o	.0131 (.0031)	.0224 (.0047)	.0224
ab^m	-.0205 (.0037)	-.0208 (.0065)	-.0208
ab^p	-.0137 (.0050)	-.0140 (.0095)	-.0140
b^o	.0126 (.0029)	.0187 (.0049)	.0187
b^m	-.0132 (.0032)	-.0178 (.0057)	-.0178
b^p	-.0108 (.0066)	.0050 (.0120)	.0050
C_1	.0354 (.0026)	.0367 (.0046)	.0347 (.0008)
C_2	.0360 (.0028)		.0306 (.0011)
C_3	.0362 (.0032)	.0251 (.0043)	.0344 (.0033)
c^o	-.0076 (.0014)	-.0079 (.0025)	-.0079
ac^o	.0119 (.0014)	~~-~~.0146 (.0027)	.0146
ac^m	.0001 (.0016)	-.0001 (.0031)	-.0001
bc^o	.0000 (.0019)	.0013 (.0033)	.0013
bc^m	0.0063 (.0019)	0.0010 (.0034)	0.0010
WSQER	3.6×10^{-3}	12.5×10^{-3}	7.2×10^{-3}
$\overline{\lvert dv \rvert}$	5.85	11.75	8.53
$\overline{\sigma(v)}$	3.59	5.93	3.08
C/c	3.96×10^{-9}	8.82×10^{-7}	1.65×10^{-1}

Table 3.3

Comparison of 18 and 23 Parameter Force Fields for set A

FORCE FIELD	23(16)	18(15)	R+S
FORCE CONSTANT			
A_1	0.2850 (.0056)		
A_2	.2640 (.0050)	0.2667 (.0150)	0.2606
A_3	.2487		
B_1	.2506 (.0054)		
B_2	.2227	.2265 (.0071)	.2126
B_3			
a^o	.0152 (.0019)	.0108 (.0035)	.0132
a^m	-.0234 (.0032)	-.0131 (.0077)	-.0112
a^p	-.0178 (.0024)	-.0128 (.0053)	-.0121
ab^o	.0221 (.0022)	.0265 (.0043)	.0166
ab^m	-.0221 (.0026)	-.0172 (.0043)	-.0041
ab^p	-.0207 (.0053)	-.0016 (.0071)	-.0040
b^o	.0158	.0112	
b^m	-.0183	-.0155	
b^p	-.0187	.0057	.0154
C_1	.0304 (.0018)	.0341 (.0036)	.0357
C_2	.0282 (.0018)		
C_3	.0401	.0219 (.0044)	.0332
c^o	-.0102 (.0010)	-.0084 (.0020)	-.0072
ac^o	.0145 (.0009)	.0134 (.0022)	.0123
ac^m	.0024 (.0012)	.0000 (.0026)	
bc^o	-.0029 (.0022)	-.0073 (.0030)	-.0107
bc^m	0.0037 (.0015)	-.0039 (.0021)	-.0067
WSQER	2.0×10^{-3}	4.1×10^{-3}	
$\lvert\overline{dv}\rvert$	5.78	8.02	
$\overline{\sigma(v)}$	3.92	5.41	
C/c	4.28×10^{-6}	1.63×10^{-6}	

Table 3.4

Comparison of 18 and 23 Parameter Force Fields for set B

FORCE FIELD	23(23)	18(18)
FORCE CONSTANT		
A_1	0.3001 (.0223)	
A_2	.2719 (.0223)	0.2090 (.0180)
A_3	.2487 (.0224)	
B_1	.2485 (.0077)	
B_2	.2227 (.0080)	.2091 (.0089)
B_3	.2051 (.0081)	
a^o	.0144 (.0048)	-.0057 (.0073)
a^m	-.0316 (.0112)	.0168 (.0110)
a^p	-.0162 (.0057)	-.0003 (.0061)
ab^o	.0177 (.0043)	.0127 (.0053)
ab^m	-.0257 (.0053)	-.0187 (.0067)
ab^p	-.0222 (.0079)	.0061 (.0104)
b^o	.0158 (.0034)	.0112 (.0056)
b^m	-.0183 (.0038)	-.0155 (.0060)
b^p	-.0187 (.0087)	.0057 (.0127)
C_1	.0336 (.0038)	.0526 (.0062)
C_2	.0368 (.0032)	
C_3	.0401 (.0034)	.0400 (.0058)
c^o	-.0063 (.0018)	-.0011 (.0033)
ac^o	.0179 (.0035)	.0110 (.0019)
ac^m	.0089 (.0039)	-.0066 (.0032)
bc^o	.0021 (.0021)	.0010 (.0031)
bc^m	0.0059 (.0022)	0.0018 (.0032)
WSQER	1.1×10^{-3}	4.6×10^{-3}
$\overline{\lvert dv \rvert}$	4.40	8.07
$\overline{\sigma(v)}$	3.60	5.77
C/c	3.16×10^{-11}	1.50×10^{-9}

Table 3.5

Comparison of 18 and 23 Parameter Force Fields for set C

FORCE FIELD	23(16)	18(15)
FORCE CONSTANT		
A_1		
A_2	0.2719	0.1666 (.0218)
A_3	.2508 (.0054)	
B_1	.2485	
B_2	.2375 (.0078)	.1717 (.0173)
B_3	.1899 (.0056)	
a^o	.0144	-.0057
a^m	-.0316	.0168
a^p	-.0162	-.0003
ab^o	.0158 (.0034)	-.0105 (.0083)
ab^m	-.0276 (.0035)	.0000 (.0083)
ab^p	-.0145 (.0057)	.0273 (.0096)
b^o	.0131 (.0030)	-.0121 (.0081)
b^m	-.0121 (.0029)	-.0013 (.0089)
b^p	-.0072 (.0066)	.0579 (.0182)
C_1	.0336	.0622 (.0115)
C_2	.0340 (.0028)	
C_3	.0365 (.0035)	.0465 (.0084)
c^o	-.0083 (.0017)	-.0013 (.0056)
ac^o	.0201 (.0011)	.0125 (.0035)
ac^m	.0105 (.0021)	-.0044 (.0042)
bc^o	.0004 (.0022)	-.0127 (.0051)
bc^m	0.0067 (.0023)	-.0075 (.0065)
WSQER	0.3×10^{-3}	1.5×10^{-3}
$\lvert\overline{dv}\rvert$	3.74	7.54
$\overline{\sigma(v)}$	4.48	8.24
C/c	3.60×10^{-7}	4.14×10^{-9}

Table 3.6

Comparison of 18 Parameter Force Fields for sets A, B and C

FORCE FIELD	18(15) ← 18(18) → 18(15)		
FORCE CONSTANT			
A	0.2667	0.2090	0.1666
B	.2265	.2091	.1717
a^o	.0108	-.0057	-.0057*
a^m	-.0131	.0168	.0168*
a^p	-.0128	-.0003	-.0003*
ab^o	.0265	.0127	-.0105
ab^m	-.0172	-.0187	.0000
ab^p	-.0016	.0061	.0273
b^o	.0112*	.0112	-.0121
b^m	-.0155*	-.0155	-.0013
b^p	.0057*	.0057	.0579
C_1	.0341	.0526	.0622
C_3	.0219	.0400	.0465
c^o	-.0084	-.0011	-.0013
ac^o	.0134	.0110	.0125
ac^m	.0000	-.0066	-.0044
bc^o	-.0073	.0010	-.0127
bc^m	-.0039	0.0018	-.0075

Force Constants marked thus * are not varied in calculation.

Table 3.7

Comparison of 23 Parameter Force Fields for sets A, B and C

FORCE FIELD	23(16) ← 23(23) → 23(16)		
FORCE CONSTANT			
A_1	0.2850	0.3001	
A_2	.2640	.2719	0.2719*
A_3	.2487*	.2487	.2508
B_1	.2506	.2485	.2485*
B_2	.2227*	.2227	.2375
B_3		.2051	.1899
a^o	.0152	.0144	.0144*
a^m	-.0234	-.0316	-.0316*
a^p	-.0178	-.0162	-.0162*
ab^o	.0221	.0177	.0158
ab^m	-.0221	-.0257	-.0276
ab^p	-.0207	-.0222	-.0145
b^o	.0158*	.0158	.0131
b^m	-.0183*	-.0183	-.0121
b^p	-.0187*	-.0187	-.0072
C_1	.0304	.0336	.0336*
C_2	.0282	.0368	.0340
C_3	.0401*	.0401	.0365
c^o	-.0102	-.0063	-.0083
ac^o	.0145	.0179	.0201
ac^m	.0024	.0089	.0105
bc^o	-.0029	.0021	.0004
bc^m	0.0037	0.0059	0.0067

Force Constants marked thus * are not varied in calculation

Table 3.8

Comparison of 18 Parameter Force Fields for sets A, B and C
Diagonal Force Constants only

FORCE FIELD	Set A 18(4) ←	Set B 18(18) →	Set C 18(4)
FORCE CONSTANT			
A	0.2198	0.2090	0.2081
B	.2112	.2091	.2004
C_1	.0499	.0526	.0469
C_2	0.0401	0.0400	0.0400
WSQER	$13.6x10^{-3}$	$4.6x10^{-3}$	$2.9x10^{-3}$
$\overline{\lvert dv \rvert}$	11.76	8.07	11.39
$\overline{\sigma(v)}$	4.15	5.77	5.16
C/c	$2.81x10^{-1}$	$1.50x10^{-9}$	$1.30x10^{-1}$

Off-Diagonal Force Constants from Set B

Table 3.9

Comparison of 18 Parameter Force Fields for sets A,B,C and Z
Diagonal Force Constants only

FORCE FIELD	Set A 18(4)	Set B 18(4)	Set C 18(4)	Set Z
FORCE CONSTANT				
A	0.2679	0.2541	0.2492	0.2622
B	.2232	.2185	.2086	.2147
C_1	.0351	.0381	.0340	.0367
C_2	0.0256	0.0282	0.0301	0.0251
WSQER	5.1×10^{-3}	5.9×10^{-3}	2.9×10^{-3}	
$\overline{\mid dv \mid}$	9.20	9.27	11.68	
$\overline{\sigma(v)}$	2.90	2.73	3.21	
C/c	3.13×10^{-1}	1.90×10^{-1}	1.27×10^{-1}	

Off-Diagonal Force Constants from Set Z

Table 3.10

Comparison of 23 Parameter Force Fields for sets A, B and C
Diagonal Force Constants only

FORCE FIELD	Set A ← 23(5)	Set B 23(23)	→ Set C 23(5)
FORCE CONSTANT			
A_1	0.2965	0.3001	
A_2	.2727	.2719	0.2719*
A_3	.2487*	.2487	.2498
B_1	.2483	.2485	.2485*
B_2	.2227*	.2227	.2300
B_3		.2051	.1930
C_1	.0346	.0336	.0336*
C_2	.0367	.0368	.0349
C_3	0.0401*	0.0401	0.0361
WSQER	$5.5x10^{-3}$	$1.1x10^{-3}$	$0.9x10^{-3}$
$\overline{\lvert dv \rvert}$	8.24	4.40	6.98
$\overline{\sigma(v)}$	3.22	3.60	3.68
C/c	$2.90x10^{-1}$	$3.16x10^{-11}$	$1.82x10^{-1}$

Off-Diagonal Force Constants from Set B

Force constants marked thus * are not varied in calculation.

Table 3.11

Comparison of 23 Parameter Force Fields
for sets B and Z
Diagonal Force Constants only

FORCE FIELD	Set B 23(9)	Set Z
FORCE CONSTANT		
A_1	0.2626	0.2644
A_2	.2328	.2361
A_3	.2128	.2128
B_1	.2466	.2479
B_2	.2220	.2247
B_3	.2001	.1922
C_1	.0376	.0354
C_2	.0365	.0360
C_3	0.0380	0.0362
WSQER	1.8×10^{-3}	
$\overline{\lvert dv \rvert}$	5.45	
$\overline{\sigma(v)}$	2.41	
C/c	1.05×10^{-1}	

Off-Diagonal Force Constants from Set Z

Table 3.12

Frequency Errors for individual molecules calculated using 18 Parameter Force Fields

MOLECULE	dv	WSQER	dv	WSQER	dv	WSQER
	Set Z		Set A			
1. Benzene	14.8	1.26	9.1	0.56		
2. Hexadeutero Benzene	13.0	0.57	7.4	0.30		
3. Fluoro Benzene	10.5	1.23	6.4	0.56		
4. Fluoro Pentadeutero Benzene	9.7	0.81	7.3	0.31	Set B	
5. 1,2 difluoro Benzene	7.8	0.24	8.9	0.44	9.9	0.52
6. 1,3 difluoro Benzene	12.1	1.18	12.8	1.37	8.9	0.91
7. 1,4 difluoro Benzene	7.1	0.29	3.6	0.21	6.6	0.34
8. 1,4 difluoro Tetradeutero Benzene	11.6	0.42	9.2	0.37	8.1	0.43
9. 1,2,3 trifluoro Benzene						
10. 1,2,4 trifluoro Benzene	7.5	0.36			3.7	0.09
11. 1,3,5 trifluoro Benzene	16.2	1.00			11.1	0.54
12. 1,3,5 trifluoro Deutero Benzene						
13. 1,3,5 trifluoro Dideutero Benzene						
14. 1,3,5 trifluoro Trideutero Benzene	6.7	0.08	Set C		1.7	0.01
15. 1,2,3,4 tetrafluoro Benzene	14.2	0.66	7.0	0.14	12.2	0.73
16. 1,2,3,5 tetrafluoro Benzene	15.4	1.67	6.3	0.28	10.6	0.93
17. 1,2,4,5 tetrafluoro Benzene	10.8	0.56	10.6	0.50	6.0	0.14
18. Pentafluoro Benzene	13.8	1.27	5.2	0.29		
19. Pentafluoro Deutero Benzene	19.8	0.64	9.3	0.21		
20. Hexafluoro Benzene	25.0	0.26	10.9	0.05		
		$x10^{-3}$		$x10^{-3}$		$x10^{-3}$

Table 3.13

Frequency Errors for individual molecules calculated using 23 Parameter Force Fields

MOLECULE	dv	WSQER	dv	WSQER	dv	WSQER
	Set Z		Set A			
1. Benzene	8.9	0.62	7.7	0.36		
2. Hexadeutero Benzene	6.2	0.18	6.3	0.30		
3. Fluoro Benzene	4.9	0.30	5.0	0.36		
4. Fluoro Pentadeutero Benzene	5.3	0.15	4.3	0.10	Set B	
5. 1,2 difluoro Benzene	5.8	0.12	4.5	0.09	4.9	0.16
6. 1,3 difluoro Benzene	7.1	0.49	8.4	0.51	4.9	0.18
7. 1,4 difluoro Benzene	5.5	0.35	5.0	0.20	5.9	0.22
8. 1,4 difluoro Tetradeutero Benzene	4.9	0.10	5.5	0.11	2.7	0.04
9. 1,2,3 trifluoro Benzene						
10. 1,2,4 trifluoro Benzene	4.6	0.21			4.0	0.13
11. 1,3,5 trifluoro Benzene	6.2	0.11			3.4	0.04
12. 1,3,5 trifluoro Deutero Benzene						
13. 1,3,5 trifluoro DiDeutero Benzene						
14. 1,3,5 trifluoro Trideutero Benzene	4.1	0.06	Set C		2.7	0.01
15. 1,2,3,4 tetrafluoro Benzene	6.4	0.19	3.8	0.05	4.1	0.08
16. 1,2,3,5 tetrafluoro Benzene	5.1	0.17	3.7	0.06	5.3	0.16
17. 1,2,4,5 tetrafluoro Benzene	7.7	0.30	5.8	0.18	5.0	0.12
18. Pentafluoro Benzene	3.3	0.08	2.2	0.03		
19. Pentafluoro Deutero Benzene	8.3	0.11	1.8	0.01		
20. Hexafluoro Benzene	11.0	0.05	5.7	0.01		
		$x10^{-3}$		$x10^{-3}$		$x10^{-3}$

Table 3.14

SECTION 3.5 Discussion of the Force Fields.

Discussion of the Frequency Errors

Introduction

Before discussing the force fields from the point of view of the force constants which constitute them, they are considered from the point of view of their ability to reproduce the observed frequencies.

Discussion

As expected the 23 parameter force fields give a better fit to the observed frequencies than the 18 parameter force fields. The WSQER for the 18 parameter field for set Z is 12.53×10^{-3}, compared with 3.61×10^{-3} for the 23 parameter field, a considerable reduction in error for the addition of only five force constants. This demonstrates the significance of the introduction of the concept of substituent dependance.

Taking the smaller WSQER values for the Di- and Tetrafluoro Benzenes, the sum over all twenty molecules of the individual WSQER values (see Table 3.13) for the 18 parameter force fields for sets A, B and C is 5.48×10^{-3}. So dividing the molecules into three sets and fitting a different 18 parameter force field to each set is not as effective as fitting a 23 parameter force field to all the molecules.

Extending the arguments to include the 23 parameter force fields for sets A, B and C, it is again seen that these fields give a much better fit to the observed frequencies than the 18 parameter fields. Taking the smaller WSQER values for the Di- and Tetrafluoro Benzenes, the sum over all twenty molecules of the individual WSQER values (see Table 3.14) for the 23 parameter force fields for sets A, B and C is 2.10×10^{-3}. This reduction in error is not particularly large when compared with the WSQER of 3.61×10^{-3} for set Z in view of the reduction in the number of frequencies to which the fields were fitted.

Conclusion

The 23 parameter force fields are far better at reproducing the observed frequencies than the 18 parameter force fields, showing the significance of substituent dependance. For the 23 parameter fields, the fields for sets A, B and C are not much better at reproducing the observed frequencies than the field for set Z, showing that the changes in the frequencies on going through the molecules from Benzene to Hexafluoro Benzene are accounted for, to a large extent, by the introduction of substituent dependance into the field for set Z, whilst reducing the number of frequencies to which this field is fitted is not so important in reducing the errors.

Comparison of Force Fields with Whiffen's Benzene Field

Introduction

The two sets A and Z include the observed frequencies for Benzene. Therefore for the force fields fitted to these sets to be valid, those force constants which occur in the force field for Benzene must be in agreement with Whiffen's tilde force constants for Benzene (12).

Discussion

This agreement will not necessarily be exact so it has to be decided what error limits are to be placed on the force constants calculated here. Following Scherer (115), the actual error in a force constant is taken as:

$$d(\phi_i) = \sigma(\phi_i) \left| \frac{\overline{|dv|}}{\overline{\sigma(v)}} \right|^2 \qquad 11$$

where $d(\phi_i)$ is the actual error in the ith force constant,

$\sigma(\phi_i)$ is the dispersion of the ith force constant,

$\overline{|dv|}$ is the weighted average frequency error

and $\overline{\sigma(v)}$ is the weighted average dispersion of the calculated frequencies.

Both $\overline{|dv|}$ and $\overline{\sigma(v)}$ are calculated from the frequencies which are calculated using the force field of which ϕ_i is a member. The values of both these quantities plus the $\sigma(\phi_i)$ values are given together with the appropriate force fields in Tables 3.3 to 3.12.

The term $\overline{|dv|}/\overline{\sigma(v)}$ is squared since the force constants are determined from the eigen values, which are proportional to the squares of the frequencies.

For the 23 parameter force field for set Z,

$$\left| \overline{|dv|}/\overline{\sigma(v)} \right|^2 = 2.66$$

so $$d(\phi_i) = 2.66\ \sigma(\phi_i)$$

is taken as the actual error in the force constants. The range of solutions for the Benzene force constants in the 23 parameter force field for set Z, calculated using this relationship, are given in Table 3.15 together with Whiffen's tilde force constants.

FORCE FIELD	23 PARAMETER F.F.	WHIFFEN'S F.F.
FORCE CONSTANT		
A_1	+.2912 to +.2409	.286
a^o	+.0173 to +.0055	.012
a^m	-.0280 to -.0014	-.022
a^p	-.0204 to -.0024	-.017
C_1	+.0423 to +.0285	.029
c^o	-.0113 to -.0039	-.010
ac^o	+.0156 to +.0082	.014
ac^m	+.0044 to -.0042	.000

Table 3.15

As can be seen the tilde force constants all lie within the indicated ranges so it is concluded that the 23 parameter field for set Z is a valid field. If the dispersions were taken as the actual errors in the force constants some of the tilde force constants would lie outside the indicated ranges. Most notable of these is A_1, for which the range would be +.2760 to +0.2568 compared with the tilde value of .286.

Using equation 11 to calculate the actual errors in all of the other fields for sets A and Z it is found that the tilde force constants always lie within the indicated ranges.

Conclusions

Using equation 11 as the definition of actual error in a force constant all the force fields calculated for sets A and Z are valid. This is the method apparently used by Scherer (115) to calculate the actual errors in force constants but he does not explain it. It allows for the fact that the statistical error in a calculated frequency is not generally equal to the actual error, which is the difference between the observed and calculated frequencies. However, it is rather general in that it makes no attempt to correlate the actual error in a specific frequency with any particular force constant. Also it appears to overestimate the errors in some force constants so whether it gives the true error in a given force constant is doubtful.

Discussion of the force fields for set Z

Introduction

Three force fields were fitted to the frequency data for set Z, the 23(23) field, the 23(9) field and the 18(18) field (see Table 3.3). These force fields are the starting points for the other calculations so they are considered first, but before this is done it is instructive to consider briefly what results might be expected. Since the fields are fitted to identical frequency data it is to be expected that the force fields are very similar. Therefore, for the 23(23) and the 18(18) fields:

A_2 (23) should equal A (18), i.e. A in the 18 parameter field should represent the mid-point of A_1, A_2, A_3 in the 23 parameter force field:

B_2 (23) should equal B (18);

C_1 (23) should equal C_1(18);

C_3 (23) should equal C_3(18);

C_2 (23) should equal $\frac{1}{2}$ (C_1 + C_3) for the 18 field;

the off-diagonal force constants in the two fields should be equal.

The 23(9) field is calculated as a mid-point between the 18(18) and the 23(23) fields. If the off-diagonal force constants for these two fields are equal, then the diagonal force constants in the 23(9) field should equal those in the 23(23) field.

Discussion

Comparing the 23(23) and 18(18) parameter force fields, it is seen that the off-diagonal elements in the two fields are similar, except for b^p. Since for both fields a^m, a^p, ab^m, ab^p and b^m are all negative and for the 23(23) field b^p is also negative, it is reasonable to expect b^p to be negative for the 18(18) field. Since, it is not, doubt is cast on the acceptability of the 18(18) field. However, since for both fields the actual error in b^p is larger than the force constant itself, this result alone is not very significant.

A comparison of the diagonal force constants must include the 23(9) field which is the initial field for the calculation of the 23(23) field and is itself calculated from the 18 parameter field allowing only the 9 diagonal force constants to vary. For the A force constants, A_2 in the 23(9) field is almost identically equal to A in the 18(18) field, with A_1 and A_3 fairly equally spaced above and below, as would be expected. However, these A force constants are higher than their equivalent force constants in the 23(23) field. For the B force constants again, B_2 in the 23(9) field is almost identical to B in the 18(18) field, with B_1 and B_3 fairly equally spaced above and below. These B force constants are closer to those for the 23(23) field than the A force constants but are still different. Since these three fields are fitted to the same data, this lack of agreement between them is disappointing and it suggests that either the 23(23) field or the 18(18) and 23(9) fields are unacceptable.

The C force constants, so far not discussed, show clearly that the 18(18) and 23(9) fields are the unacceptable ones. Comparing the C_1 and C_3 force constants for the 23(23) and 18(18) fields, the C force constants are similar but for the 23(23) field C_3 is slightly higher than C_1, whereas for the 18(18) field C_3 is considerably lower than C_1. It would be expected for the 23(9) field that C_1 and C_3 would be similar to C_1 and C_3 in the 18(18) field and that C_2 in the 23(9) field would be approximately equal to $(C_1 + C_3)/2$ in the 18(18) field. This latter condition is satisfied, for the 18(18) field $(C_1 + C_3)/2 = .0309$ compared with a value for C_2 of .0306 in the 23(9) field. The C_1 force constants in the two fields are similar but the C_3 force constants are very different. C_3 in the 23(9) field is almost the same as C_1. It would appear that the inherent value of C_2 in the 18(18) field, together with the appropriate off-diagonal force constants are totally controlling the value of C_3. Removing the condition that $C_2 = (C_1 + C_3)/2$ in the 23(9) field allows the C_3

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value to rise by 40%.

Conclusions

The behaviour of the diagonal force constants, especially the C constants, in the 18(18) and 23(9) force fields makes them unacceptable. However, the 23(23) field is acceptable. It obeys the Benzene condition, the force constants do not change in an erratic manner and, as will be seen later, the changes in the A, B and C force constants are in the same direction as those found by Scherer (115) for these force constants in the Chloro Benzenes, i.e. decreases in the A and B force constants and increases in the C force constants on going through the series from 1(HH) to 3(FF). The introduction of substituent dependance in this field, thereby allowing for changes in the force field on going through the molecules from Benzene to Hexafluoro Benzene causes a considerable reduction in the WSQER. Not allowing for changes in the force constants in the 18 parameter field is probably the reason for its failure.

Discussion of the 23 Parameter Force Fields for Sets B and Z.

Introduction

The next step is to compare the 23 parameter force fields for sets A, B, C and Z, starting with the fields for sets B (Table 3.5) and Z (Table 3.3). The set B molecules, i.e. the Di, Tri and Tetra Fluoro Benzenes represent the mid-section of the set Z molecules. Therefore, it is to be expected that the changes in the force fields on going from set Z to set B would be slight but, since the number and range of frequencies to which the set B field is fitted are smaller, the variances in the force constants for this field should also be smaller than the variances in the force constants for set Z.

Discussion

The off-diagonal force constants in the two fields are similar but the variances or dispersions for the set B force constants are slightly larger than those for the set Z field. The B force constants are similar in the two fields with again slightly larger dispersions for the set B force constants. The two sets of C force constants are slightly different, C_1 in the set B field is greater than C_1 in the set Z field and C_3 in the set B field is less than C_3 in the set Z field, whereas reducing the number of frequencies might be expected to have the opposite effect. The most significant differences in the diagonal force constants, however, occur in the A force constants; each force constant in set B being about 12% higher than the equivalent force constant in set Z. Also the dispersions of these force constants in set B are twice as large as those in set Z.

This behaviour is not observed in the field midway between these two fields, i.e. the 23(9) field obtained for set B from the 23(23) field for set Z varying only the diagonal force constants (see Table 3.12). For this field the A and B force constants, as expected, have hardly changed from the values for set Z. The C force constants have risen slightly, C_1 is now greater than C_2, though this is not too significant when the errors in the force constants are taken into account. Going from this 23(9) field to the 23(23) field for set B, the B force constants hardly change, the C force constants change slightly and the A force constants change significantly. Of course, it must be remembered that in going from the 23(9) to the

23(23) field the off-diagonal force constants are being allowed to vary as well as the diagonal force constants. Therefore, changes in the A force constants will be associated with changes in the off-diagonals. It is interesting to note that the WSQER is reduced from 1.8×10^{-3} for the 23(9) field to 1.1×10^{-3} for the 23(23) field, a not particularly great reduction in error considering the changes in the force constants.

This 23(23) field does appear to be the correct 23 parameter force field for set B, since taking as the initial field a previously calculated 18 parameter force field for set B (calculated before all the frequency assignments were made) the 23 parameter force field given in Table 3.5 is still the final field.

The explanation of these anomalous force constant changes appears to be due to a near linear dependance in the matrix C for this calculation. The ratio $|C| / \prod_i c_{i,i}$ is 3.16×10^{-11} for the field for set B compared with 3.96×10^{-9} for the field for set Z. Aldous and Mills (96), in their studies on the Methyl Halides, considered that the equations were ill conditioned if the ratio was of the order of 10^{-3}. However, one of the molecules they studied was Methyl Fluoride (72) for which $|C|$ was 2.76×10^{-7} and $\prod_i c_{i,i}$ was 4.68×10^{-5}. Both the ratios given above for the calculations considered here are much smaller than 10^{-3} but this ratio is always the ratio of two large numbers. For the field for set B, $|C|$ is 7.71×10^{34} and for the force field for set Z, $|C|$ is 8.60×10^{41}. In neither case is C approaching singularity. However, the ratio $|C| / \prod_i c_{i,i}$ for set B is 100 times smaller than that for set Z.

The correlation coefficients for the A force constants in the field for set Z are,

	A_1	A_2	A_3
A_1	1.0	0.9355	0.8947
A_2		1.0	0.9635
A_3			1.0

and those for set B are,

	A_1	A_2	A_3
A_1	1.0	0.9694	0.9544
A_2		1.0	0.9901
A_3			1.0

The correlation coefficients in the field for set Z are large and those in the field for set B approach unity. The changes in the A force constants on going from set Z to set B are

	Set Z	Set B	B - Z
A_1	.2664	.3001	.0337
A_2	.2361	.2719	.0358
A_3	.2128	.2487	.0359

The set B force constants all rise by nearly the same amount and it is this near linear dependancy which is causing the anomalous changes in the A force constants A_1, A_2, A_3.

Conclusion

Due to a near linear dependance in the A force constants the 23 parameter force field for set B is unacceptable. The reason for this near linear dependance would appear to be that on going from set Z to set B the number of frequencies to which the fields are fitted is reduced and for set B the number of frequencies in the perturbation calculation is too small to put enough controls on the force field.

Discussion of the 23 Parameter Force Fields for Sets A, B and C

Introduction

If the 23 parameter force field for set B is unacceptable, then any field calculated from it, when not all force constants are allowed to vary (i.e. the 23 parameter force fields for set A (Table 3.4) and set C (Table 3.6)), must also be unacceptable. However, it is still of interest to compare the three 23 parameter force fields for sets A, B and C (A comparison of the three fields is given in Table 3.8).

Discussion

For the off-diagonal force constants the yy meta and para interactions are all negative, as they are in the 23 parameter force field for set Z, and there are no great changes on going through the series from set A to set C. Of course, it must be remembered that some of these force constants are not allowed to vary on going from set B to sets A and C.

Examining the diagonal force constants for each set individually, it is seen that there is a decrease in value going through the two series A_1, A_2, A_3 and B_1, B_2, B_3 and an increase in value going through the series C_1, C_2, C_3 (except for C_1 to C_2 in set A). This is shown graphically in Figures 3.5 and 3.6. The vertical lines represent the actual errors in the force constants (Figure 3.6 shows that the anomalous values of C_1 and C_2 in set A are not significant when considering the errors in the two force constants and the small difference between them). However, there is no clear pattern of change in value for the individual force constants when going from set A, through set B, to set C. This random behaviour

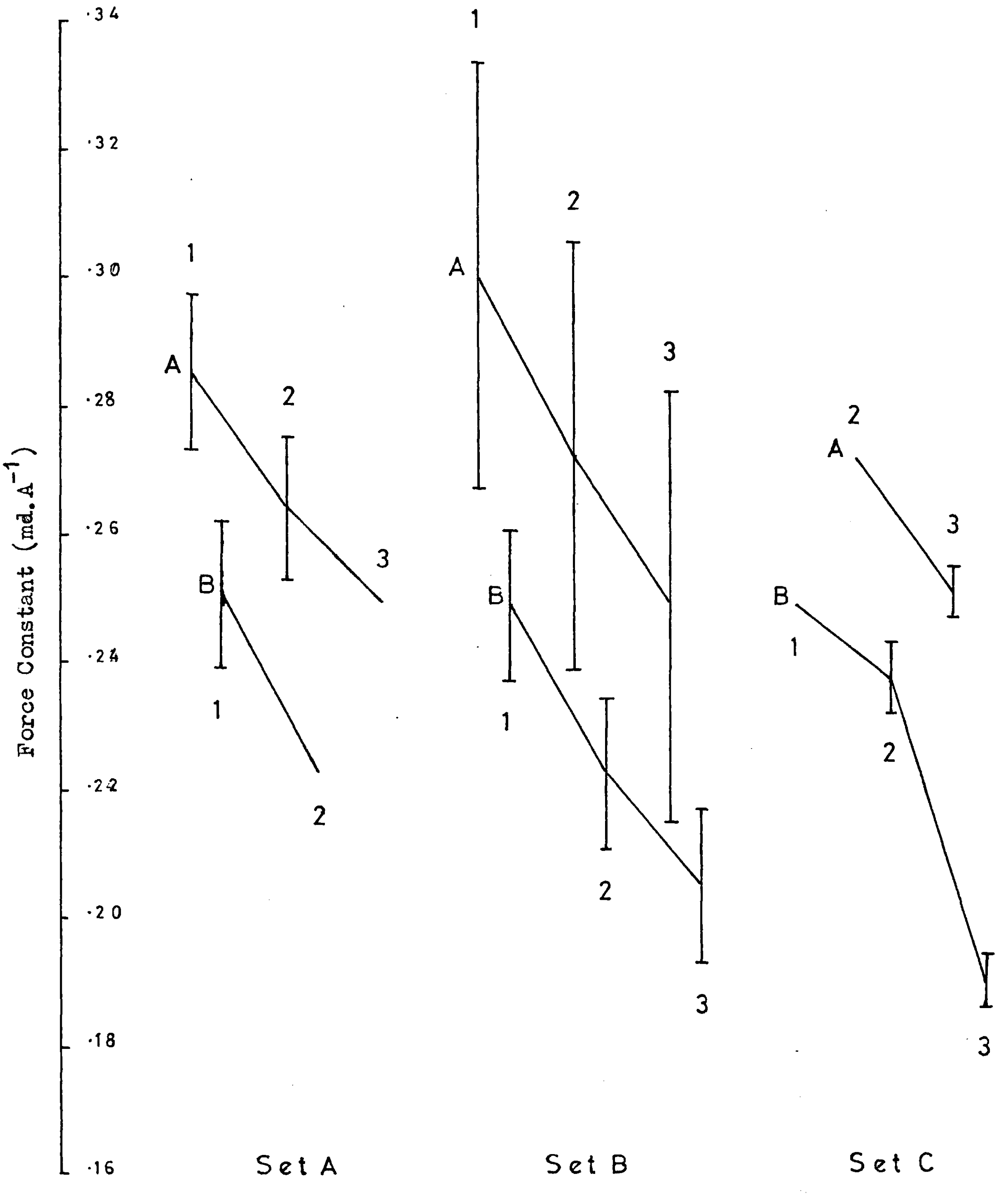


Figure 3.5 Diagonal Force Constants for the 23 Parameter Force Fields for sets A, B and C (Out-of-Plane Angle Bends)

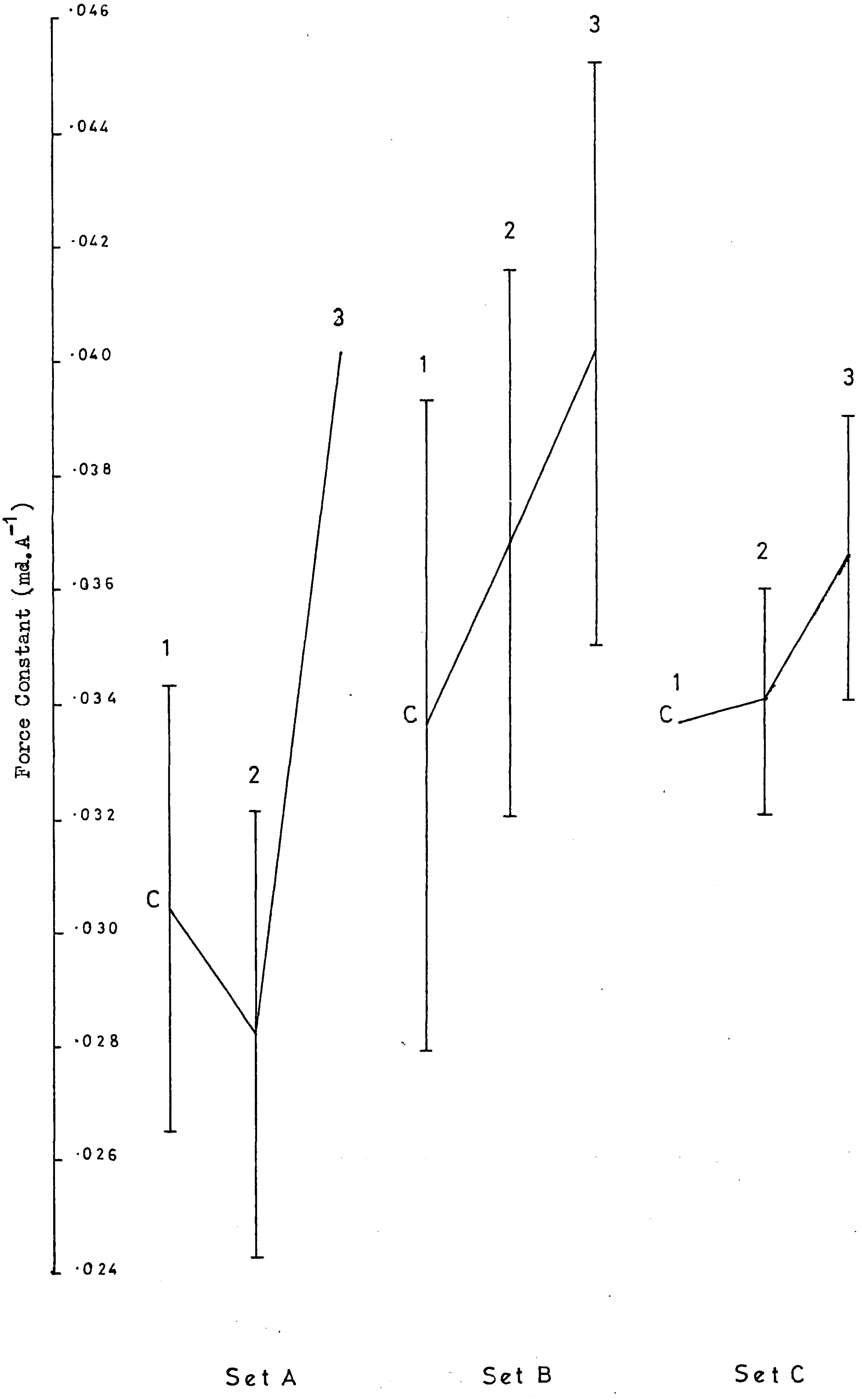


Figure 3.6 Diagonal Force Constants for the 23 Parameter Force Fields for sets A, B and C (Special Torsions)

is also seen in the force fields for sets A, B and C calculated using the off-diagonal force constants for set B (see Table 3,11).

Conclusions

As pointed out in the Introduction, the 23 Parameter Force Fields for sets A and C must be unacceptable since they are calculated from the field for set B. This is confirmed by a comparison of these force fields with the 23 parameter force field for set Z and by the unpredictability of the changes in the force constants on going from set A, through set B, to set C.

Discussion of the 18 Parameter Force Fields for sets A, B and C

Introduction

Returning to the 18 parameter force fields, it has already been decided that the field calculated for set Z is unacceptable and it is, therefore, doubtful if the fields for sets A, B and C, which are calculated from the field for set Z, will be acceptable. However, since the field for set B is calculated from that for set Z, allowing for all force constants to vary, this cannot be decided until the force constants are known. Even if they are unacceptable, it is still of interest to examine briefly and compare the various 18 parameter force fields which might be expected to be similar.

Discussion

Since the only field so far accepted is the 23 parameter force field for set Z, any other acceptable field must agree with it. Comparing this field with the 18 parameter field for set B (Table 3.5), it is immediately obvious that they are not at all alike. Therefore, the 18 parameter force field for set B is unacceptable and, since the fields for set A (Table 3.4) and for set C (Table 3.6) are calculated from it without allowing all force constants to vary, they too must be unacceptable.

In the fields for sets A, B and C (see Table 3.7) the similarity of the off-diagonals is not retained; in fact, many change sign on going from one set to another. For the diagonal force constants there is a steady decrease in A and B on going from set A to set C and a steady increase in C_1 and C_3 (This is shown graphically in Figure 3.7). These changes, especially for the C force constants, are large.

Also calculated are diagonal force constants for sets A, B and C using the off-diagonals from: the 18 parameter force field for set B (Table 3.9); and the 18 parameter force field for set Z (Table 3.10). In the case of these fields, the diagonal force constants hardly change, showing that the large changes noted above occur only in conjunction with the somewhat random changes in the off-diagonal force constants. The small changes that do occur in the A and B force constants conform to the same decreasing pattern and, comparing the 18 parameter force fields for set Z with those calculated for sets A, B and C using the off-diagonal force constants for set Z (see Table 3.10), the diagonal force constants for set Z are slightly biased towards those for set A, which probably reflects the preponderance of data for the molecules in this set.

Conclusions

By comparison with the 23 parameter force field for set Z, it is seen that the 18 parameter force fields for sets A, B and C are unacceptable.

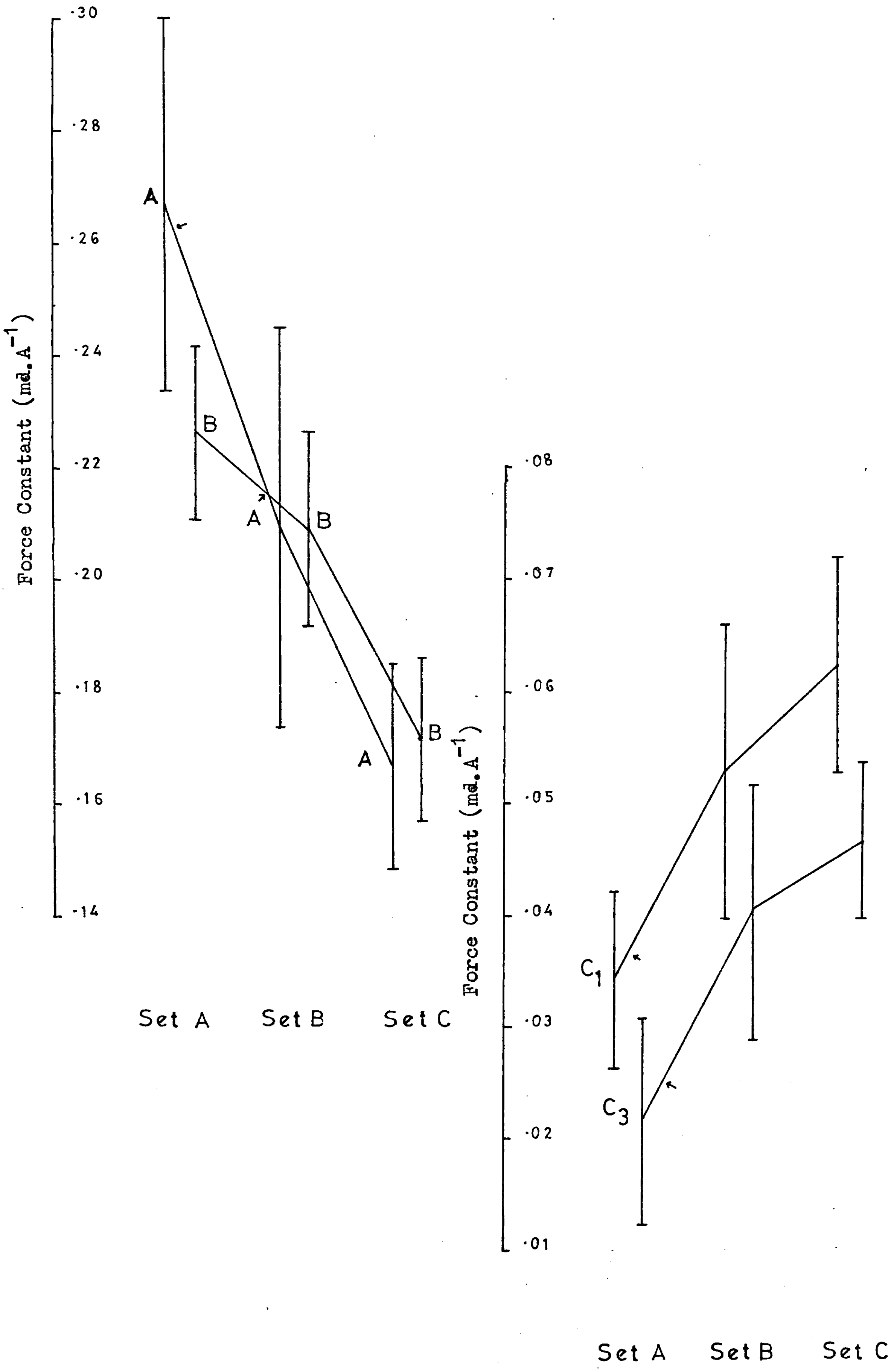


Figure 3.7 Diagonal Force Constants for the 18 Parameter Force Fields for sets A, B and C

Discussion of the Force Fields for Sets A, B and C

Finally, comparing the 18 and 23 parameter force fields (Tables 3.4 to 3.6), it is seen that for sets B and C in each case the two fields are completely unalike, showing how far apart they have become although they can all be traced back to the same field. In the case of the two fields for set A they are similar except for the C force constants. Also the force constants agree where applicable with Radcliffe and Steele's 15 parameter force field except, again, for the C force constant.

General Conclusion

The conclusions from these acceptability tests are that the 23 parameter force field for set Z is the only field capable of expressing the Potential Energy function for the out-of-plane vibrations of the Fluorine substituted Benzenes. This conclusion agrees with that reached from the study of which fields give the best fit to the observed vibrational frequencies.

The failure of the 18 parameter force field for set Z is due to the non-allowance of force field changes on going through the molecules from Benzene to Hexafluoro Benzene.

The failure of the 23 parameter force fields for sets A, B and C is due to the fact that the number of frequencies to which these fields are fitted is too small to put adequate controls on the force field.

It might appear that the 18 parameter force fields for sets A, B and C would be acceptable since they avoid these two pitfalls. By dividing the molecules into three sets, allowances are made for changes in the force fields and by not allowing for substituent dependance the number of force constants is reduced. However, a comparison of the 23 parameter force field for set Z with the 18 parameter force fields for sets A, B and C showed that these fields too are unacceptable.

Comparison with Scherer's Force Field for the Chloro Benzenes.

Introduction

As previously mentioned, one of the reasons why the 23 parameter force field for set Z is accepted, is its similarity to Scherer's 23 parameter force field for the Chloro Benzenes (115). This similarity is now examined.

Discussion

Before the two fields can be compared, Scherer's field has to be expressed in terms of y and ϕ internal coordinates, using the conversion factors given in Section 3.3. The conversion , in fact, can only be made exactly for one molecule at a time and these factors are therefore only an approximation. To compare the two fields with the greatest accuracy it would be necessary to repeat the calculations for the Chloro Benzenes using y and ϕ internal coordinates. However, the Chloro Benzene field calculated using the expressions given in Section 3.3 is adequate for the comparison discussed here. A final point before the comparison can be made concerns the units of the force constants. When When comparing force constants for molecules with different substituents it is necessary to remove the scaling factors introduced to give all internal coordinates the units of length. The force constants are now expressed in millidynesx Angstroms.

Comparison of 23 Parameter Force Fields for the Chloro Benzenes and the Fluoro Benzenes

FORCE FIELD	CHLORO BENZENES y,T	 y,ϕ	 y,ϕ	FLUORO BENZENES y,ϕ
FORCE CONSTANT				
A_1	0.381	0.265	0.311	0.313
A_2	.365	.249	.293	.277
A_3	.352	.236	.277	.250
B_1	.200	.150	.434	.419
B_2	.187	.137	.396	.380
B_3	.175	.125	.361	.325
a^o	-.061	.081	.095	.013
a^m	.003	-.014	-.016	-.017
a^p	-.012	-.012	-.014	-.013
ab^o	-.049	-.002	-.004	.018
ab^m	.003	-.011	-.020	-.029
ab^p	-.011	-.011	-.020	-.019
b^o	-.023	.015	.045	.021
b^m	.003	-.010	-.029	-.022
b^p	-.006	-.006	-.017	-.018
C_1	.133	.033	.064	.069
C_2	.138	.035	.068	.070
C_3	.178	.045	.088	.070
c^o	-.033	-.008	-.016	-.015
ac^o	-.100	.011	.017	.017
ac^m	.023	-.0004	-.0006	.0001
bc^o	-.077	.012	.029	.000
bc^m	0.022	0.003	0.007	0.011
	md.A^{-1}	md.A^{-1}	md.A^{+1}	md.A^{+1}

Table 3.16

The two force fields are given in Table 3.16.

The agreement between the two fields is remarkably good. For the off-diagonal force constants the worst discrepancies occur in the three yy^o interactions, a^o, ab^o, b^o. This could be a consequence of the approximations used in calculating the field for the Chloro Benzenes. For the diagonal force constants, A_1 and C_1, the two force constants which involve only Hydrogen substituents, are almost identical in the two fields. There is a steady decrease going through the series A_1, A_2, A_3 and B_1, B_2, B_3 in both fields, the rate of decrease being greater in both series for the Fluoro Benzenes field. For the C force constants, there is a small increase on going through the series C_1, C_2, C_3 in both fields, in this case the rate is slightly greater for the Chloro Benzenes field.

Conclusions

The similarity of these two fields is interesting in that it suggests that the frequency differences between a Chloro Benzene molecule and the equivalent Fluoro Benzene are, to a large extent, due to mass rather than electronic effects. Considering just the diagonal y force constants, the opinion of Radcliffe and Steele (24) that naive rehybridization arguements would suggest that the force required for unit angular displacement out of the plane of the ring are independant of substituent, is supported for the Chlorine and Fluorine force constants but not for the Hydrogen force constants.

Discussion of the Diagonal Force Constants

Introduction

The decrease in the A and B force constants in going through the series from 1 to 3 having been noted, the question that now arises is why do these changes occur. The increase in the C force constants is slight and much smaller than the errors in the force constants (see Figure 3.8) and, therefore, is not considered further. The force constants for the Fluoro Benzenes are shown in Figure 3.8. The vertical lines indicate the actual errors in the force constants and the two arrows the positions of the A_1 and C_1 force constants for Benzene. The C force constants are plotted on two different scales, one ten times the other.

Discussion

Onee of the factors which might be expected to influence the results would be interference between neighbouring substituents due to overlapping Van der Wadl's radii. Using values given by Pauling (120), this possibility is investigated for both the Chloro and the Fluoro Benzenes, using Figure 3.9. It is seen that: Fluorine, Fluorine; Fluorine, Hydrogen; and Hydrogen, Hydrogen neighbours have no overlap or overlap only slightly. This would suggest that $A_1 \sim A_2 \sim A_3$ and $B_1 \sim B_2 \sim B_3$ for the Fluoro Benzenes. For the Chloro Benzenes; Chlorine, Chlorine and Chlorine, Hydrogen neighbours overlap considerably. This would suggest that $A_1 < A_2 < A_3$ and $B_1 < B_2 < B_3$. The fact that all these predicted trends are contrary to the actual ones and also that the considerable degree of overlap in the Chloro Benzenes is contrary to their known planarity (115) invalidates the hypothesis that overlapping Van der Wadl's

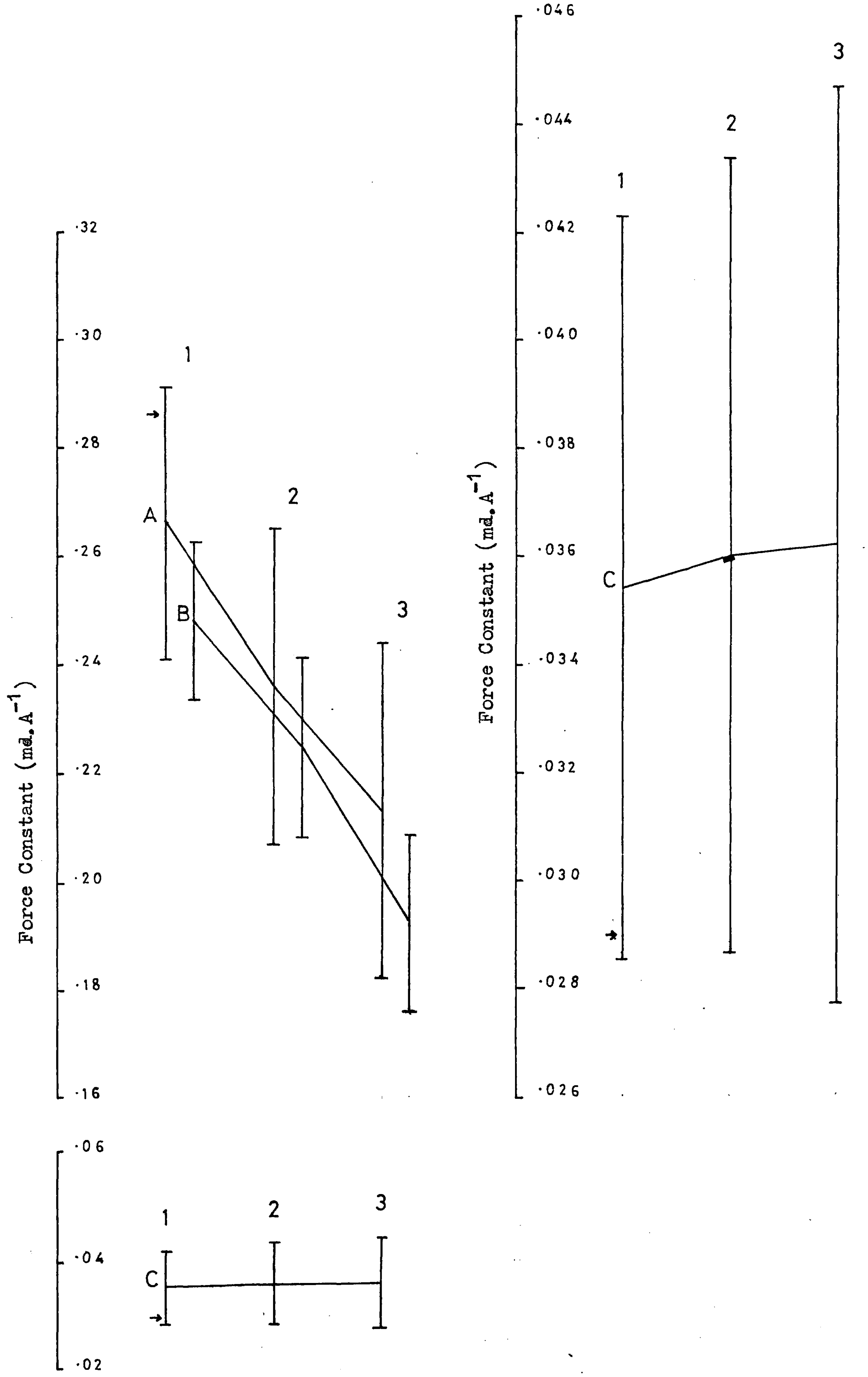
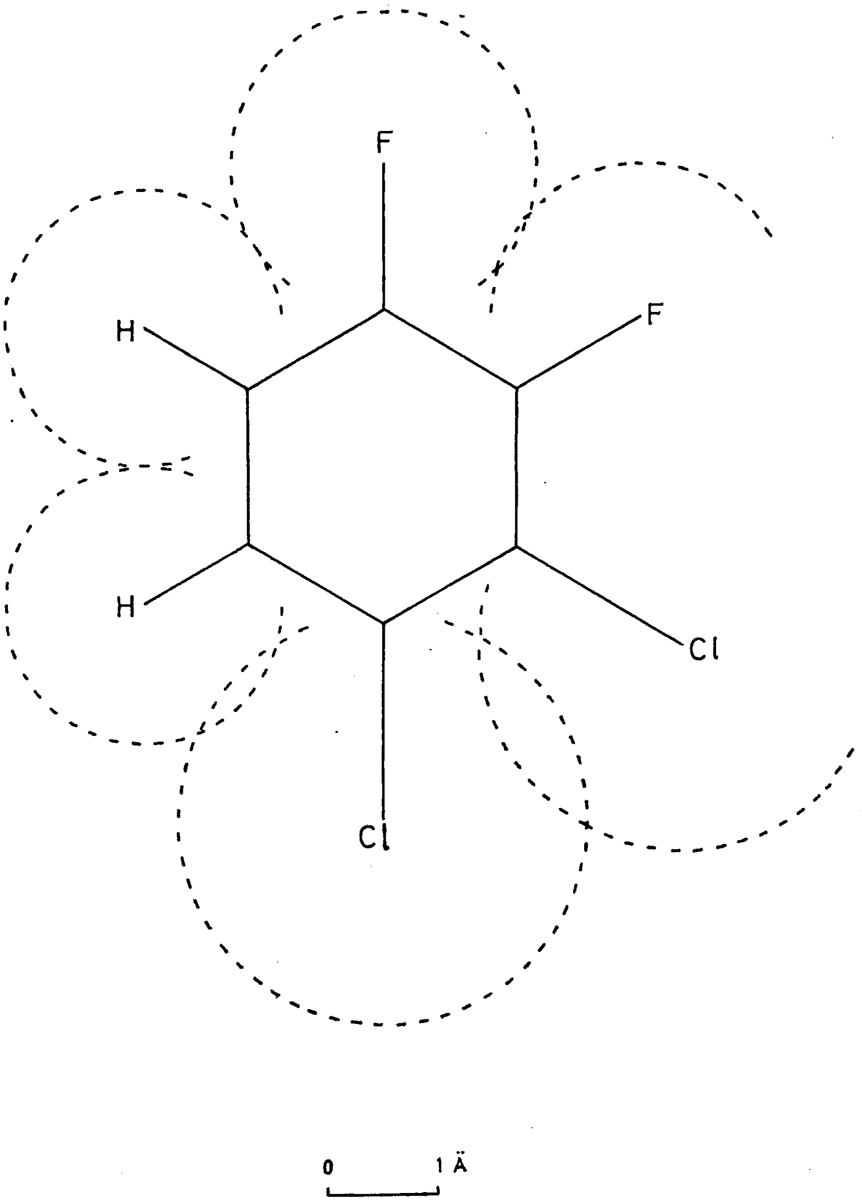


Figure 3.8 Diagonal Force Constants for the 23 Parameter Force Field for set Z



Scale: 2 A to 3 cm

Van der Waál's Radii	
H	1.20 A
F	1.35 A
Cl	1.80 A

Bond Lengths	
C-C	1.395 A
C-H	1.084 A
C-F	1.300 A
C-Cl	1.700 A

Figure 3.9 Van der Waál's Radii

radii are influencing the results. The reason is that Van der Wall's radii strictly apply only along bond axes.

Another factor which might be expected to influence the results would be electrostatic attraction and repulsion between the atoms. If it is assumed that the bond moment of a C-H bond is 0.3D, with Hydrogen at the positive end of the dipole, and the bond moment of a C-F bond is 0.65D, with Fluorine at the negative end of the dipole (see Chapter Seven), the change in energy on moving a Hydrogen atom 1A out of the molecular plane, when its neighbouring substituents are Hydrogen atoms (i.e. A_1 force constant), is $+2.16x10^{-15}g.cm^2.sec^{-2}$ (increase in energy) whilst the change in energy on moving a Hydrogen atom 1A out of the molecular plane, when its neighbouring substituents are one Hydrogen and one Fluorine atom (i.e. A_2 force constant), is $-3.42X10^{-15}g.cm^2.sec^{-2}$ (decrease in energy). Therefore,

$$dV(A_1) - dV(A_2) = +5.58x10^{-15}g.cm^2.sec^{-2}$$

when considering changes in Potential Energy due to electrostatic forces.

The actual change in energy for a change in one internal coordinate is $V = \frac{1}{2}f\ (dR)^2$, so for a 1A movement of the substituent out of the molecular plane

$$dV\ (A_1) - dV(A_2) = 150x10^{-15}g.cm^2.sec^{-2}$$

Therefore, the energy changes due to electrostatic forces can only explain a small fraction of the actual energy differences between the A_1 and A_2 force constants. This applies also to all other pairs of similar force constants.

The major cause of the differences between the force constants is probably electron attraction and repulsion. When a substituent moves out of the plane of the Benzene ring, some sp^3 character is introduced into the electron orbitals of the Carbon atom to which the substituent is attached. Since Fluorine is highly electronegative (i.e. it attracts electrons to itself away from the ring), the energy changes due to rehybridization would be expected to be smaller, if the moving substituent has Fluorine as its neighbours tather than Hydrogen. Therefore, the predicted trends are $A_1 > A_2 > A_3$ and $B_1 > B_2 > B_3$, the same as those observed. Also, since Chlorine is not so highly elctronegative as Fluorine, the trends would be predicted to be the same, but not so steep, as with Fluorine and, again, this is what is observed.

Conclusion

Therefore, on a qualitative basis, electron flow can explain the differences between the force constants. To give a quantitative explanation would probably require calculations of a quantum-mechanical type.

CHAPTER FOUR The Computer Programs

In Chapter One the theory of normal coordinate analysis, the primary aim of which was the accurate calculation of force constants, was outlined. In Chapter Three it was applied to the out-of-plane vibrations of the Fluoro Benzenes. In this chapter it is not intended to describe in great detail the computer programs used in the application of this theory but to outline briefly the general techniques.

SECTION 4.1 Programs GZEVAL 1-4

These four programs are basically the same in that they use identical input data and make identical calculations. For a given molecule the input data consists of:-

the molecular geometry,

the coding used to construct the B matrix (i.e. the type of internal coordinate and the atoms involved),

the masses of the atoms,

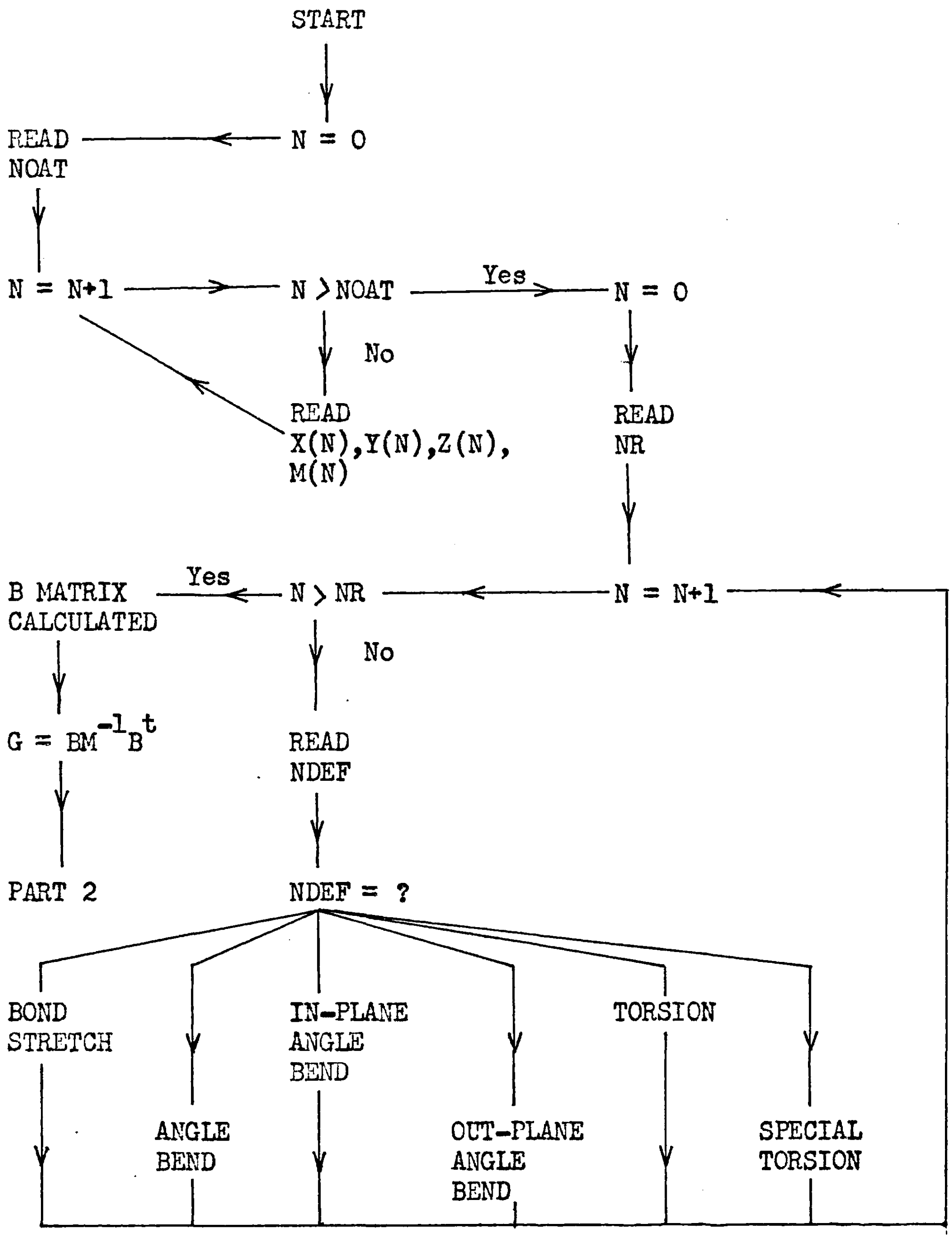
the force field,

the unsymmeterized Z matrices,

the U matrices - one for each symmetry block,

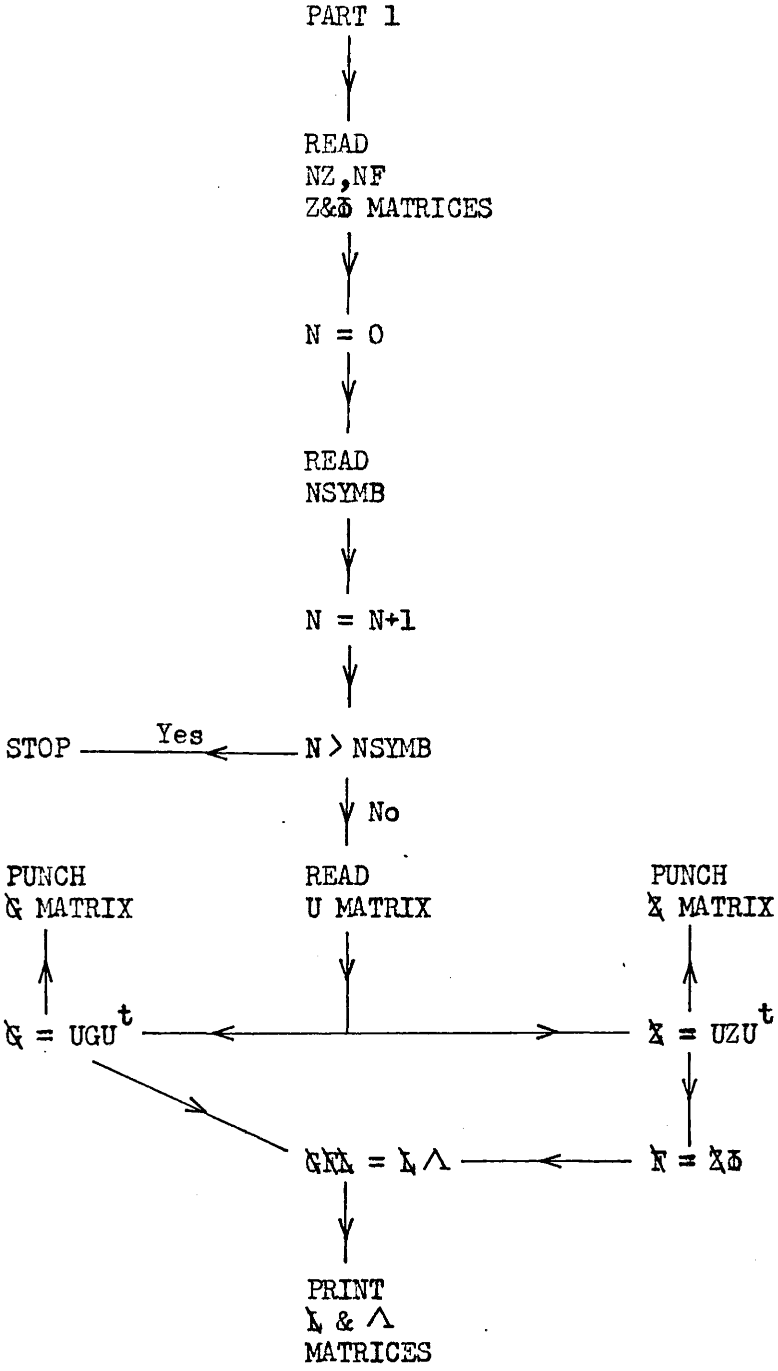
plus the dimensions of the various matrices where required.

The end points of the calculation are the eigen vectors and eigen values for this molecule but these are not necessarily the required data. The mode of operation is outlined briefly in Figure 4.1.



NOAT = Number of Atoms
NR = Number of Internal Coordinates
NDEF = Number Code for Deformation

Figure 4.1. Flow Diagram for GZEVAL 1-4.



NZ = Number of Z Matrix Elements
NF = Number of Force Constants
NSYMB = Number of Symmetry Blocks

Figure 4.1 (continued).

The programs differ in the type and quantity of output data and this depends on the purpose of the calculation. If it forms the first part of a series of calculations on force fields, then the important output data are the symmetrized G and Z matrices, punched on cards, ready for input to the programs GZDATA 1-3 and MLTPRB 1. If the force field is known and no further calculations are envisaged then the important output data are the eigen vectors and eigen values (expressed as frequencies). Other output can consist of a print-out of the B, $\mathfrak{G}$ and $\mathfrak{Z}$ matrices and the input data to check on its accuracy.

The final point in this section concerns the calculation of the eigen vectors and eigen values of the matrix $\mathfrak{G}\mathfrak{F}$. It can be diagonalized as it is but since it is an unsymmetrical matrix the following method is preferable.

First the $\mathfrak{G}$ matrix is diagonalized,

$$\mathfrak{G}D = D\,\Gamma$$

where D is the eigen vector matrix

and Γ is the eigen value matrix for $\mathfrak{G}$.

Since $\quad DD^t = E$

$$\mathfrak{G} = D\,D^t$$

and if $\quad \overline{D} = D^{\frac{1}{2}}$

$$\mathfrak{G} = \overline{DD}^t \qquad 1$$

let $\quad A = \overline{D}^t\mathfrak{F}D \qquad 2$

and A can be diagonalized so that

$$AY = Y\Lambda' \qquad 3$$

where Y is the eigen vector matrix

and Λ' the eigen value matrix for A.

Premultiplying equation 3 by $\overline{\mathbf{D}}$ and substituting for A,

$$\overline{DD}^{t}\mathbf{F}\overline{D}Y = \overline{D}Y\Lambda'$$

therefore $\mathbf{G}\mathbf{F}\overline{D}Y = \overline{D}Y\Lambda'$

and the eigen vector matrix for GF is

$$\mathbf{L} = \overline{D}Y$$

and the eigen value matrix is

$$\Lambda = \Lambda'$$

The advantage of this method is that the two matrices to be diagonalized $\mathbf{G}$ and A are symmetrical and time is therefore saved in the computing, since the time to diagonalize a symmetric matrix is proportional to n^2 and for an unsymmetric matrix it is proportional to n^3, where the dimensions of the matrix are n by n. The calculation of the eigen values and eigen vectors is done in a standard subroutine using Jacobi's method.

<u>SECTION 4.2</u> Program GZEVAL 9

This program uses the same input data as the other GZEVAL programs but calculates the cartesian displacements of the atoms in a given normal coordinate. Using the relationships from Chapter One $R = B_q$, $S = UR$ and $S = \mathbf{L}Q$, it follows that

$$Q = \mathbf{L}^{-1}UBq$$

and the matrix $\mathbf{L}^{-1}UB$ can be calculated for each symmetry block in turn, provided that $\mathbf{L}$ can be inverted. This means that the set of symmetry coordinates must have no redundancies. However redundancies frequently do occur and these can be difficult to detect and remove. Therefore the general method proposed by Gussoni and Zerbi (13) is used to remove the redundant symmetry coordinates.

The G matrix is diagonalized

$$\mathbf{G}D = D\Gamma$$

and if there are redundant symmetry coordinates some of the elements of Γ are zero. Therefore if $\Gamma_i = 0$, then the ith column of D, D_i can be removed. D' is the matrix D with the ith column removed and Γ' is the eigen value matrix, then

$$\mathbf{G}D' = D'\Gamma'$$

This equation is still valid since only zero values have been removed but D' is no longer square and cannot be an eigen vector matrix. However since

$$D'D'^t = \mathbf{E}$$

$$D'^t\mathbf{G}D' = \Gamma'$$

The matrix D'^t is considered to be a new symmetry matrix so that the new non-redundant symmetry coordinates S' are related to the old S via the transformation

$$S' = D'^{t}S \qquad 4$$

and $$S' = D'^{t}UR \qquad 5$$

Therefore $$\mathbf{G}' = D'^{t}\mathbf{G}D' = \Gamma'$$

and D'^{t} diagonalizes $\mathbf{G}$ so that its eigen vector matrix is E, the identity matrix, and its eigen value matrix is identical to itself.

In the new symmetry coordinates the $\mathbf{F}$ matrix is

$$\mathbf{F}' = D'^{t}\mathbf{F}D'$$

and therefore the matrix A is

$$A' = \Gamma'^{\frac{1}{2}}\,\mathbf{F}'\,\Gamma'^{\frac{1}{2}} \qquad 6$$

where $\Gamma'^{\frac{1}{2}}$ is equivalent to the matrix $\bar{D}$ introduced in equation 2. Substituting for $\mathbf{F}'$ in equation 6

$$A' = \Gamma'^{\frac{1}{2}}\,D'^{t}FD'\,\Gamma'^{\frac{1}{2}}$$

and A' is equivalent to the matrix A defined by equation 2 except that the rows and columns corresponding to redundant coordinates have been removed.

Therefore $$A'Y' = Y'\Lambda$$

and $$\mathbf{L}' = \Gamma'^{\frac{1}{2}}Y' \qquad 7$$

All the redundant symmetry coordinates have been removed therefore $\mathbf{L}'$ can be inverted, so that from equation 7 it follows that

$$(\mathbf{L}')^{-1} = Y'^{t}(\Gamma')^{-\frac{1}{2}}$$
$$= \mathbf{L}'^{t}(\Gamma')^{-1}$$

since $\quad Y'Y'^{t} = E$

The normal coordinates Q are related to the symmetry coordinates S' by the transformation

$$S' = \mathbf{L}'Q$$

Therefore $\quad Q = (\mathbf{L}')^{-1}\,D'^{t}UBq \qquad 8$

and all these quantities can be calculated.

The reverse transformation can be shown to be

$$q = M^{-1}B^{t}U^{t}D'(\Gamma')^{-1}\mathbf{L}'Q \qquad 9$$

and if $\quad q = T_1Q \quad$ and $\quad Q = T_2q$

it follows that

$$T_1 = M^{-1}T_2^{\,t}$$

In the program GZEVAL 9 T_2 is the matrix calculated, which can then be converted to T_1. T_1 is important in connection with the theory of Gribov (see Section 5.7).

SECTION 4.3 Programs GZDATA 1 and 2

The sole purpose of GZDATA 1 is to check the data prior to input to the perturbation program. This input data consists of:-

the force field matrix Φ and the weight matrix P,

the number of molecules,

then for each molecule in turn

the number of symmetry blocks,

the observed frequency matrix Λ^{obs} and the weight matrix W,

then for each symmetry block in turn,

the symmetrized G and Z matrices,

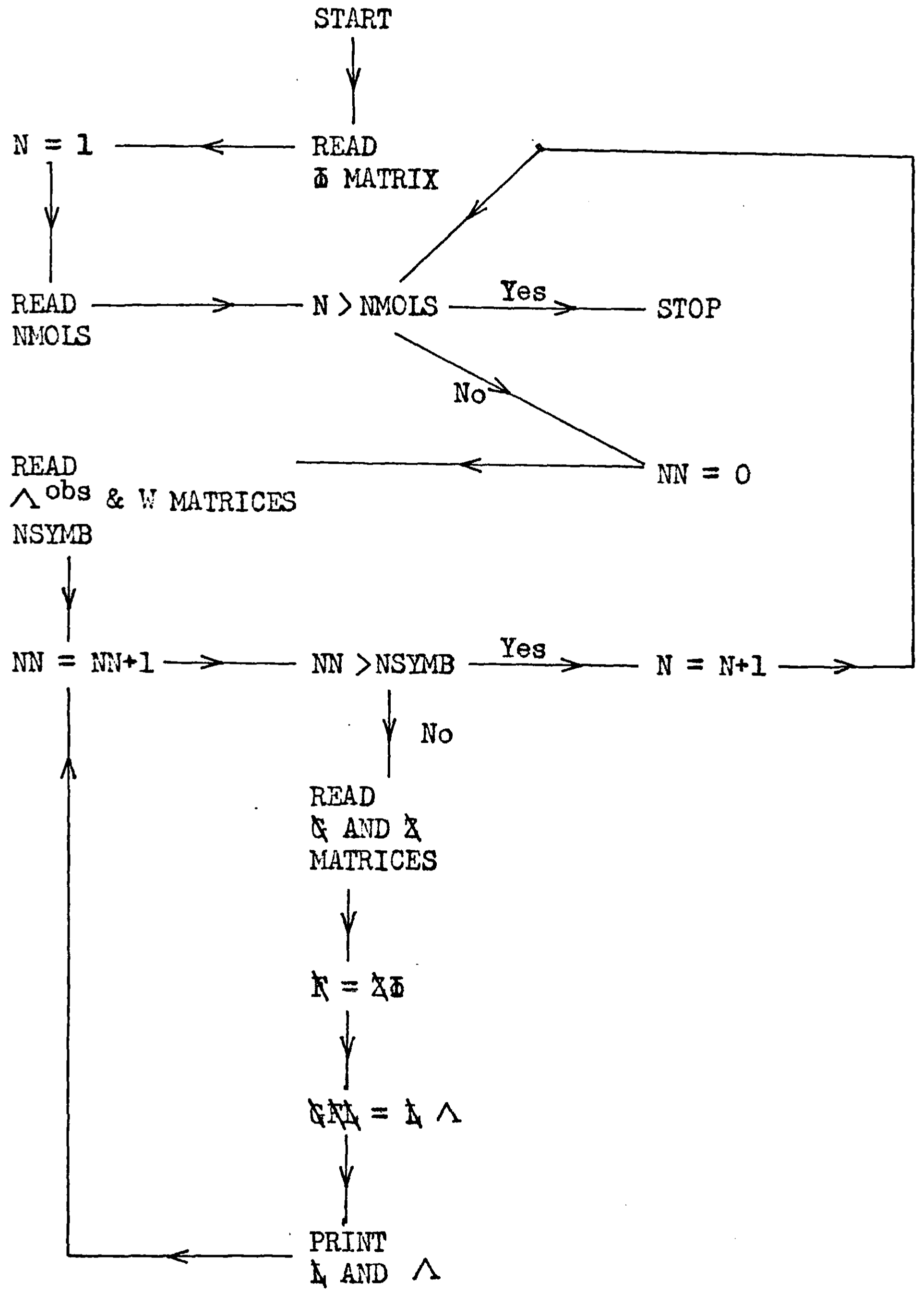
plus the dimensions of the matrices and various individual pieces of data where required.

The mode of operation is outlined in Figure 4.2.

Program GZDATA 2 uses the same input data as GZDATA 1 and makes the same calculations. It also calculates the weighted square-error sum and the weighted average frequency error, using equations 8 and 9, Section 3.4, both for the molecules individually and all molecules using the same force field.

SECTION 4.4 Program GZDATA 3

This program uses the same input data as GZDATA 1 and 2. It does not proceed the perturbation program but follows the calculation of the final force field. It calculates the variances (or standard deviations) and the correlation coefficients of the force constants; the error and the standard deviation of each frequency; the weighted square-error sum, the weighted average frequency error and the weighted average standard deviation, both for the individual molecules and for all molecules which use the same force field. Its mode of operation is similar to that for GZDATA 1 and 2, shown in Figure 4.2, except that in



NMOLS = Number of Molecules

Figure 4.2 Flow Diagram for GZDATA 1 & 2 each symmetry block following the calculation of the eigen vectors and eigen values, the Jacobian for this block is also determined. The Jacobians for all the symmetry species of all the molecules then form a final master Jacobian, dimension n by m, which relates all the frequencies to the force constants. (n is the total number of frequencies and m is the number of force constants). The matrix C is calculated

$$C = P^t J^t W J P$$

where P is the force constant weight matrix (see Section 1.9) and W is the diagonal matrix of frequency weighting factors.

The standard deviation of the ith calculated eigen value $\sigma(\lambda_i)$ is given by (96),

$$\sigma^2(\lambda_i) = \left| J P C^{-1} P^t J^t \right|_{i,i} \sigma_c^2$$

where $\sigma_c^2 = \sum_i w_i (\lambda_i^{obs} - \lambda_i^{calc})^2 / (n-m)$

as given in Section 3.1, equation 2.

To calculate the standard deviation in the ith frequency $\sigma(v_i)$, an upper and lower limit for this frequency are calculated,

v_i^{upper} from $\lambda_i + \sigma(\lambda_i)$,

v_i^{lower} from $\lambda_i - \sigma(\lambda_i)$.

Then $\sigma(v_i) = (v_i^{upper} - v_i^{lower})/2$

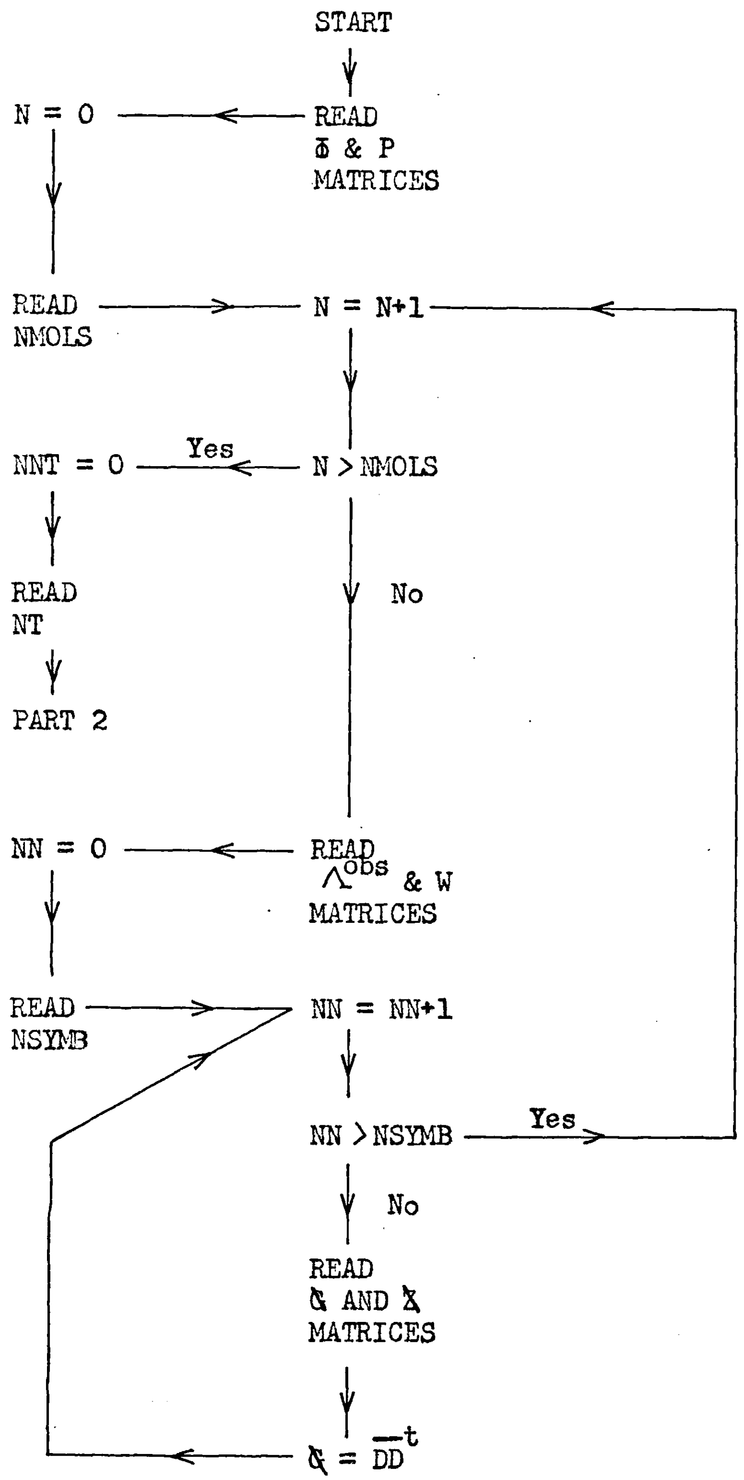
The error in the ith frequency is simply

$$dv_i = v_i^{calc} - v_i^{obs}$$

The weighted square-error sum, the weighted average frequency error and the weighted average standard deviation are calculated using equations 8,9 and 10 (Section 3.4) and the variances and correlation coefficients using equations 1 and 3 (Section 3.1).

SECTION 4.5 Program MLTPRB 1

This is the perturbation program which calculates the final force constants from the initial trial set. Its mode of operation is shown in Figures 4.3 and 4.4. In the first part (Fig.4.3) all the input data are collected (the data are identical to that for GXDATA 1 to 3) and stored, ready for use in the second part. To save time G is diagonalized in the first part (since G is independent of the force constants it does not change) and the matrix $\overline{D}$ is stored. In the second part (Fig.4.4) the new force constants are calculated. As shown this is repeated a number of times. Four is usually sufficient so that complete convergence is achieved.



NT = Number of Perturbation Cycles

Figure 4.3 Flow Diagram for MLTPRB 1 (Input Data).

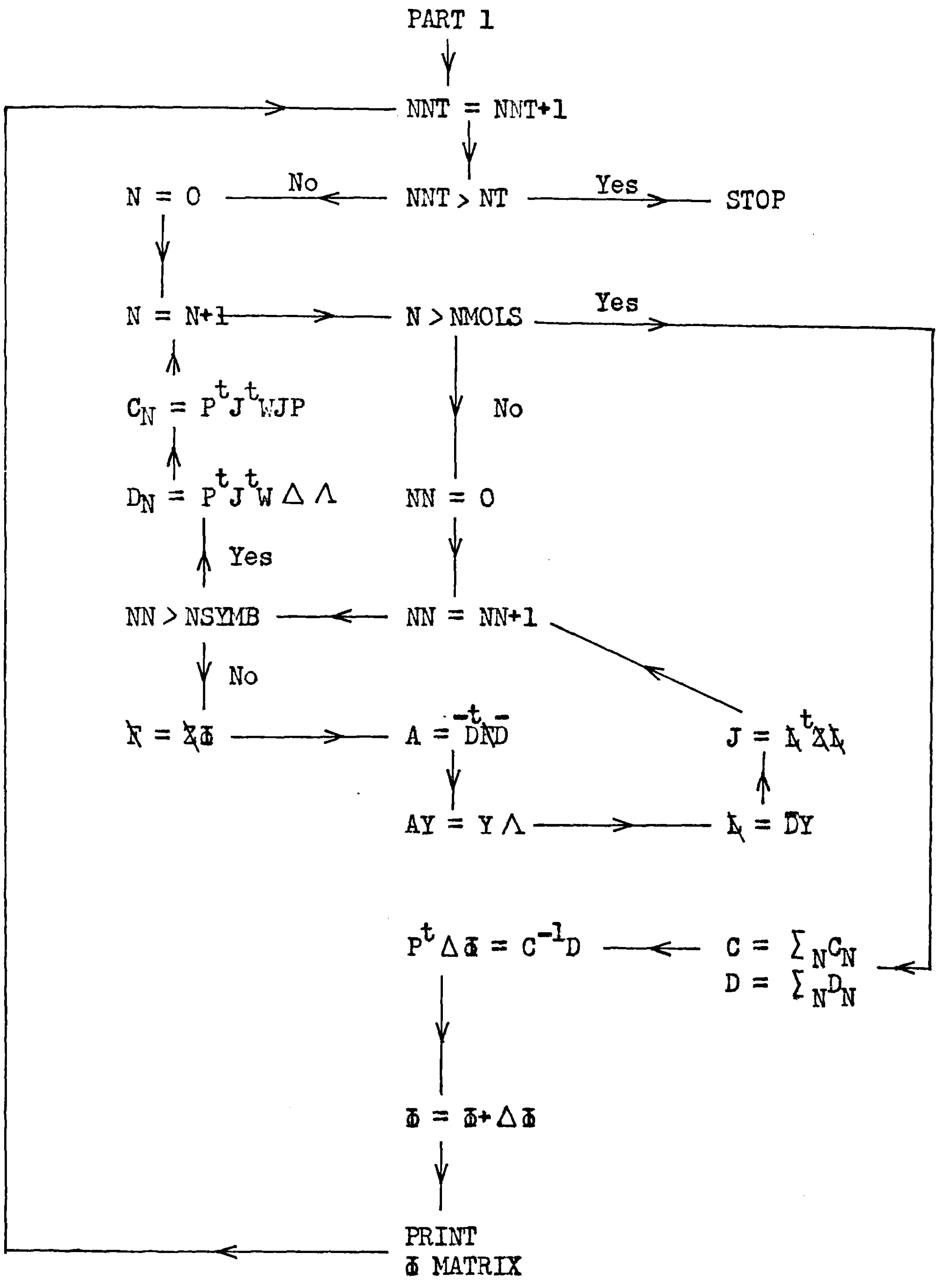


Figure 4.4 Flow Diagram for MLTPRB 1 (Force Field Calculation)

PART II

Absolute Infrared Intensities

INTRODUCTION

In the introduction to Part I the three characteristics of an infrared band were discussed. They were;

i. Frequency,

ii. Intensity,

iii. Shape.

In Part II the information that can be obtained from infrared band intensities is examined.

Infrared band intensities are closely related to movements of of electronic charges in a molecule during a vibration. Since this vibration involves, usually, all atoms in a given molecule, it is difficult to relate these changes to movements of individual bonds.

$\partial\mu/\partial Q$, the change in dipole moment with respect to the change in a normal coordinate for a particular band, is proportional to the square root of the absolute infrared intensity of that band so its value can be calculated, apart from the sign. Provided all $\partial\mu/\partial Q$ values for the infrared bands of a given symmetry species and the eigen vectors, which relate changes in the symmetry coordinates to changes in the normal coordinates, are known, then the $\partial\mu/\partial S$ values, the change in dipole moment with respect to the change in a symmetry coordinate, for that symmetry species can be calculated.

However, these values still relate to the molecule as a whole and what is usually required is an interpretation of $\partial\mu/\partial Q$ in terms of the dipole moments of bonds (bond moments) and the changes in dipole moments of bonds with respect to a deformation of that bond (bond moment derivatives).

The Bond Moment Hypothesis attempts to do this but the constraints it places on the understanding of changes in dipole moment are so rigid that the values calculated for bond moments and bond derivatives are not generally transferable between molecules and rarely even transferable between different symmetry species of the same molecule. However, the idea of transferability, or that similar molecules display similar properties, is a basic tenet of physical chemistry and it is, therefore, desirable to postulate a theory which allows for the tranfer of bond moments and bond moment derivatives between similar molecules.

Steele and Wheatley (156) examined the infrared active vibrations of Benzene and Hexafluoro Benzene and concluded that for the out-of-plane vibrations, besides the contribution to the change in the dipole due to reorientation of the bond moments as the atoms move, there is a contribution from the redistribution of electronic charge in the p_z orbitals of the carbon atoms forming the Benzene ring. This "rehybridization moment" is of the same magnitude and direction in both Benzene and Hexafluoro Benzene.

In Part II the infrared intensities of the out-of-plane vibrations of 1,4 difluoro Benzene and 1,3,5 trifluoro Benzene are measured and the results examined to see if they support the idea that a rehybridization moment acts during the out-of-plane vibrations of Benzene and molecules which are derivatives of Benzene. To analyse these measurements and interpret them in terms of bond parameters, use is made of the electro-optical theory of Gribov (136, 137, 138). This theory gives a general expression for $\partial\mu/\partial Q$

in terms of bond moments and bond moment derivatives, which Gribov refers to as electro-optical parameters, and can be applied to all molecules.

In Chapter Five the general methods involved in calculating infrared intensities and interpreting them in terms of bond parameters are outlined. In Chapter Six the measurement of the intensities of the b_{3u} vibrations of 1,4 difluoro Benzene and the a_2'' vibrations of 1,3,5 trifluoro Benzene is described. Finally, in Chapter Seven the results from these measurements are analysed.

CHAPTER FIVE General Theory of Absolute Infrared Intensities

SECTION 5.1 Induced Emission and Absorption of Radiation.

There are two processes involved in an induced vibrational transition which occurs when electromagnetic radiation interacts with an absorbing medium (Cottrell (121), p.20). They are

i. Induced Absorption in which a quantum of radiation of energy hw and frequency w is absorbed by a molecule M to give an excited molecule M*.

$$M + hw \rightarrow M^*$$

ii. Induced Emission in which a quantum of radiation of energy hw and frequency w interacts with an excited molecule M* to give another quantum of the same energy and frequency, while the molecule reverts to a lower energy state.

$$M^* + hw \rightarrow M + 2hw$$

To the approximation that all nuclear motions are harmonic the quantised vibrational energy of a molecule is

$$E_{vib} = \sum_i (n_i + \tfrac{1}{2})\, hw_i$$

where n_i is the quantum number associated with the ith vibrational frequency w_i and it can have values 0,1,2,3 ....

and the summation is over all vibrational modes.

The lowest energy level or ground level of a molecule is when all $n_i = 0$. The level for which all $n_i = 0$ except one, n_j which equals 1 is the jth fundamental level. The selection rule which has to be obeyed for a vibration, or transition between two energy levels, to occur is that $dn_i = \pm 1$. This means that not only are transitions allowed between states 0 and 1 (the fundamental vibration) but between any two energy states provided the rule is obeyed. Thus for diatomic molecules (only one fundamental vibration) transitions are allowed between states 1 and 2, 2 and 3, etc. and for polyatomic molecules from any state $n_1, n_2, \ldots n_i \ldots$ to state $n_1, n_2 \ldots n_{i+1} \ldots$ etc. These transitions give rise to hot bands which occur at the same frequency as the fundamental (in the harmonic oscillator approximation) and therefore cannot be separated from it (122). (It must be remembered that the very great majority of molecules are in the ground state and the fundamental vibration is always the dominant one).

If the number of molecules per unit volume in lower state '' (the quantum number of the state being n'') is N(n''), the number of transitions giving rise to induced absorption from lower state '' to upper state ' (the quantum number of this state being n') is

$$N^+ = \sum_{n''} N(n'') \, B_{n''n'} \, p(w) \qquad 1$$

where $B_{n''n'}p(w)$ gives the rate of transfer of molecules from state '' to state '. $B_{n''n'}$ is the Einstein coefficient of induced absorption and p(w) is the radiation density of frequency w, which is given by

$$w = (E' - E'')/h \qquad 2$$

where E' is the energy of the upper state and E'' is the energy of the lower state.

The summation in equation 1 is over all lower states (thus hot bands are included).

Similarly if the number of molecules per unit volume in state ' is N(n') the number of transitions giving rise to an induced emission from upper state ' to lower state '' is

$$N^- = \sum_{n'} N(n') \, B_{n'n''} \, p(w) \qquad 3$$

where $B_{n'n''}p(w)$ gives the rate of transfer of molecules from state ' to state ''. $B_{n'n''}$ is the Einstein coefficient of induced emission.

The summation in equation 3 is over all upper states.

Each induced transition (whether emission or absorption) is accompanied by an exchange of energy hw of the absorbing medium with the radiating field. Therefore the net change in energy of the radiating field on traversing a small distance dl of absorbing medium of unit cross section is

$$\begin{aligned} -dI(w) &= hw \, (N^+ - N^-) \, dl \\ &= hw \, p(w) \, S \, dl \qquad 4 \end{aligned}$$

where $$S = \sum_{n''} N(n'')B_{n''n'} - \sum_{n'} N(n')B_{n'n''} \qquad 5$$

The fact that change of energy is -dI(w) shows that this is an energy loss.

The intensity of a radiating field is related to the radiation density by the expression

$$I(w) = cp(w)$$

Therefore substituting for p(w) in equation 4 and rearranging

$$\frac{-dI(w)}{I(w)} = \frac{hw}{c} \quad S\, dl \qquad 6$$

This expression can be integrated between the limits $I_o(w)$ the initial intensity of frequency w and I(w) the intensity after traversing distance l through the absorbing medium.

Therefore $$\int_{I_o(w)}^{I(w)} \frac{-dI(w)}{I(w)} = \frac{hw}{c} \quad S \int_o^l dl$$

$$\ln\left|I_o(w)/I(w)\right| = \frac{hw}{c} \quad S\, l \qquad 7$$

SECTION 5.2 The Einstein Coefficients

It is now required to examine the exact form of the Einstein coefficients of induced absorption and emission introduced in Section 5.1. They are in fact equal for a transition between state ' and state ''.

i.e. $$B_{n''n'} = B_{n'n''}$$

This does not mean that for transitions between the two states there is no net loss in energy from the radiating field as the population of the lower energy state is always greater than that of the upper state.

The Einstein coefficient of induced absorption is given by

$$B_{n''n'} = \frac{8\,^{3}}{3\hbar^{2}} \left| \int \Psi^{*}(n'')\ \underline{\mu}\ \Psi(n')\,d\tau \right|^{2} \qquad 8$$

where $\Psi(n')$ is the wave function of the upper energy state

and $\Psi^{*}(n'')$ is the complex conjugate of the wave function of the lower energy state.

$\underline{\mu}$ is the dipole moment of the system.

The limits of integration are ± infinity and integration is over all space.

(It is not proposed to derive equation 8 here, an excellent explanation of it is given in Barrow (2), Chapter 4).

For convenience, let

$$I = \int \Psi^{*}(n'')\ \underline{\mu}\ (n')\ d\tau$$

If $\underline{\mu}$ is invariant during a vibration

$$I = \mu \int \Psi^{*}(n'')\ \Psi(n') = 0$$

since $\Psi^{*}(n'')$ and $\Psi(n')$ are orthogonal.

Therefore unless there is a change in the dipole moment of the molecule during a vibration there can be no interaction with electromagnetic radiation and hence no Infra Red band.

The definition of dipole (or electric) moment of a molecule is (as given by Wilson, Decius and Cross (8), p.5) a vector quantity whose direction is that of a line joining the centre of charge of negative charges with the centre of charge of the positive charges and whose magnitude is the length of that line multiplied by the total negative or positive charge (which are equal in a neutral molecule). It can be resolved into components μ_x, μ_y and μ_z (denoted generally by μ_q) along the three coordinates x, y and z (denoted generally by q). The value of μ_q is given by

$$\mu_q = \sum_i e_i q_i$$

where e_i is the charge on the ith particle

and q_i is its coordinate.

The summation i is over all particles.

When the molecule vibrates the charged particles, which define the dipole moments, move and the dipole moment changes. The most convenient coordinate used to define a vibrating molecule are the Normal Coordinates (see Section 1.4) so that $\mu_q(Q_1,Q_2 \ldots)$ the instantaneous dipole moment, which is a function of the normal coordinates, can be expanded as a Taylor series (see Section 1.2) in the Normal Coordinates. Therefore

$$\mu_q(Q_1,Q_2 \ldots .) = \mu_q(Q_1^e,Q_2^e \ldots .) + \sum_i (Q_i - Q_i^e) \left|\frac{\partial \mu}{\partial Q_i}\right|_e + \text{higher terms} \qquad 9$$

where Q_1^e etc. are the equilibrium normal coordinates

and $\mu_q(Q_1^e,Q_2^e \ldots)$ is the qth component of the dipole moment at equilibrium.

The summation i is over all normal coordinates.

In the double harmonic oscillator approximation the higher terms are ignored. It is a double harmonic oscillator approximation since here the assumption of electrical harmonicity is made and in Section 1.2, when considering the Potential Expression, the assumption of mechanical harmonicity was made.

The wave functions can also be expressed in terms of the normal coordinates.

$$\Psi = \phi \prod_i \psi (Q_i) \qquad 10$$

where ϕ is the electronic wave function

and $\psi(Q_i)$ is the vibrational wave function for the ith normal coordinate.

Multiplication is over all normal coordinates.

The rotational wave functions are not considered.

Since the molecule is always in the ground electronic state for the transitions considered here the electronic wave function normalizes to unity. Therefore substituting for μ using equation 9 and $\Psi^*(n'')$ and $\Psi(n')$ using equation 10, equation 8 becomes

$$I = \int \prod_i \psi''(Q_i) \sum_q \left[\mu_q^e + i \frac{\partial \mu_q}{\partial Q_i} dQ_i \right] \prod_i \psi'(Q_i) d\tau \qquad 11$$

where $\psi''(Q_i) = \psi^*(n'', Q_i)$

$\psi'(Q_i) = \psi(n', Q_i)$

$dQ_i = Q_i - Q_i^e$

and $\mu_q^e = \mu_q(Q_1^e, Q_2^e \ldots .)$

The summation over q is necessary since μ has been resolved into its three components. For convenience it will now be dropped. Later it will be shown why it is not normally required.

I is now expanded and divided into two parts I_1 and I_2.

$$I_1 = \mu_q^e \int \prod_i \psi''(Q_i) \prod_i \psi'(Q_i) d\tau \qquad 12$$
$$= 0$$

This follows since only the ith vibration is being considered, for which

$$\int \psi''(Q_i)\ \psi'(Q_i) = 0$$

$$I_2 = \sum_i \left[\frac{\partial \mu_q}{\partial Q_i}\right]_e \int \psi''(Q_1)\psi'(Q_1) \int \psi''(Q_2)\psi'(Q_2) .. \int \psi''(Q_i) dQ_i \psi'(Q_i)\ d\tau \qquad 13$$

Again, since only the ith vibration is being considered, only the ith term in the summation remains.

Now $$\int \psi''(Q_1)\psi'(Q_1) = 1 \text{ etc.}$$

Since for these terms n'' = n'

Therefore

$$I_2 = \left[\frac{\partial \mu_q}{\partial Q_i}\right]_e \int \psi''(Q_i)\ dQ_i\ \psi'(Q_i)$$

This integral is equal to zero except when n' = n'' + 1.

Then $$I_2 = \left[\frac{h(n'' + 1)}{8\pi^2 c w_i}\right]^{\frac{1}{2}} \left[\frac{\partial \mu_q}{\partial Q_i}\right]_e \qquad 14$$

(For an explanation of this integration see Wilson, Decius and Cross (8), p.37 and Appendix III).

Returning to equation 8 and substituting for I

$$B_{n''n'} = \frac{\pi}{3hcw_i} \left[\frac{\partial\mu_q}{\partial Q_i}\right]^2_e (n'' + 1) \qquad 15$$

where $n' = n'' + 1$ and w_i is the frequency of the ith band.

The derivation of $B_{n'n''}$, the Einstein coefficient of induced emission is very similar to that of $B_{n''n'}$. In this case

$$I_2 = \left[\frac{\partial\mu_q}{\partial Q_i}\right]_e \int \psi'(Q_i)dQ_i\psi''(Q_i)$$

The integral is equal to zero except when $n'' = n' - 1$

Then $$I_2 = \left[\frac{hn'}{8\pi^2 cw_i}\right]^{\frac{1}{2}} \left[\frac{\partial\mu_q}{\partial Q_i}\right]_e$$

but since $n' = n'' + 1$ this is identical to equation 14 and $B_{n''n'} = B_{n'n''}$ as previously stated.

SECTION 5.3 The Intensity of a Theoretical Band

Returning to equation 5 and substituting for the Einstein coefficients

$$S = \frac{\pi}{3hcw_i} \left[\frac{\partial\mu_q}{\partial Q_i}\right]^2_e \sum_{n''} N(n'').(n'' + 1) - \sum_{n'} N(n').n' \qquad 15$$

Since n' and n'' are quantum numbers for the same system and $n' = n'' + 1$, it follows that

$$S = \frac{\pi}{3hcw_i}\left[\frac{\partial \mu_q}{\partial Q_i}\right]^2_e \sum_{n''}(n'' + 1).\left|N(n'') - N(n'' + 1)\right| \qquad 16$$

At equilibrium the population of energy states follow the Boltzmann distribution. Therefore

$$\frac{N(n'')}{N_T} = \frac{\exp(-un'')}{Q_v}$$

where $u = hcw/kT$

$N_T = \sum_{n''} N(n'')$, the total number of moleculew per unit volume

and $Q_v = \sum_{n''} \exp(-un'')$, the vibrational partition function.

Therefore substituting for $N(n'')$ and $N(n'' + 1)$ in equation 16

$$S = \frac{\pi}{3hcw_i}\left[\frac{\partial \mu_q}{\partial Q_i}\right]^2_e \frac{N_T}{Q_v} \sum_{n''}(n'' + 1)\left|\exp(-un'') - \exp(-u(n''+1))\right| \qquad 17$$

If $T_{n''} = (n''+1)\left|\exp(-un'') - \exp(-u(n''+1))\right|$

Then $T_o = 1 - e^{-u}$

$T_1 = 2(e^{-u} - e^{-2u})$

$T_2 = 3(e^{-2u} - e^{-3u})$

etc.

Therefore $\sum_{n''} T_{n''} = 1 + e^{-u} + e^{-2u} \ldots$

$= Q_v$

Therefore equation 17 becomes

$$S = \frac{\pi}{3hcw_i}\left[\frac{\partial \mu_q}{\partial Q_i}\right]^2_e N_T \qquad 18$$

Substituting for S in equation 7

$$\ln \left| I_o(w)/I(w) \right| = \frac{\pi}{3c^2 w_i} \quad N_T \, \ell \, w \left[\frac{\partial \mu_q}{\partial Q_i} \right]^2_e \qquad 19$$

If $N_T = pN$

where p is the molar concentration

and N is Avagadro's Number

Substituting in equation 19 and rearranging

$$\frac{1}{p\ell} \quad \frac{\ln I_o(w)/I(w)}{w} = \frac{\pi N}{3c^2 w_i} \left[\frac{\partial \mu_q}{\partial Q_i} \right]^2_e \qquad 20$$

The only approximations made in deriving this equation are those of electrical and mechanical harmonicity. It applies to all allowed transistions which are accompanied by an exchange of energy hw_i between the absorbing medium and the radiating field. It is also temperature independent, the increase in hot band absorption exactly cancelling the increase in induced emission as the temperature is raised (123).

SECTION 5.4 The Intensity of an Experimental Band

An experimentally observed infra red band does not have an infinitely narrow band width as assumed in equation 20. In fact the time development or Heisenberg approach to spectral absorption (see Section 2.3, Hexafluoro Benzene) shows that even a perfectly harmonic band would have some broadening due to uncertainty. Therefore in equation 20, $\left| \ln (I_o(w)/I(w)) \right| / w$ is replaced by an integral over the entire band. Equation 20 thus becomes

$$\Gamma_i = \frac{1}{pl} \int_{Band} \frac{\ln \left| I_o(v)/I(v) \right|}{v} \, dv = \frac{\pi N}{3c^2 w_i} \left[\frac{\partial \mu_q}{\partial Q_i} \right]^2_e \qquad 21$$

where Γ_i is the intensity of the ith band.

Since the integration on the right hand side of Equation 21 is over an experimentally observed infra red band, the harmonic frequency w is replaced by the actual frequency v. w_i, the frequency of the fundamental transition, is a constant for a given band and so is $\left| \partial \mu / \partial Q_i \right|_e$. Therefore Γ_i is also constant for a given band.

An alternative definition of intensity is

$$A_i = \frac{1}{pl} \int_{Band} \left| \ln I_o(v)/I(v) \right| dv = \frac{\pi N_v}{3c^2 w_i} \left[\frac{\partial \mu_q}{\partial Q_i} \right]^2_e \qquad 22$$

where the frequency factor v is not included on the right hand side. The Γ definition of intensity is preferred here.

The broadening of infra red bands in the gas phase is due mainly to two factors.

1. Anharmonicity. In Section 5.1 the assumption that the fundamental and all hot band transitions occur at the same frequency was made. This would be the case if the Potential Energy function was perfectly harmonic. Unfortunately it is not, the spacing between the energy levels, and therefore the transition frequencies, decrease as the quantum number increases. These differences in frequency

are very small and the bands are not resolved. The overall shape of the band is therefore a sharp rise on the high frequency side due to the fundamental transition and a fall on the low frequency side, which can best be described as fairly steep, due to transitions involving energy levels with high quantum numbers and therefore low populations. The integration in equation 21 is carried out over all transitions. w_i should still be taken as the harmonic frequency of the band. Unfortunately harmonic frequencies are known for only a few molecules and so w_i is taken as the frequency of the fundamental transition. (This is not the same as the harmonic frequency as anharmonicity causes a slight decrease in the energy level with $n = 1$).

2. Rotational Fine Structure. In Section 5.2 the rotational part of the wave function was ignored and although the intensity of the vibration transition is the required quantity, in the gas phase there are transitions in which not only the vibrational quantum numbers change but also rotational quantum numbers. For most molecules this rotational fine structure is not resolved and the observed spectrum has one of the familiar type A, B or C band shapes discussed in Section 1.15. When measuring the intensity of an infra red band the integration $\int \ln \left|I_0(v)/I(v)\right| / v.dv$ or $\int \ln\left|I_0(v)/I(v)\right| dv$ is carried out over all the rotational fine structure. When using A for the intensity it is necessary to include a correction factor in equation 22 to allow for the inclusion

of the rotational structure in the integrated intensity (124), but as shown by Crawford (125) when using no correction factor is required. Therefore within the confines of the double harmonic oscillator approximation equation 21 is still exact.

SECTION 5.5 The Measurement of Intensity.

Having defined the intensity of a band as

$$\Gamma = \frac{1}{pl} \int_{\text{Band}} \frac{\ln \left| I_o(v)/I(v) \right|}{v} \, dv$$

the first question that arises is how are I_o and I measured from an infra red band. In Section 5.1 $I_{o(v)}$ was defined as the initial intensity of the radiating field at frequency v and I(v) was defined as the intensity after traversing distance l through the absorbing medium, i.e. the sample thickness.

When recording an infra red spectrum three traces are required:-

1. A Background trace without any absorbing sample in the sample beam.

2. A Sample trace with the sample in the sample beam.

3. A 100% absorption trace with the sample beam blocked off.

Then I_o is the distance between the 100% and background traces,

and I is the distance between the 100% and sample traces (see figure 5.1).

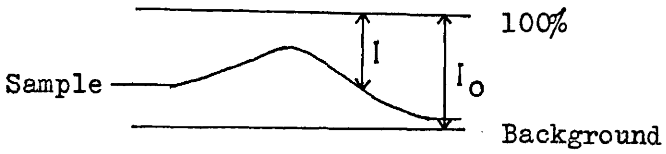


Figure 5.1

This technique of recording three traces is basically that followed whether a single or a double beam spectrometer is being used. Of course the sample has to be contained within a cell and therefore the background trace is recorded with an empty cell in the sample beam. In the gas phase empty means evacuated since the cells used are quite long and any air present could affect the results. When using a double beam spectrometer the need for recording a background trace could be avoided by using two matched cells, one containing the sample in the sample beam, the other empty in the reference beam. The background is obtained by joining the two wings of the spectrum, where no sample absorption occurs, with a straight line. However, this method is not entirely satisfactory and it is usually preferable to record a separate background trace. In this case it does not matter whether an empty cell is placed in the reference beam or not. The only condition is that no alteration is made to the reference beam in the course of the experiment.

The next question is how is the integral in equation 21 evaluated.

If $$f(v) = \frac{\ln|I_0(v)/I(v)|}{v}$$

then $$\Gamma = \frac{1}{p\mathrm{I}} \int_{\mathrm{Band}} f(v)\, dv$$

and $\int_{\mathrm{Band}} f(v)\, dv$ is the area between the line defined by $f(v)$ and the line $f = 0$. This can be evaluated using the Trapezoidal Rule (Heading (4), p.370). If the limits of integration are v_o and v_n such that at these points

$$I_o(v) = I(v) \quad \text{i.e. } f(v) = 0$$

The band is divided into n equal subdivisions each of width Δv where

$$\Delta v = (v_n - v_o)/n$$

Neglecting the curve of the n arcs so that each subdivision is trapezoidal in shape (provided Δv is small enough this is a reasonable approximation), the area under the band is given by

$$\int_{\mathrm{Band}} f(v)dv = \Delta v/2 \left| (f(v_o) + f(v_1)) + (f(v_1) + f(v_2)) + \dots (f(v_{n-1}) + f(v_n)) \right|$$

$$= \Delta v/2. \left| 2\sum_i f(v_i) - f(v_o) - f(v_n) \right| \qquad 23$$

where i goes from 0 to n.

Actually since $f(v_o) = f(v_n) = 0$

Therefore $$\int_{\mathrm{Band}} f(v)\, dv = \sum_i f(v_i)\, \Delta v$$

and this result (going from right to left) would follow directly from decreasing the width of the subdivision so that $\Delta v \rightarrow dv$ and the function becomes continuous.

The reason that the Trapezoidal Rule is introduced is that in practice it is frequently more convenient to divide the band into several sections and evaluate the area under each section separately, each with a different Δv. (This applies especially to type C gas phase bands where the Q branch is much sharper than the P and R branches and requires a much smaller subdivision). In this case the end functions are important.

It would therefore appear that $I_0(v)$ and $I(v)$ can be measured and $\int_{\text{Band}} \frac{\ln |I_0(v)/I(v)|}{v} dv$ evaluated. This assumes that the sample can be irradiated with light of frequency v and the values $I_0(v)$ and $I(v)$ measured without any other radiation being present. This is not the case in practice. For any radiation to reach the sample there must be a finite slit width and at any time the sample is being irradiated with light over a range of frequencies. This applies whether the spectrometer is a prism or grating instrument (see Figure 5.2).

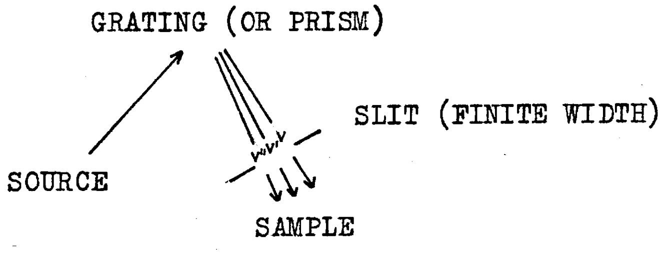


Figure 5.2

Therefore no spectrometer measures $I_0(v)$ or $I(v)$ at a single frequency but instead it measures the integral of the intensities over a range of frequencies. However it is still possible to measure the intensity of an infra red band using the Wilson-Wells theorem (126).

If $T(v')$ is the apparent registered by the instrument at setting v' (i.e. the central frequency admitted by the slit), then

$$T(v') = \int I(v)\, g(v,v')\, dv$$

where $g(v,v')$ is the fraction of the light of actual frequency v which is registered by the instrument at setting v'. (This is known as the slit function since the size of the slit determines the range of frequencies).

The integration is carried out over all values of v for which $g(v,v') \neq 0$.

Therefore what is recorded is not I_o and I but T_o and T, so an apparent intensity B is introduced where

$$B = \frac{1}{pl}\int_{\text{Band}} \ln\left|T_o(v')/T(v')\right| dv'$$

$$= \frac{1}{pl}\int_{\text{Band}} \ln\left|\frac{\int I_o(v)g(v,v')dv}{\int I(v)g(v,v')dv}\right| dv'$$

Wilson and Wells (126) showed that

$$\lim_{pl \to 0} B = A \qquad 24$$

where A is defined in equation 22.

This theorem also applies to Γ, so that

$$\lim_{pl \to 0} \Gamma\,(\text{apparent}) = \Gamma\,(\text{true}) \qquad 25$$

For equations 24 and 25 to be true the following conditions must be obeyed.

1. The incident intensity I_o does not vary rapidly over the band.

2. Either the variation of $\ln\left|I_o(v)/I(v)\right|$ with v can be neglected in the resolved spectral range, or the resolution of the instrument does not change appreciably over the entire band being studied.

The first condition is relatively easily obeyed since I_o will not vary much provided water vapour and carbon dioxide are excluded from the absorbing path. This can be achieved either by evacuation of the spectrometer, a fairly difficult process, or by absorbing these gases using, usually, Silica Gel and Potassium Hydroxide. In the liquid phase the second condition is also obeyed but difficulties may arise in the gas phase, since here a vibrational absorption band contains many rotational lines, which give rise to rapid fluctuations in I even though these lines may not be resolved by the spectrometer. However, provided the pressure in the sample cell is high enough, this fine structure is completely smeared out to give a smooth band, in which case the condition is satisfied. This pressure broadening can be achieved either by using a sufficiently high pressure of the gas itself, or more usually, by the addition of an infra red transparent and chemically inert gas (e.g. Nitrogen or Argon) to the sample. The pressure required for complete broadening depends on the sample being studied (and therefore the type of rotational fine structure), the nature of the broadening gas and the resolution of the spectrometer. Penner and Weber (127) proposed the condition that there is sufficient total pressure when the variation of β (= $\int_{\mathrm{Band}} \ln (T_o(v')/T(v'))dv')$ with pl is linear.

Therefore provided the two conditions are upheld the true intensity can be obtained from the apparent either by plotting B versus pl and extrapolating to zero concentration or by plotting Bpl versus pl in which case A is the slope at the origin of the tangent to this curve. Both these methods can give rise to considerable ambiguity in fixing a value for A, especially in the gas phase where the data with the largest relative errors, i.e. low pressures and low band areas, are relied on most heavily. However if the condition of Penner and Weber (127) mentioned above is satisfied, then A=B and both are equal to the slope of the curve of β versus pl. These methods of measuring A apply also to Γ, of course. They are discussed in terms of A since this is the intensity definition Wilson and Wells (126) used.

This discussion on the calculation of Γ has assumed a prior knowledge of p and l. l is the distance between the two inner walls of the cell, which contains the sample, and since this is fairly large in gas phase work its calculation requires only conventional measuring techniques. p is the molar concentration and its calculation in gas phase work requires a knowledge of the pressure of the absorbing gas and the ideal gas laws. In Chapter 6 this is discussed in greater detail in connection with the experimental work.

SECTION 5.6 The Dipole Moment Derivative

According to Equation 21,

$$\Gamma_i = \frac{N\pi}{3c^2 w_i} \left[\frac{\partial \mu_q}{\partial Q_i}\right]_e^2$$

where $\partial \mu_q / \partial Q_i$ is the change in dipole moment of the molecule along the cartesian axis q with respect to the change in the ith normal coordinate. The subscript e indicates that it measured at the equilibrium normal coordinate.

In equation 11 a summation over the 3 cartesian coordinates x, y and z was introduced but subsequently dropped for reasons of convenience. If this summation is now reintroduced equation 21 becomes

$$\Gamma_i = \frac{N\pi}{3c^2 w_i} \left[\left[\frac{\partial \mu_x}{\partial Q_i}\right]_e^2 + \left[\frac{\partial \mu_y}{\partial Q_i}\right]_e^2 + \left[\frac{\partial \mu_z}{\partial Q_i}\right]_e^2 \right] \qquad 26$$

Frequently the change in dipole moment is orientated along a fixed direction for all vibrations of a particular symmetry species and provided the cartesian axes are chosen to coincide with the symmetry axes only one component of the dipole moment derivative is non-zero. This is the case when in the symmetry point group of the molecule under consideration the three translations T_x, T_y and

T_z each transforms as a separate symmetry species. For a molecule of lower symmetry there may be two or even three non-zero components of the dipole moment derivative in the same symmetry species and in this case since there is only one intensity value for a given band only the sum $\sum_q \left[\partial\mu_q/\partial Q_i\right]_e^2$ can be evaluated and no information about the orientation of the change in the dipole moment can be gained. For a doubly degenerate band $\partial\mu_x/\partial Q_{ia} = \partial\mu_y/\partial Q_{ib}$ and in this case

$$\Gamma_i = \frac{N\pi}{3c^2 w_i}\left[\left[\frac{\partial\mu_x}{\partial Q_{ia}}\right]_e^2 + \left[\frac{\partial\mu_y}{\partial Q_{ib}}\right]_e^2\right]$$

$$= \frac{2N\pi}{3c^2 w_i}\left[\frac{\partial\mu_x}{\partial Q_{ia}}\right]_e^2$$

Alternatively this equation could be arrived at by considering that a doubly degenerate band is a superimposition of two bands of the same frequency so that the intensity of one of them is $\Gamma_i/2$. Similar reasoning applies to triply degenerate bands only in this case a factor of 3 is involved.

Therefore assuming only one component of the dipole moment derivative is non-zero the derivation of $\partial\mu/\partial Q_i$ from Γ_i is quite straightforward except for the choice of sign. Leaving this point aside for the present, the next step is to interpret the dipole moment derivatives $\partial\mu/\partial Q$ in terms of more easily understandable molecular properties. Therefore, if $\partial\mu/\partial S_j$ is the change in dipole moment with respect to the change in the jth symmetry coordinate,

$$\frac{\partial \mu}{\partial S_j} = \sum_i \frac{\partial \mu}{\partial Q_i} \times \frac{\partial Q_i}{\partial S_j} \qquad 27$$

From equation 80, section 1.12

$$S = \mathbf{L}Q$$

therefore $Q = \mathbf{L}^{-1}S$

and $\dfrac{\partial Q_i}{\partial S_j} = \mathbf{L}^{-1}_{i,j}$

Substituting in equation 27

$$\frac{\partial \mu}{\partial S_j} = \sum_i \mathbf{L}^{-1}_{i,j} \frac{\partial \mu}{\partial Q_i} \qquad 28$$

where the summation is over all $\partial\mu/\partial Q_i$ for the symmetry species under consideration. Therefore they all must be known. Also the eigen vector matrix must be known and it must not be singular (i.e. must contain no redundancies). Assuming these conditions are fulfilled the question of the sign of the dipole moment derivative introduces considerable uncertainty into its interpretation in terms of the symmetry coordinates since all possible sign combinations must be included in the calculations. In general if there are n fundamental vibrations in a given symmetry species, there are 2^n different sign combinations and 2^n sets of solutions. It is only necessary to calculate 2^{n-1} sets however, since the other 2^{n-1} sets differ only in sign. Only one of these 2^n sets is physically correct.

To decide which of the solutions is the correct one, all solutions must be calculated and compared to see which set (or sets) conform best to some expected pattern. If isotopic data is available a second 2^n sets of solutions can be calculated (provided that the isotopic and original molecules belong to the same symmetry point group) and the correct set will have the same values for corresponding $\partial\mu/\partial S_j$ s in the two molecules. If the isotopic molecule is of lower symmetry than the original the comparison can be made by calculating all possible values for $\partial\mu/\partial S$ for the original molecule and then use these values to calculate alternative possible sets of intensities for the isotopic molecule which are then compared with the experimental results. As in the case of the frequencies of isotopic molecules, where the invariance of the potential energy under isotopic substitution led to the isotope sum and product rules, so this invariance of the dipole moment function under isotopic substitution also leads to isotope rules, as shown by Crawford (128) and Decius (129). This means that there is a limit to the amount of extra data that can be obtained by isotopic substitution but these rules can provide a useful check on the accuracy of the intensity measurements. If no isotopic data exists comparison with a similar molecule can form the basis for the selection of a particular set of solutions. This method relies on the assumption of the transferability of dipole moments, a particularly insecure assumption. In certain cases the sign of the dipole moment derivative can be obtained from vibration-rotation studies (130). Also, provided the molecule is small, quantum mechanical calculations can be used to obtain theoretical values of the $\partial\mu/\partial S_j$ s which are compared with the experimental values to help choose the correct sign combination (131).

By a similar approach to that used above to derive $\partial\mu/\partial S_j$, the rate of change of dipole moment with respect to the kth internal coordinate $\partial\mu/\partial R_k$ can be obtained.

$$\frac{\partial\mu}{\partial R_k} = \sum_j \frac{\partial\mu}{\partial S_j} \frac{\partial S_j}{\partial R_k} \qquad 29$$

From equation 74, Section 1.11

$$S = UR$$

Therefore $\frac{\partial S_j}{\partial R_k} = u_{j,k}$

Substituting in equation 29

$$\frac{\partial\mu}{\partial R_k} = \sum_j u_{j,k} \frac{\partial\mu}{\partial S_j} \qquad 30$$

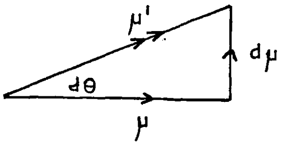
Since usually an internal coordinate occurs only once in the symmetry coordinates for a particular symmetry species, the summation in equation 30 can be dropped. Therefore

$$\frac{\partial\mu}{\partial R_k} = u_{j,k} \frac{\partial u}{\partial S_j} \qquad 31$$

This interpretation of the dipole moment derivative in terms of internal coordinates, which are intimately connected with the bonds in molecules, is not entirely accurate.

As an example consider what happens when a bond is rotated through a small angle $d\Theta$ about one end. If u is the dipole moment of the bond before rotation, μ' the dipole moment after rotation and du the change in dipole moment, then

$$\vec{\mu}' = \vec{\mu} + \vec{d\mu}$$



Resolving μ' into its two componenta μ and $d\mu$

$$\mu = \mu' \cos d\,\Theta = \mu'$$

$$d\mu = \mu' \sin d\,\Theta = \mu' d\Theta$$

These expressions arise for the fact the $d\Theta$ is small, so that

$$\cos d\Theta \rightarrow 1$$

$$\sin d\Theta \rightarrow d\Theta$$

Therefore it follows that

$$d\mu/d\Theta = \mu$$

This simple theory implies that both an in plane and an out-of-plane angle bend have the same change in dipole moment with respect to the bond rotating about one end which is equal to the dipole moment of the bond. This however is not the case in practice as will be seen later.

This in fact is one of the assumptions of zero-order bond moment hypothesis which attempts to explain dipole moment derivatives in terms of Bond Moments, the dipole moment of a bond, and Bond Moment Derivatives, the change in bond moment with respect to deformation (either bending or stretching) of that bond. The three assumptions, as given by Hornig and McKean (132), are

1. When a bond is stretched by dr, a moment $(d\mu/dr)\ dr$ is produced in the direction of that bond.

2. When a bond is bent through an angle $d\theta$, a moment $\mu_o\ d\theta$ (where μ_o is the effective bond moment) is produced in the plane of bending and perpendicular to the direction of the bond.

3. When any one bond is bent or stretched no moments are produced in other bonds.

The first two assumptions follow from the one given by Straley (133) that the bond moment lies directly along the bond and continues to do so when the molecule is deformed by vibration. The third assumption implies that when two or more bonds are deformed the resulting moments are strictly additive.

Hornig and McKean (132) reviewed in some detail the literature concerned with the zero-order bond moment hypothesis and showed that in practice the three assumptions are not generally valid. They tabulated many values for bond moments and bond moment derivatives and in many cases not only are they not transferable between similar molecules but not even transferable between different symmetry species of the same molecule. For instance for ethylene, there are three different values for C-H bond moment calculated from the intensities of vibrations of the three different infra red active symmetry species. They also discussed some of the factors which give rise to these inconsistencies and concluded that $\partial\mu/\partial S$ is a more meaningful quantity than μ and $\partial\mu/\partial r$.

Coulson (134) also reviewed the factors which cause the breakdown of the bond moment hypothesis. They include: lone pairs of electrons, which have dipole moments which can change during a vibration but which are not incorporated into any bond moments; hybridization changes during the deformation of a bond, which affect the molecule as a whole and not just the bond being deformed; and incomplete orbital following of a bond during a vibration so that the dipole is not orientated along the bond. These factors will be discussed later in Chapter 7 in reference to the Fluorine substituted Benzenes under consideration.

Therefore, although the interpretation of dipole moment derivatives in terms of bond properties would be desirable in view of the simplicity of the model, the zero-order bond moment hypothesis is inadequate since it ignores factors other than μ and $\partial\mu/\partial r$ which can contribute to the change in dipole moment. Sverdlov (135) has advanced a theory in which it is assumed that the bond moment vector departs from the bond direction during a vibration, under the influence of atoms not connected with that bond. This necessitates the introduction of components of the change in bond moment with respect to each type of bond distortion, perpendicular to the bond. Therefore the number of parameters is increased by a factor of three and since they cannot all be determined, even for the simplest molecules, the theory has no practical advantages. However, the theory of Gribov (136,137,138) in which the dipole moment derivative is interpreted in terms of the "electro-optical" parameters of a molecule offers a more hopeful means of explaining dipole moment derivatives than the zero-order bond moment hypothesis.

SECTION 5.7 The Electro-Optical Theory of Gribov.

This theory gives a general expression for the dipole moment derivative in terms of the bond properties, bond moment and bond moment derivatives, which Gribov refers to as electro-optical parameters. The derivation of this expression is outlined below.

The dipole moment of a molecule $\vec{\mu}$ can be split into a series of components

$$\vec{\mu} = \vec{\mu}_{up} + \vec{\mu}_{pol} + \sum_k \vec{\mu}_k$$

where $\vec{\mu}_k$ is the bond moment of the kth bond and these bond moments are considered to be transferable between molecules,

$\vec{\mu}_{up}$ represents the contribution to the dipole moment of the molecule from unpaired electrons

and $\vec{\mu}_{pol}$ represents the contribution to the dipole moment of the molecule from off-axis polarization of the bonds.

If $\vec{e}_k$ is a unit vector directed along the kth bond and μ_k is the magnitude of the kth bond, then

$$\vec{\mu} = \vec{\mu}_{up} + \vec{\mu}_{pol} + \sum_k \mu_k \vec{e}_k$$

If it is assumed that the contributions to the dipole moment from unpaired electrons and off-axis polarization can be resolved into components along the bonds, then

$$\vec{\mu}_{up} + \vec{\mu}_{pol} = \sum_k \mu_k' \vec{e}_k$$

and

$$\vec{\mu} = \sum_k (\mu_k + \mu_k') \vec{e}_k$$

The two components of the dipole moment along the kth bond can be combined so that

$$\vec{\mu} = \sum_k \mu_k \vec{e}_k$$

but μ_k can no longer be considered as a transferable bond moment.

In the case of planar molecules, in which there are no bonds perpendicular to the plane of the molecule it may be necessary to consider certain electron orbitals as constituting a bond perpendicular to this plane.

The dipole moment can be resolved into three components in the x, y and z directions. Therefore $\vec{\mu}_q$, the component of the dipole moment in the direction q, is

$$\vec{\mu}_q = \sum_k \mu_k (\vec{e}_k)_q \qquad 32$$

where $(\vec{e}_k)_q$ is the component of the kth unit vector along the coordinate q.

Differentiating equation 32 with respect to Q_i

$$\frac{\partial \vec{\mu}_q}{\partial Q_i} = \sum_k \vec{e}_k \frac{\partial \mu_k}{\partial Q_i} + \sum_k \mu_k \frac{\partial \vec{e}_k}{\partial Q_i} \qquad 33$$

For convenience the subscript q is dropped from $\vec{e}_k$ but it must be remembered that it specifically refers to direction q, as defined by the dipole moment derivative $\partial \mu_q / \partial Q_i$.

In terms of R_j, the jth internal coordinate, equation 33 becomes

$$\frac{\partial \vec{\mu}_q}{\partial Q_i} = \sum_j \left[\sum_k \vec{e}_k \frac{\partial \mu_k}{\partial R_j} + \sum_k \mu_k \frac{\partial \vec{e}_k}{\partial R_j} \right] \frac{\partial R_j}{\partial Q_i} \qquad 34$$

From equation 25, section 1.4

$$R = LQ$$

Therefore $\dfrac{\partial R_j}{\partial Q_i} = l_{j,i}$

and substituting in equation 34

$$\frac{\partial \vec{\mu}_q}{\partial Q_i} = \sum_j \left[\sum_k \vec{e}_k \frac{\partial \mu_k}{\partial R_j} + \sum_k \mu_k \frac{\partial \vec{e}_k}{\partial R_j} \right] l_{j,i} \qquad 35$$

where the summation j is over all internal coordinates and the summation k is over all bonds.

$\partial \mu_k / \partial R_j$ is the change in the dipole moment of the kth bond with respect to the change in the jth internal coordinate. In this form all possible terms are included.

In order to simplify manipulation of the expression the terms are expressed in matrix form. Therefore $\partial \mu_k / \partial R_j$ is the k,jth element of the rectangular matrix $|\partial \mu / \partial R|$, dimension nb by nr, and $\vec{e}_k$ is the kth element of row matrix $|e|$, dimension nb, where

nb is the number of bonds

and nr is the number of internal coordinates.

μ_k is the kth element of the row matrix $|\mu|$, dimension nb. The elements of $|\mu|$ and $|\partial \mu / \partial R|$ make up the electro-optical parameters of the molecule.

To express $\partial \vec{e}_k / \partial R_j$ in matrix form requires a more detailed examination. If $\vec{r}_k$ indicates both the magnitude and direction of the kth bond and $(\vec{r}_k)_q$ is the component of r_k in direction q. Then

$$(\vec{r}_k)_q = r_k \vec{e}_k$$

where r_k is the magnitude of $\vec{r}_k$ and $\vec{e}_k$ refers specifically to direction q as previously mentioned. Therefore if the change in the kth bond is $\Delta \vec{r}_k$ the component in direction q is

$$\begin{aligned} \Delta (\vec{r}_k)_q &= \Delta (r_k \vec{e}_k) \\ &= \vec{e}_k \Delta r_k + r_k \Delta \vec{e}_k \end{aligned}$$

Therefore $$\Delta \vec{e}_k = \frac{1}{r_k}\left[\Delta(\vec{r}_k)_q - \vec{e}_k \ \Delta r_k\right]$$

and $$\frac{\partial \vec{e}_k}{\partial R_j} = \frac{1}{r_k}\left[\frac{\partial(\vec{r}_k)_q}{\partial R_j} - \vec{e}_k \ \frac{\partial r_k}{\partial R_j}\right]$$

The bond vector $\vec{r}_k$ is defined by the two atoms which constitute the bond. If these atoms are labelled a - the terminal atom and b - the initial atom, then

$$(\vec{r}_k)_q = q_a - q_b$$

where q_a and q_b are the qth coordinates of atoms a and b respectively. Therefore

$$\frac{\partial(\vec{r}_k)_q}{\partial R_j} = \frac{\partial q_a}{\partial R_j} - \frac{\partial q_b}{\partial R_j}$$

where $\partial q_a/\partial R_j$ is the change in the qth coordinate of atom a with respect to the change in the jth internal coordinate.

From section 1.2 it is known that q and R are connected through the B matrix such that

$$R = B_q$$

B cannot be inverted so a matrix A is defined such that

$$q = AR$$

and $$AB = BA = E$$

Since $$BM^{-1}B^tG^{-1} = E$$

it follows that

$$A = M^{-1}B^tG^{-1}$$

Since the coordinate for only one direction is involved and not all three directions as in the B matrix, A_q is defined in only one direction, therefore

$$A_q = M^{-1} B_q^t G^{-1}$$

where the dimensions of the matrices are: A_q, na by nr; M^{-1}, na by na; B_q^t, na by nr; G^{-1}, nr by nr,

where na is the number of atoms.

Therefore $$\sum_{j,k} \frac{\partial(\vec{r}_k)_q}{\partial R_j} = \sum_{j,k} \left[\frac{\partial q_a}{\partial R_j} - \frac{\partial q_b}{\partial R_j} \right]$$

$$= \Delta A_q$$

$$= \Delta M^{-1} B_q^t G^{-1}$$

where Δ is a rectangular matrix, dimension nb by na. Its kth row, which refers to the kth bond, has element + 1 in the column corresponding to the terminal atom of the kth bond, -1 in the column corresponding to the initial atom of the kth bond and 0 in all other columns.

$\partial r_k/\partial R_j$ is the change in length of the kth bond with respect to the change in the jth internal coordinate. If this is a bending coordinate then $\partial r_k/\partial R_j$ equals zero. If it is a stretching coordinate and $k = j$, i.e. internal coordinate ∂R_j refers to the stretching of the kth bond then $\partial r_k/\partial R_j$ equals unity. If $k \neq j$ $\partial r_k/\partial R_j$ does not necessarily equal zero since the stretching of one bond can affect the length of another so these terms must be included. Therefore, when ∂R_j is a stretching coordinate $\vec{e}_k\ \partial r_k/\partial R_j$

is the k,jth element of square matrix $|E|$, dimension nb by nb, and when ∂R_j is a bending coordinate $\vec{e}_k \; \partial r_k/\partial R_j$ is the k,jth element of the rectangular null matrix $|0|$, dimension nb by nb-nr. Therefore

$$\sum_{j,k} \vec{e}_k \frac{\partial r_k}{\partial R_j} = |E,0|$$

where rectangular matrix $|E,0|$ has dimensions nb by nr.

If S^{-1} is a diagonal matrix, dimension nb by nb, whose k,kth element is $1/r_k$ and L_i is the ith column of the eigen vector matrix L, equation 35 expressed in matrix form is

$$\partial\mu_q/\partial Q_i = \left[\| e \| \, \| \partial\mu/\partial R | + \| \mu \| S^{-1} \left(\Delta M^{-1} B_q^t G^{-1} - \| E,0 \| \right) \right] L_i \qquad 36$$

Equation 36 is a general expression for the dipole moment derivative in terms of the electro-optical parameters μ_k and $\partial\mu_k/\partial R_j$. There is a problem in that G when expressed in internal coordinates is usually singular and cannot be inverted. However since any given $\partial\mu_q/\partial Q_i$ belongs to a particular symmetry species it follows that the complete G and L matrices are not required, only the G_Γ and L_Γ matrices for that particular symmetry species. According to equation 75, section 1.12

$$UU^t = U^tU = E$$

where the matrix U connects the symmetry coordinates S with the internal coordinates R, and U and $\partial\mu_q/\partial Q_i$ belong to the same symmetry species Γ.

Equation 36 can be rewritten as

$$\partial\mu_q/\partial Q_i = \Big[\lfloor e \rfloor\lfloor \partial\mu/\partial R \rfloor U^t + \lfloor \mu \rfloor S^{-1} (\Delta M^{-1}B_q^t U^t U G^{-1} U^t - \lfloor E,0 \rfloor U^t)\Big]\ UL_i \qquad 37$$

Also from section 1.12

$\mathcal{L} = UL$

thus $\mathcal{L}_i = UL_i$

and $\mathcal{G} = UGU^t$

thus $\mathcal{G}^{-1} = UG^{-1}U^t$

Therefore equation 37 becomes

$$\partial\mu_q/\partial Q_i = \Big[\lfloor e \rfloor\lfloor \partial\mu/\partial R \rfloor U^t + \lfloor \mu \rfloor S^{-1} (\Delta M^{-1}B_q^t U^t \mathcal{G}^{-1} - \lfloor E,0 \rfloor U^t)\Big]\mathcal{L}_i \qquad 38$$

where $\mathcal{L}_i$ is the ith column of the eigen vector matrix for symmetry species Γ.

Equation 38 can be extended to include all the dipole moment derivatives for a given symmetry species. Therefore

$$\lfloor \partial\mu_q/\partial Q \rfloor = \lfloor D\,Mu \rfloor + \lfloor Mu \rfloor\ \mathcal{L} \qquad 39$$

where $\partial\mu_q/\partial Q_i$ is the ith element of row matrix $\lfloor \partial\mu_q/\partial Q \rfloor$, dimension ns.

$$\lfloor DMu \rfloor = \lfloor e \rfloor\lfloor \partial\mu/\partial R \rfloor U^t \qquad 40$$

and is a row matrix dimension ns.

$$\lfloor Mu \rfloor = \lfloor \mu \rfloor S^{-1}(\Delta M^{-1}B_q^t U^t G^{-1} - \lfloor E,0 \rfloor U^t) \qquad 41$$

and is also a row matrix dimension ns.

Where ns is the number of symmetry coordinates.

$\mathcal{L}$ is invertable so that

$$\lfloor \partial\mu_q/\partial Q \rfloor \mathcal{L}^{-1} = \lfloor DMu \rfloor + \lfloor Mu \rfloor \qquad 42$$

If Γ and Λ still contain redundancies they can be replaced by Γ' and Λ' respectively, provided the symmetry matrix U is replaced by V ($= D^{1t}U$) - see Section 4.2. Equation 38 becomes

$$\partial u_q/\partial Q_i = \Big[\{ e \}\{\partial\mu/\partial R\} V^t + \{ \mu \} S^{-1} (\Delta M^{-1} B_q^t V^t (\Gamma')^{-1} - \{ E,0 \} V^t)\Big] L_i' \qquad 43$$

and in this form all matrices can be calculated.

SECTION 5.8 The application of the theory of Gribov.

If in equation 38 the bond moments and bond moment derivatives were known, the dipole moment derivates could be calculated and compared with the experimentally derived values. However, they are not usually known beforehand so they have to be calculated from the dipole moment derivatives. The other data required are calculated in a Normal Coordinate Analysis, described fully in Part I. If in the matrix $\{\partial\mu/\partial R\}$ only the terms for the change in a bond moment with respect to the stretching of that bond are retained all terms can be calculated but the theory reverts to being the bond moment hypothesis. If all terms in the matrices $\{\partial\mu/\partial R\}$ and $\{ \mu \}$ are retained then the number of unknowns greatly exceeds the number of observables, for one molecule. This is a weak point of the theory and as pointed out by Tanabe and Saeki (139,140) can result in only being able to calculate linear combinations of certain terms, which cannot be resolved into individual components. However, starting with a set of trial parameters which were assumed to be transferable between similar molecules and using a perturbation technique similar to that used for the calculation of force constants, Tanabe and Saeki applied the theory with some success to the three Methylene Chloride molecules (CH_2Cl_2, $CHDCl_2$ and CD_2Cl_2) (139) and to a larger series of thirteen Chloro Methanes (140).

This perturbation approach is ideal when a large number of intensities are being considered but for small numbers of intensities direct expansion of the relevant equations is preferable and using this method the application of the theory to the vibrations considered in Part II is examined. They are the out-of-plane vibrations of 1,4 difluoro Benzene - the B_{3u} symmetry species and 1,3,5 trifluoro Benzene - the A_2'' symmetry species. For both these molecules nq (the number of normal coordinates) and ns (the number of symmetry coordinates) both equal 3, therefore G and L can be inverted, nr (the number of internal coordinates) is 12 and nb (the number of bonds) is 12. Since only out-of-plane vibrations are considered, matrix $\{ E \}$ is not applicable and therefore the matrix $\{ E, 0 \}$ is ignored. From section 4.2 it follows that

$$T_{1q} = M^{-1} B_q^t U^t \mathbf{G}^{-1} \mathbf{L} \qquad 44$$

and therefore taking $\{ u \} S^{-1} \Delta T_{1q}$ to the left hand side, equation 42 becomes

$$\left[\{ \partial\mu_q / \partial Q \} - \{ \mu \} S^{-1} \Delta T_{1q} \right] \mathbf{L}^{-1} U = \{ e \} \{ \partial\mu / \partial R | \qquad 45$$

On the left hand side only $\lfloor \mu \rfloor$ the matrix of bond moments cannot be evaluated. Of the twelve bonds six are C - X bonds and six are C - C bonds and the bond moment of the C - F bond is denoted by μ_{CF} and the bond moment of the C - H bond is denoted by μ_{CH}. It is assumed that the bond moment of a C - C bond is zero.

If
$$X = \left[\lfloor \partial\mu_q/\partial Q \rfloor - \lfloor \mu \rfloor S^{-1} \Delta T_{1q} \right] L^{-1} \qquad 46$$

where X is a row matrix, dimension ns = 3 for both molecules, by substituting values for μ_{CF} and μ_{CH}, 8 X matrices can be evaluated for each molecule. (There are $8 = 2^3$ X matrices due to the sign uncertainty of $\partial\mu_q/\partial Q_i$). Therefore equation 45 becomes

$$XU = \lfloor e \rfloor \lfloor \partial\mu/\partial R \rfloor \qquad 47$$

The matrices X and U are known so the values of the elements of XU can be calculated.

The question that now arises is what are the matrices $\lfloor e \rfloor$ and $\lfloor \partial\mu/\partial R \rfloor$. For a planar molecule, the component of the e vector, the unit vector directed along a bond, in the direction perpendicular to the plane of the molecule (arbitarily defined as the z direction) is zero. However, as will be considered in greater detail in Chapter Seven, accompanying an out-of-plane vibration, there is a redistribution of electrons (electron rehybridization) in the π-orbitals of the Benzene ring. Therefore there is a flow of electrons in the z direction and this will cause a change in dipole moment along the z axis. To allow for this the p_z orbital of each Carbon atom in the ring is defined as a bond, each with a bond moment which is zero when the molecule is planar but which has a value during an out-of-plane vibration. These pseudo-bonds are orientated along the z axis so that the components of the e vectors in the z direction (the elements of the matrix $\{ e \}$, dimension nb = 6) all have the value one. The elements of the matrix $\{ \partial\mu/\partial R \}$, dimension nb = 6 by nr = 12, are the changes in the dipole moments of the pseudo-bonds with respect to the changes in the internal coordinates. Therefore the jth element of $\{ e \} \{ \partial\mu/\partial R \}$ is

$$\sum_i \partial\mu_i/\partial R_j = \partial\mu_{RM}/\partial R_j$$

where $\partial\mu_i/\partial R_j$ is the i,th element of $\{\partial\mu/\partial R \}$ and the summation i is over all pseudo-bonds.

$\partial\mu_{RM}/\partial R_j$ is the change in dipole moment (or rehybridization moment) for the molecule as a whole with respect to the change in the jth internal coordinate. It is this overall term which is calculated.

Therefore expanding both sides of equation 47, using the U matrices given in Appendix IV, the following relationships are obtained.

For 1,4 difluoro Benzene

$\partial\mu_{RM}/\partial y_{CF} = X_1 . r'/2^{\frac{1}{2}}$ for internal coordinates $r'dy_1$ and $r'dy_4$.

$\partial\mu_{RM}/\partial y_{CH} = X_2.r/2$ for internal coordinates rdy_2, rdy_3, rdy_5 and rdy_6.

$\partial\mu_{RM}/\partial\phi_{FH} = X_3.R/2$ for internal coordinates $Rd\phi_1$ and $Rd\phi_4$.

$\partial\mu_{RM}/\partial\phi_{HF} = - X_3.R/2$ for internal coordinates $Rd\phi_3$ and $Rd\phi_6$.

The difference between a ϕ_{HF} and a ϕ_{FH} torsion coordinate is illustrated in Figure 5.3.

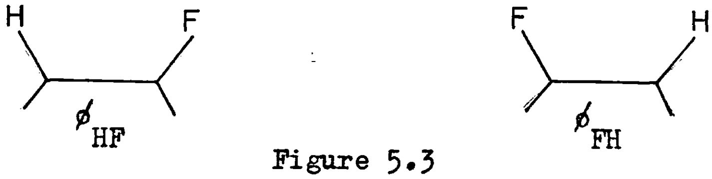


Figure 5.3

For 1,3,5 Trifluoro Benzene.

$\partial\mu_{RM}/\partial y_{CF} = X_1.r'/3^{\frac{1}{2}}$ for internal coordinates $r'dy_1$, $r'dy_3$ and $r'dy_5$.

$\partial\mu_{RM}/\partial y_{CH} = X_2.r/3^{\frac{1}{2}}$ for internal coordinates rdy_2, rdy_4 and rdy_6.

$\partial\mu_{RM}/\partial\phi_{FH} = X_3.R/6^{\frac{1}{2}}$ for internal coordinates $Rd\phi_1$, $Rd\phi_3$ and $Rd\phi_5$.

$\partial\mu_{RM}/\partial\phi_{HF} = - X_3.R/6^{\frac{1}{2}}$ for internal coordinates $Rd\phi_2$, $Rd\phi_4$ and $Rd\phi_6$.

Therefore for each set of values used for u_{CH} and u_{CH}, eight sets of results are obtained for each molecule. The correct set is decided on by comparison with the results for similar molecules.

The theory of Gribov has also been applied to some linear triatomic molecules by Thomas et.al. (141), who used equations similar to equation 35 rather than the fully expanded form of equation 38.

CHAPTER SIX The Absolute Intensity Measurements.

The molecules studied are:

1,4 difluoro Benzene - the B_{3u} species. The bands are

836.6 cm^{-1}

505.0 cm^{-1}

157.0 cm^{-1}

1,3,5 trifluoro Benzene - the A_2'' species. The bands are

847.6 cm^{-1}

664.1 cm^{-1}

205.6 cm^{-1}

SECTION 6.1 Technique and Units.

All the spectra were recorded in the gas phase, on either a Perkin-Elmer 325 grating spectrometer or a Grubb-Parsons cube interferometer, using the following technique.

First the spectrum of the evacuated cell is recorded. Before loading it into the cell, the sample, which is contained on a glass vacuum line, is degassed by freezing to liquid Nitrogen temperature, pumping on the frozen sample and then allowing it to warm to room temperature. This process is repeated until no gas bubbles appear in the sample while it is warming. The sample is also dried, by distillation under vacuum onto Phosphorus Pentoxide. Having been degassed and dried, the sample is allowed to evaporate into the gas cell and the temperature and pressure are noted. The pressure is recorded using an Ethylene Glycol manometer, open to the gas on one side while the other is under continual vacuum pumping. To minimise the possibility of error due to absorption of the sample by the Glycol the pressure is recorded as soon as possible after the tap on the gas cell is closed. The spectrum of the sample plus cell is then recorded. Finally the sample beam is blocked off and the 100% absorption trace recorded. (This only applies when using the grating spectrometer).

Where applicable, one atmosphere pressure of Nitrogen broadening gas is introduced into the cell following the introduction of the sample. The vacuum line plus a large ballast vessel is filled with dry Nitrogen at one atmosphere pressure (measured using a mercury manometer) and then the tap on the gas cell is quickly, to prevent back diffusion, opened and closed. This operation is repeated until the total pressure in the cell is one atmosphere.

As the cell has to be removed from the grating spectrometer to introduce the sample, it is necessary to ensure that it is always replaced in the same position. In the interferometer the gas cell is an integral part of the instrument so this problem does not arise.

The spectra of the band having been recorded, the area under the band is measured using the trapezoidal rule as outlined in section 5.5. (The method was checked by plotting, for one of the bands, $\ln (I_0/I)/v$ versus v and the area is obtained both by counting the squares and by use of a planimeter. All three methods gave the same result). A number of spectra are recorded at different pressures and a graph plotted of Area (β) versus Concentration (p). If the curve is a straight line then the condition of Penner and Weber (127) is satisfied and the slope obtained by the method of least squares (142).

i.e. since $\beta_j = \Gamma l \, p_j$

therefore
$$\Gamma l = \frac{\sum_j \beta_j p_j}{\sum_j p_j^2} \tag{1}$$

where the summation j is over all readings.

The standard deviation of Γl is given by (142)

$$\sigma^2 = \frac{\sum_j d_j^2}{(n-1)\sum_j p_j^2} \tag{2}$$

where $d_j = \beta_j^{obs} - \Gamma l \, p_j^{obs}$

and n is the number of readings.

This method assumes that all readings have the same absolute accuracy (142).

To obtain the absolute intensity Γ the cell length l has to be known. Since the cells are quite long, approx. 10 cm. for the grating spectrometer and approx.100 cm. for the interferometer they can be measured with sufficient accuracy using a ruler (plus calipers for the shorter cell).

As previously mentioned the pressure is measured using a Glycol manometer and therefore y, the pressure in centimeters of Glycol, must be translated into suitable concentration units. It is assumed that the sample vapour obeys the ideal gas laws, so that one mole of gas occupies $2.24136.10^4$ cm^3 at one atmosphere pressure ($1.01325.10^6$ $dyne.cm^{-2}$) and $273.15^{o}K$. Therefore it follows that

$$\text{Concentration} = \frac{y}{(273.15 + T)} \quad 1.316168 \times 10^{-5} \ \text{mole.cm}^{-3} \qquad 3$$

where T is the temperature in degrees Centigrade

and y is the pressure in centimeters of Glycol.

The density of Ethylene Glycol is taken as 1.1155 $g. cm^{-3}$ and this and all other values are taken from Kaye and Laby (1).

Therefore, if l is measured in centimeters, it follows that the units of Γ are $cm^2.mole^{-1}$. It is usually expressed in these units since then it has a value of between 1 and 10^4 for most fundamentals. If w, the frequency of the band centre, is in cm^{-1} and c, the velocity of light, 2.997925 $cm.sec^{-1}$ (1), it follows from equation 21, section 5.4, that the units of $(\partial\mu/\partial Q)$ are $cm^{3/2}.sec^{-1}$. The most convenient units for dipole moments are debyes

(ID. = 10^{-18} $g.^{\frac{1}{2}}$ $cm^{5/2}sec^{-1}$) so initially dipole moments must be expressed in $g^{\frac{1}{2}}cm^{5/2}sec^{-1}$. The dimensions of the normal coordinates Q are $mass^{\frac{1}{2}}$ x length and if the units are $g^{\frac{1}{2}}.cm$ then $(\partial\mu/\partial Q)$ is indeed in $cm^{3/2}sec^{-1}$. However on the molecular scale Q is usually expressed in $amu^{\frac{1}{2}}$ A. From equation 21, section 5.4, it follows that

$$\pm\left[\frac{\partial\mu}{\partial Q}\right] = \frac{C}{N}\left[\frac{3w\,\Gamma}{\pi}\right]^{\frac{1}{2}} N^{\frac{1}{2}} \qquad 4$$

If c/N = 4.9779 x 10^{-14} using the values from Kaye and Laby (1) and w and Γ have the previously discussed units, then evaluating equation 4 for typical values of w and Γ it will be found that

$$\pm(\partial\mu/\partial Q) = x.N^{\frac{1}{2}}.10^{-10}\ cm^{3/2}.sec^{-1}$$

where x has a value between .1 and 2.

Therefore $\quad \pm(\partial\mu/\partial Q) = x.N^{\frac{1}{2}}.10^{-10}\ \dfrac{g^{\frac{1}{2}}\ cm^{5/2}\ sec^{-1}}{g^{\frac{1}{2}}.cm}$

Since $\quad$ 1g. = N amu

and $\quad$ 1 cm = 10^8A

it follows that

$$\pm(\partial\mu/\partial Q) = x\ amu^{-\frac{1}{2}}\ D.A^{-1}$$

The eigen vector matrix L has units of $amu^{-\frac{1}{2}}$ (since $LL^t=G$). Therefore from equations 40, 41 and 42, section 5.7, it follows that the elements of the matrix $\{\partial\mu/\partial R\}$, the bond moment derivatives, have units of Debyes per Angstrom ($D.A^{-1}$) and the elements of the matrix $\{\mu\}$, the bond moments, have units of Debyes (D).

SECTION 6.2 The 1,4 difluoro Benzene Bands.

836.6 cm^{-1} Band. The spectra were recorded using a Perkin-Elmer 325 spectrometer scanning over the range 900 to 780 cm^{-1}. The sample was contained in a glass cell, length 9.35 cm, with Potassium Bromide windows sealed with selastomer. The sample pressure was between 13 and 4 cm of Glycol. Each spectrum was scanned once using a spectrometer slit width of 0.9 cm^{-1} and then the Q branch was scanned again using a slit width of 0.4 cm^{-1}, to avoid errors through inadequate resolution of the narrow Q branch. A redrawn spectrum is shown in Figure 6.1, together with the various spectrometer settings. The origin of the band at 834 cm^{-1} is not clear as it is too intense to be a normal hot band. Its most probable explanation is as a $(v_k + v_i - v_i)$ type hot band as described by Jones (143). Also there is a very weak combination band on the high frequency side of the fundamental. Following Crawford (125) both these bands are included in the summation when measuring the area. The graph of Area versus Concentration is shown in Figure 6.2 and the experimental results in Table 6.1. No measurements were taken using Nitrogen broadening.

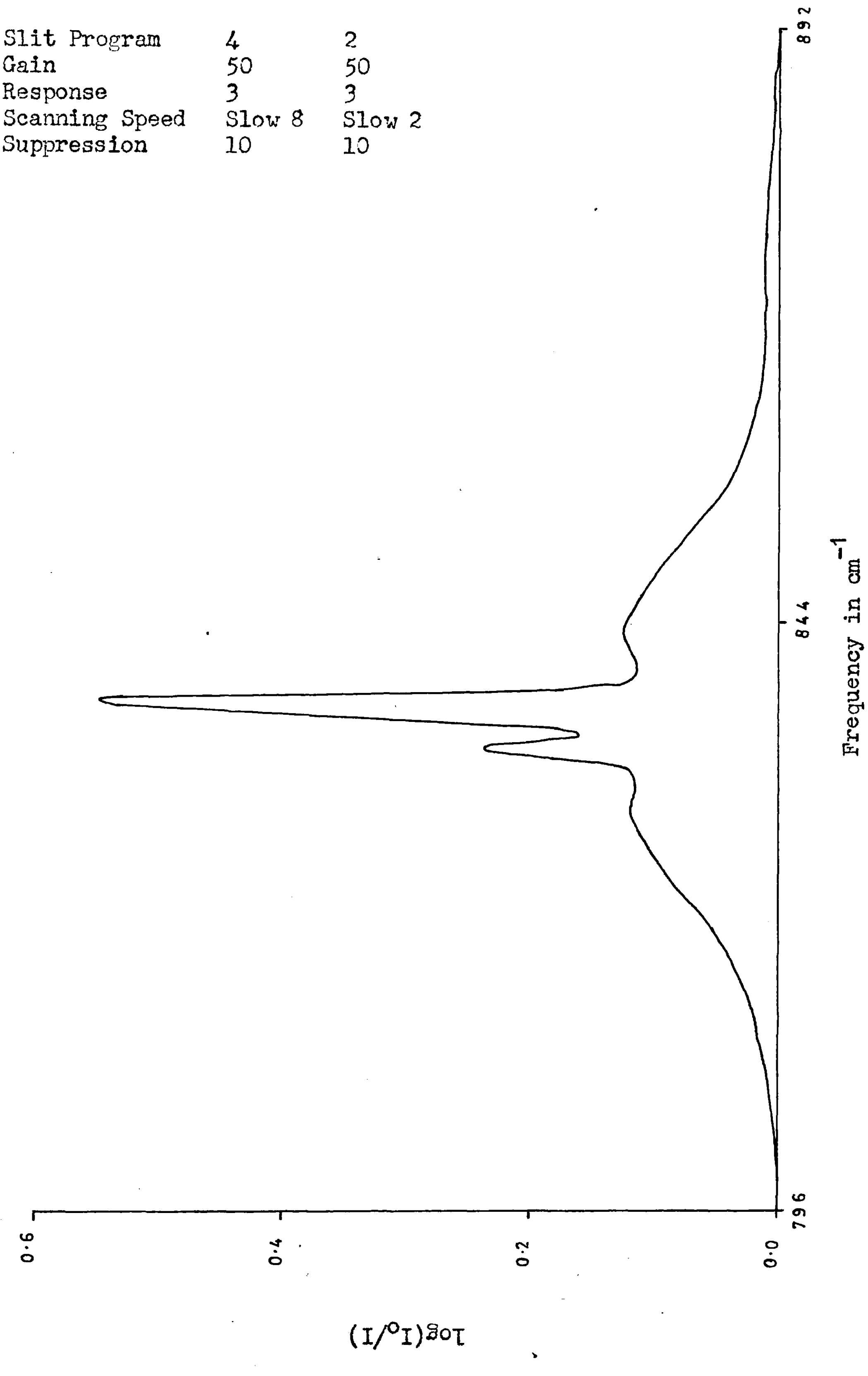
505.0 cm^{-1} Band. The spectra were recorded using a Perkin-Elmer 325 spectrometer scanning over the range 570 to 450 cm^{-1}. The sample was contained in the cell described above and the sample pressure was between 10 and 38 cm. of Glycol. The spectrometer slit widths were 1.65 cm^{-1} and 0.8 cm^{-1} for the Q branch. Aredrawn spectrum is shown in Figure 6.3, together with the spectrometer settings. The graph of Area versus Concentration is shown in Figure 6.4 and the experimental results in Table 6.2. No measurements were taken using Nitrogen broadening.

157 cm^{-1} Band. The spectra were recorded using a Grubb-Parsons cube interferometer. The sample was contained in a glass cell, length 107 cm, with Polyethylene windows and it is an integral part of the interferometer. (The optical diagram is shown in Figure 2.). The sample pressures were between 5 and 11 cm of Glycol. A background spectrum was recorded first (in Fourier Transform form on punched tape) then a series of sample spectra. The 100% absorption line is automatically computed. The tapes were processed using an Autocode program, which gives spectra in the form I (sample + background) - I (background) equals I (sample) i.e. the computer simulates a double beam instrument with an evacuated cell in the reference beam. The background (or I_0 line) is drawn by hand on the sample spectrum as a straight line joining the parts on each side of the band where no absorption occurs. The resolution or apparent slit width was 1 cm^{-1} (i.e. the fourier transform was recorded 5mm either side of top dead centre (144)) with output points every .5 cm^{-1} and the spectra were computed between 100 and 250 cm^{-1}. A redrawn spectrum is shown in Figure 6.5

and although the band envelope is not smooth (due to random noise rather than rotational fine structure) the graph of Area versus Concentration, shown in Figure 6.6, is a straight line in accordance with Beer's Law. The experimental results are given in Table 6.3. No measurements were taken using Nitrogen broadening.

Figure 6.1 Band Shape of 836.6 Band

Slit Program	4	2
Gain	50	50
Response	3	3
Scanning Speed	Slow 8	Slow 2
Suppression	10	10



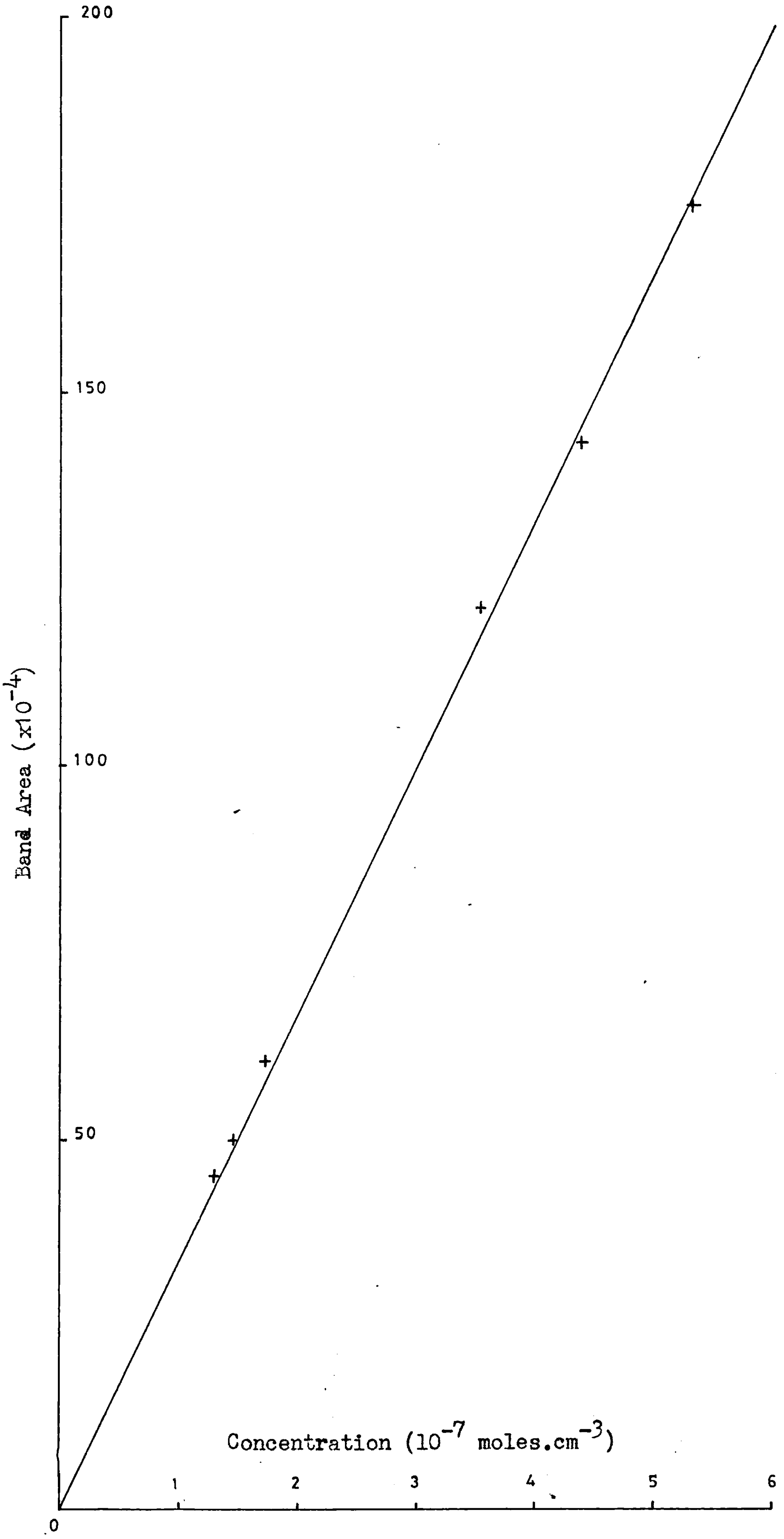


Figure 6.2 Beer's Law Plot for the 836.6 Band

The Absolute Infrared Intensity of the 836.6 cm^{-1} Band

CONCENTRATION	AREA
5.318	175.924
4.377	144.815
3.523	121.995
1.718	60.165
1.440	49.873
1.304	45.107
$x10^{-7}$	$x10^{-4}$

$\Gamma l=(33.544 \pm .326)x2.3026x10^{3}$

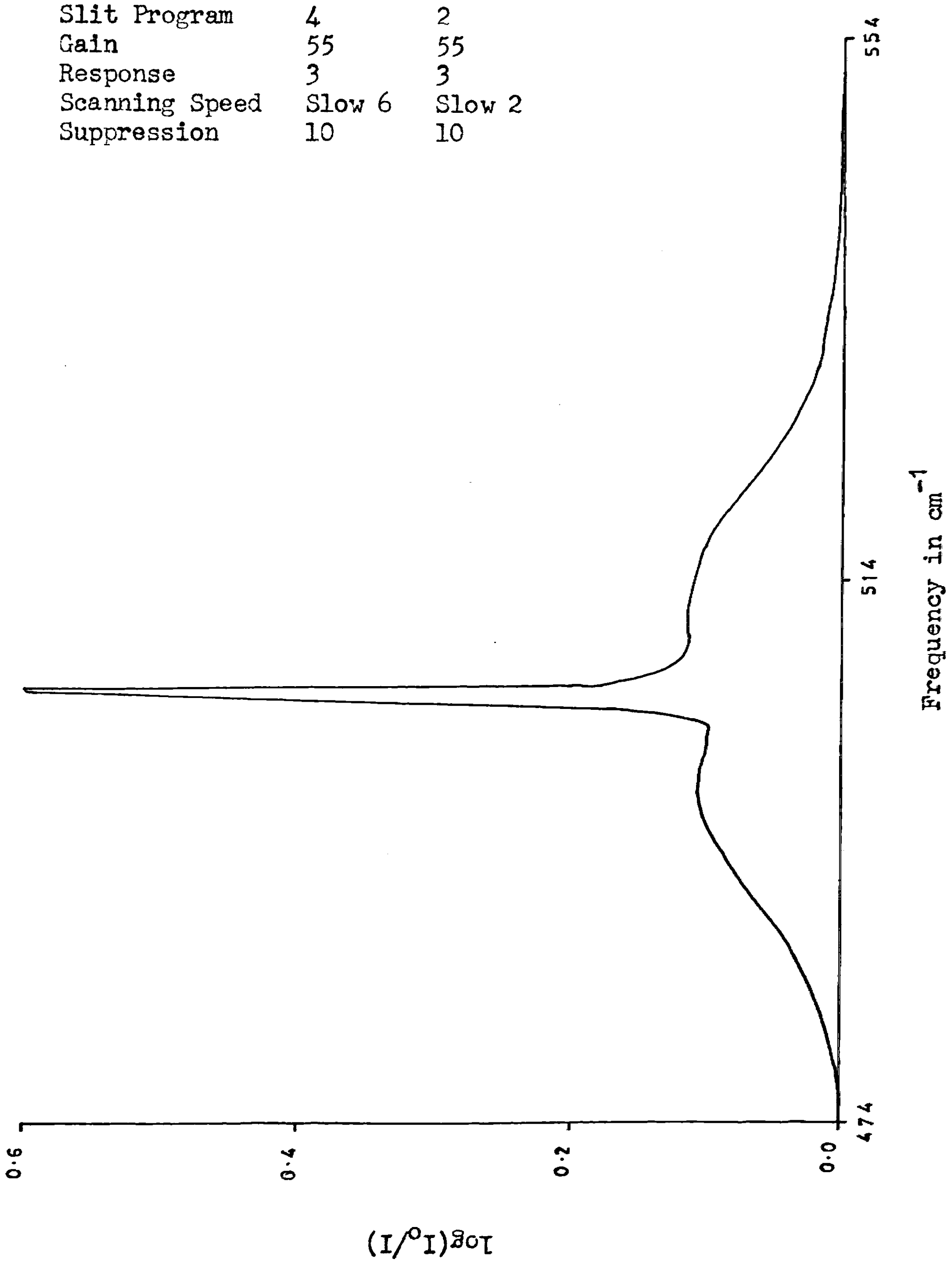
$l=9.35$ cm

$\Gamma=8261 \pm 80$ $mole^{-1}cm^{2}$

Table 6.1

Figure 6.3 Band Shape of 505.0 Band

Slit Program	4	2
Gain	55	55
Response	3	3
Scanning Speed	Slow 6	Slow 2
Suppression	10	10



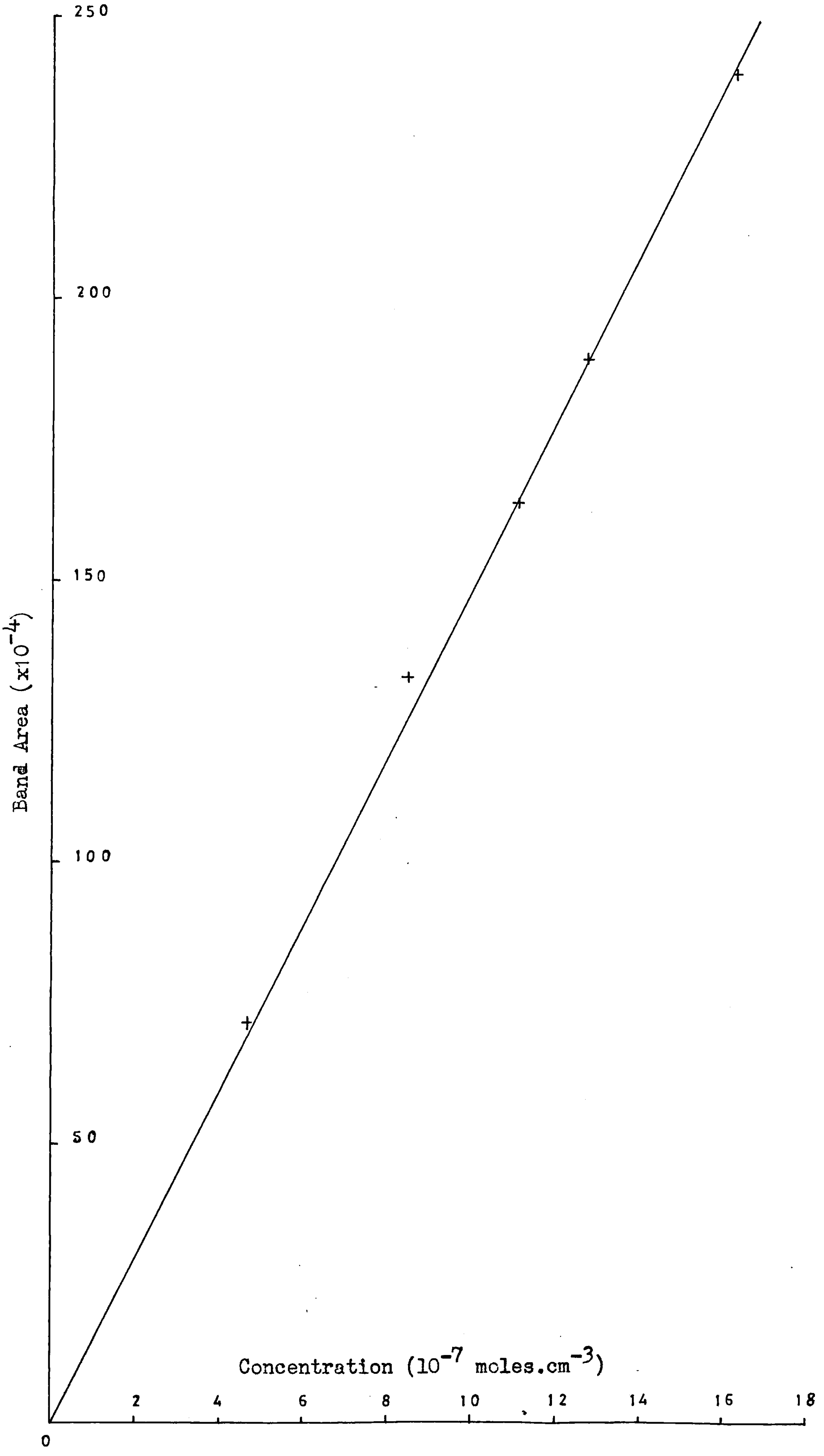


Figure 6.4 Beer's Law Plot for the 505.0 Band

The Absolute Infrared Intensity of the 505 cm^{-1} Band

CONCENTRATION	AREA
16.308	242.829
12.651	189.241
11.080	164.464
8.482	132.103
4.638	70.579
$x10^{-7}$	$x10^{-4}$

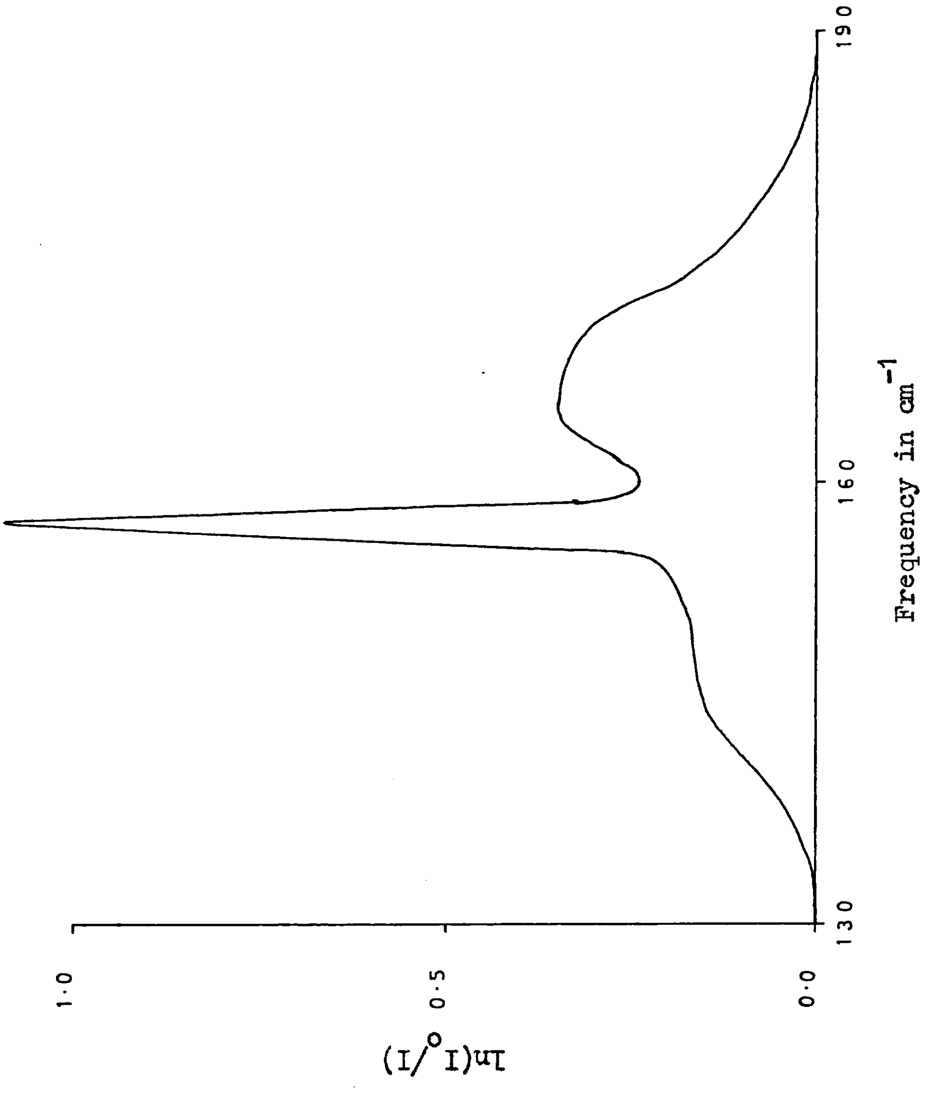
$\Gamma l=(14.985 \pm .110) x 2.3026 x 10^{3}$

$l=9.35$ cm

$\Gamma=3690 \pm 27$ $mole^{-1} cm^{2}$

Table 6.2

Figure 6.5 Band Shape of 157.C Band



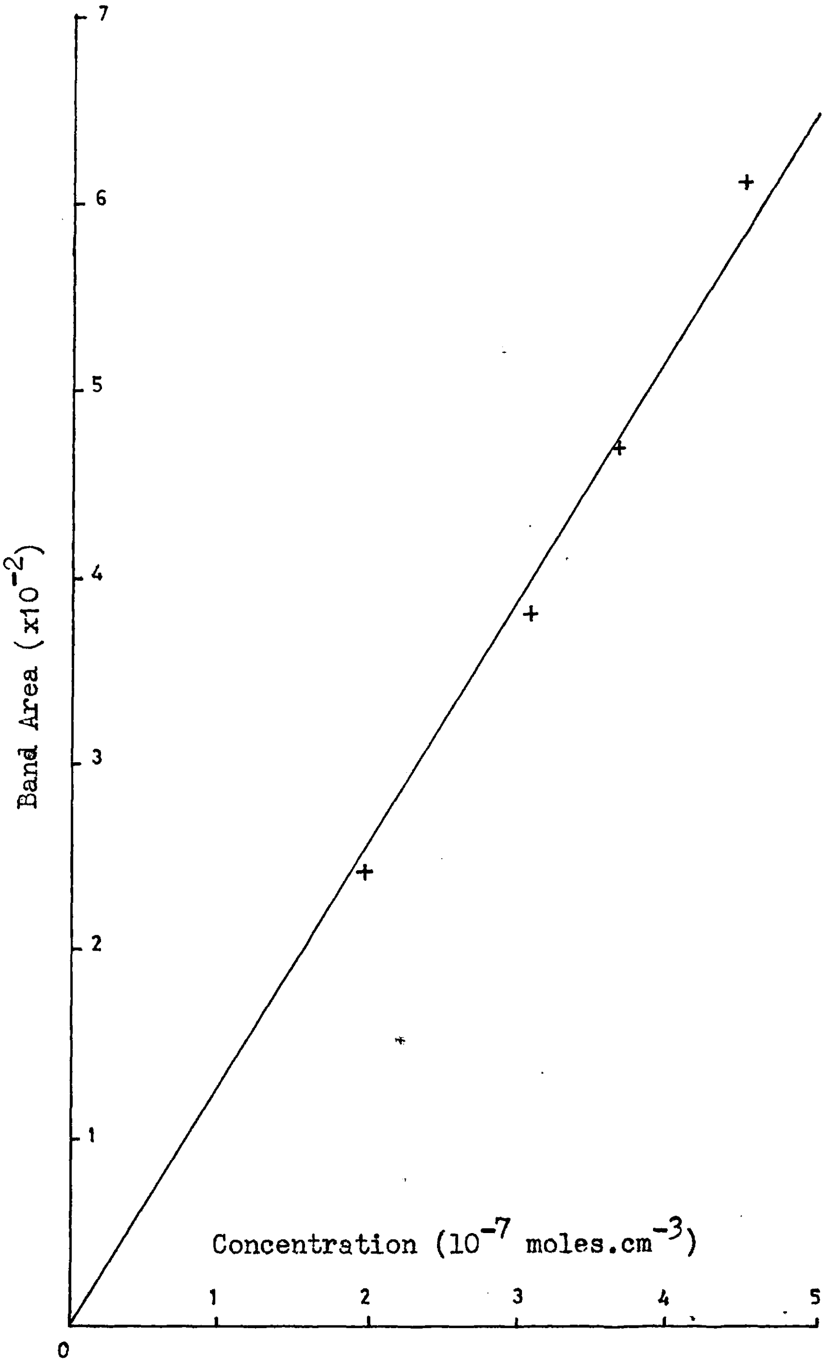


Figure 6.6 Beer's Law Plot for the 157.0 Band

The Absolute Infrared Intensity of the 157.0 cm^{-1} Band

CONCENTRATION	AREA
4.526	6.110
3.644	4.685
3.072	3.790
1.959	2.400
$x10^{-7}$	$x10^{-2}$

$\Gamma l=(1.298\pm.028)x10^{5}$

$l=107.0$ cm

$\Gamma=1213\pm27$ $mole^{-1}cm^{2}$

Table 6.3

The absolute infra red intensities and the dipole moment derivatives of the b_{3u} vibrations of 1,4 difluoro Benzene are given in Table 6.4.

BAND (cm^{-1})	($mole^{-1}cm^{2}$)	$\pm\ \partial\mu/\partial Q$ ($amu^{-\frac{1}{2}}DA^{-1}$)
836.6	8261	1.279
505.0	3690	.664
157.0	1213	.212

Table 6.4

Steele and Whiffen (145), in an earlier study, recorded the intensities of some of the fundamental bands of 1,4 difluoro Benzene including the two higher b_{3u} fundamentals. The values they obtained for the dipole moment derivatives, 1.24 $amu^{-\frac{1}{2}}$ $D.A^{-1}$ for the 836.6 cm^{-1} band and 0.55 $amu^{-\frac{1}{2}}$ $D.A^{-1}$ for the 505.0 cm^{-1} band, are in reasonable agreement with the values obtained here.

No error values are shown in Table 6.4, though they are for the intensities in Tables 6.1 to 6.3. They are calculated assuming that there is the same percentage error in Γ as in Γl, though uncertainties of the order of 1% might be expected in the value of l for the shorter cell. These errors are small, never greater than 3%, and much less than the estimate of 10% sometimes given for absolute intensities, see (146). The estimation of errors in $\partial\mu/\partial Q$ and $\partial\mu/\partial S$ has been studied by Russel et.al.(146) but their exhaustive statistical approach was not attempted here. However, although no errors are shown, they do exist and therefore exact agreement must not be expected when comparing bond moment and bond moment derivative values of similar molecules.

SECTION 6.3 The 1,3,5 trifluoro Benzene Bands

847.6 cm^{-1} Band. The spectra were recorded on a Perkin-Elmer 325 spectrometer scanning over the range 900 to 780 cm^{-1} and using the cell described in Section 6.2. Due to the high intensity of the band it was only possible to record spectra, which were not too intense at the Q branch for accurate measurement of ln (I_o/I), at low pressures (2 to 4 cm of Glycol), which have a high percentage error. Therefore the concentrations were measured using the P and R branch maxima. First spectra were recorded using pressures in the range 5 to 15 cm. of Glycol and graphs of log (I_o/I) at the P and R branch maxima versus Concentration plotted. They are shown in Figure 6.8. Then for the bands whose area could be measured, log (I_o/I) at the P and R branch maxima were measured and from these values the concentration calculated. Measurements were made on both unbroadened and Nitrogen broadened spectra but the sample concentrations were measured prior to the introduction of the Nitrogen. The two graphs of Area versus Concentration are shown in Figure 6.9 and the experimental results in Tables 6.5 and 6.6. It is seen that there is no apparent deviation from Beer's law for either curve and that the use of Nitrogen broadening causes an increase of 2.9% in the measured intensity. A redrawn spectrum is shown in Figure 6.7 and it is seen to be a fairly typical parallel band of a symmetric top molecule. Each spectrum was scanned once using a spectrometer slit width of 0.9 cm^{-1} and then the Q branch was scanned again using a slit width of 0.4 cm^{-1}.

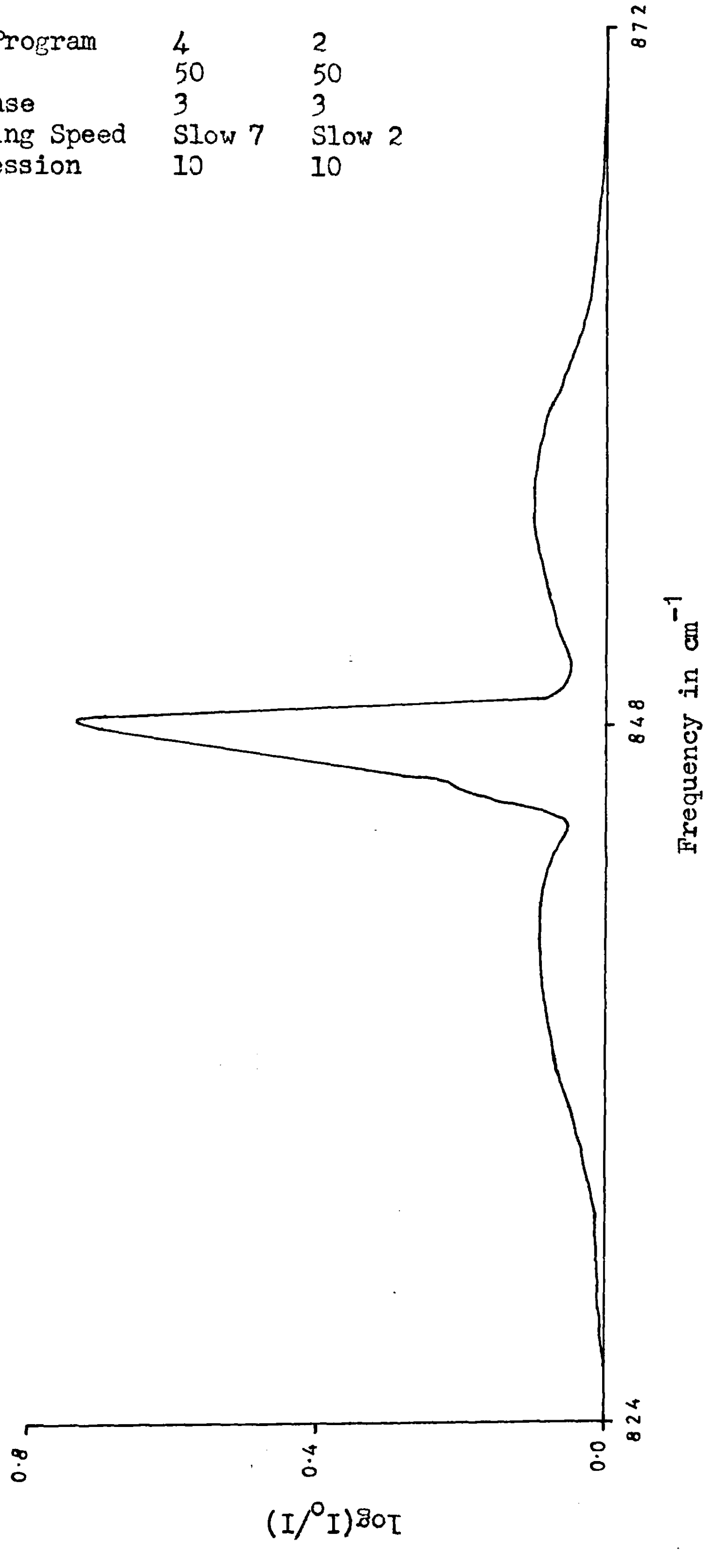
664.1 cm^{-1} Band. The spectra were recorded on a Perkin-Elmer 325 spectrometer scanning over the region 720 to 600 cm^{-1} and using the 9.35 cm cell described in section 6.2. The spectrometer slit widths were 0.9 cm^{-1} and 0.4 cm^{-1} for the Q branch. A redrawn spectrum is shown in Figure 6.10 and again it is a fairly typical parallel band of a symmetric top apart from the fact that the P branch is slightly more intense than the R branch (see also figure 6.11). This is probably due to second order coriolis interaction with another band. There is also a small peak on the R branch at 674 cm^{-1} the origin of which is not clear. The sample concentrations were measured using the P and R branch maxima. These were recorded using sample pressures of between 10 and 17 cm. of Glycol and the graphs of log (I_0/I) versus Concentration are shown in Figure 6.11. Measurements were made on both unbroadened and Nitrogen broadened spectra. The two graphs of Area versus Concentration are shown in Figure 6.12 and the experimental results in Tables 6.7 and 6.8. Again both curves appear to obey Beer's law and the use of Nitrogen broadening causes an increase in band area of 3.9%.

In recording the spectra for this band a difficulty was encountered due to the very intense CO_2 band at 667.6 cm^{-1}. By placing trays containing Potassium Hydroxide in the sample well of the spectrometer some of the Co_2 was removed from the air inside it. The remaining CO_2 still absorbed strongly but it was now possible to record spectra over the entire band except for a narrow region between 669.6 and 665.6 cm^{-1}. This region of the spectrum was obtained by extrapolation of the traces from either side. It is possible that uncertainties due to the presence of CO_2 caused the decrease in R branch intensity.

205.6 cm^{-1} Band. The spectra were recorded using a Grubb-Parsons cube interferometer, as described in Section 6.2. The sample pressures were between 8 and 42 cm of Glycol. The resolution was 1.667 cm^{-1} (i.e. the fourier transforms were recorded 3 mm either side of top dead centre) with output points every .833 cm^{-1} and the spectra were computed between 100 and 400 cm^{-1}. A redrawn spectrum is shown in Figure 6.13 and it can be seen that the band envelope is much smoother than that for 1,4 difluoro Benzene, (Figure 6.5). Even so it was not possible to obtain a satisfactory Beer's law plot of log (I_o/I) versus Concentration for the P branch maxima although the much stronger R branch maxima do give a satisfactory plot as can be seen from Figure 6.14. The graph of Area versus Concentration shown in Figure 6.15 also obey Beer's law. The experimental results are given in Table 6.9. No measurements with Nitrogen broadening were made due to difficulties through water vapour being introduced with the Nitrogen. The results for the other two bands indicate that any errors due to incomplete broadening of the spectra would be slight.

Figure 6.7 Band Shape of 847.6 Band

Slit Program	4	2
Gain	50	50
Response	3	3
Scanning Speed	Slow 7	Slow 2
Suppression	10	10



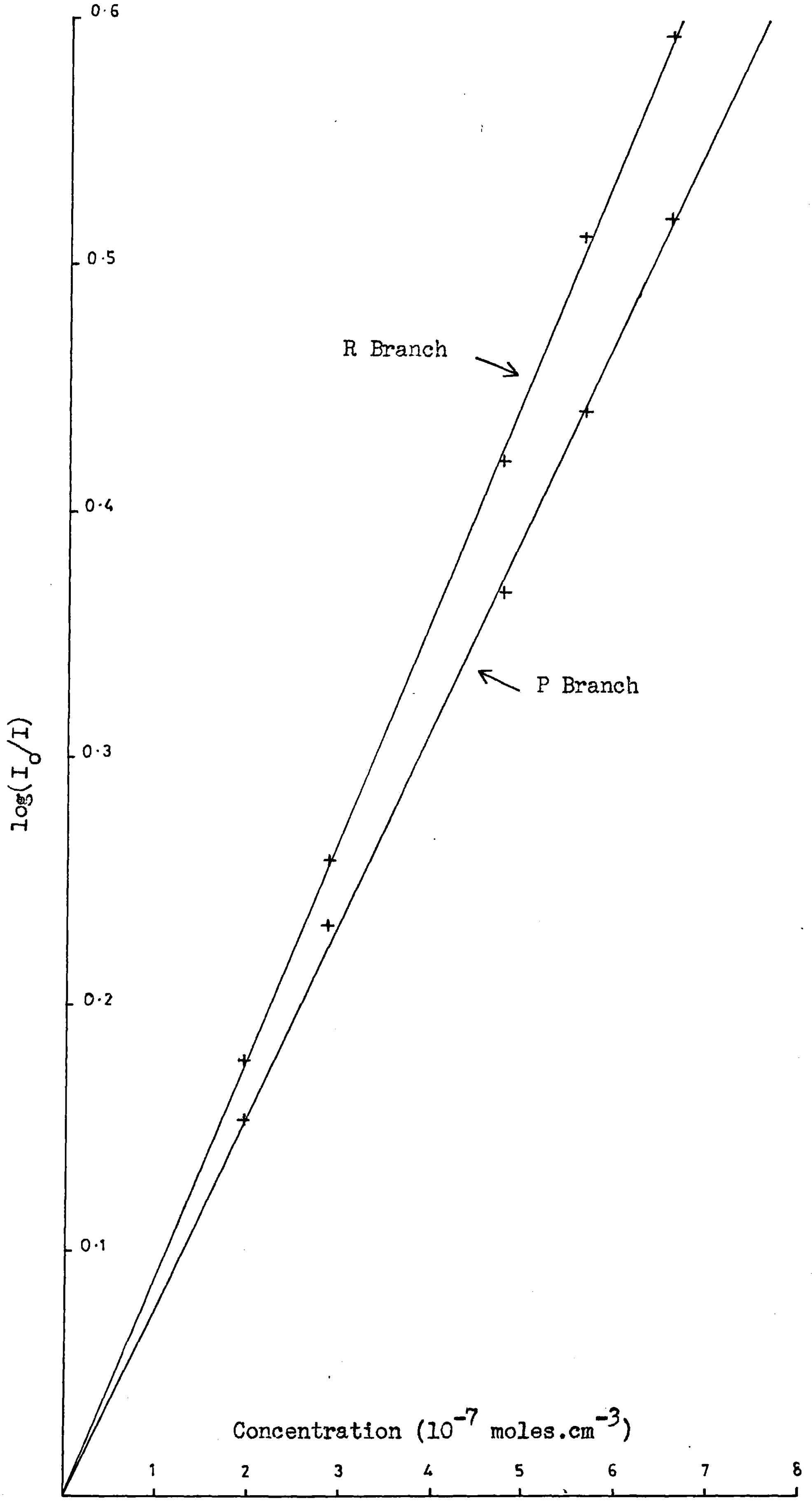


Figure 6.8 Beer's Law Plots for the P and R Branch Maxima for the 847.6 Band

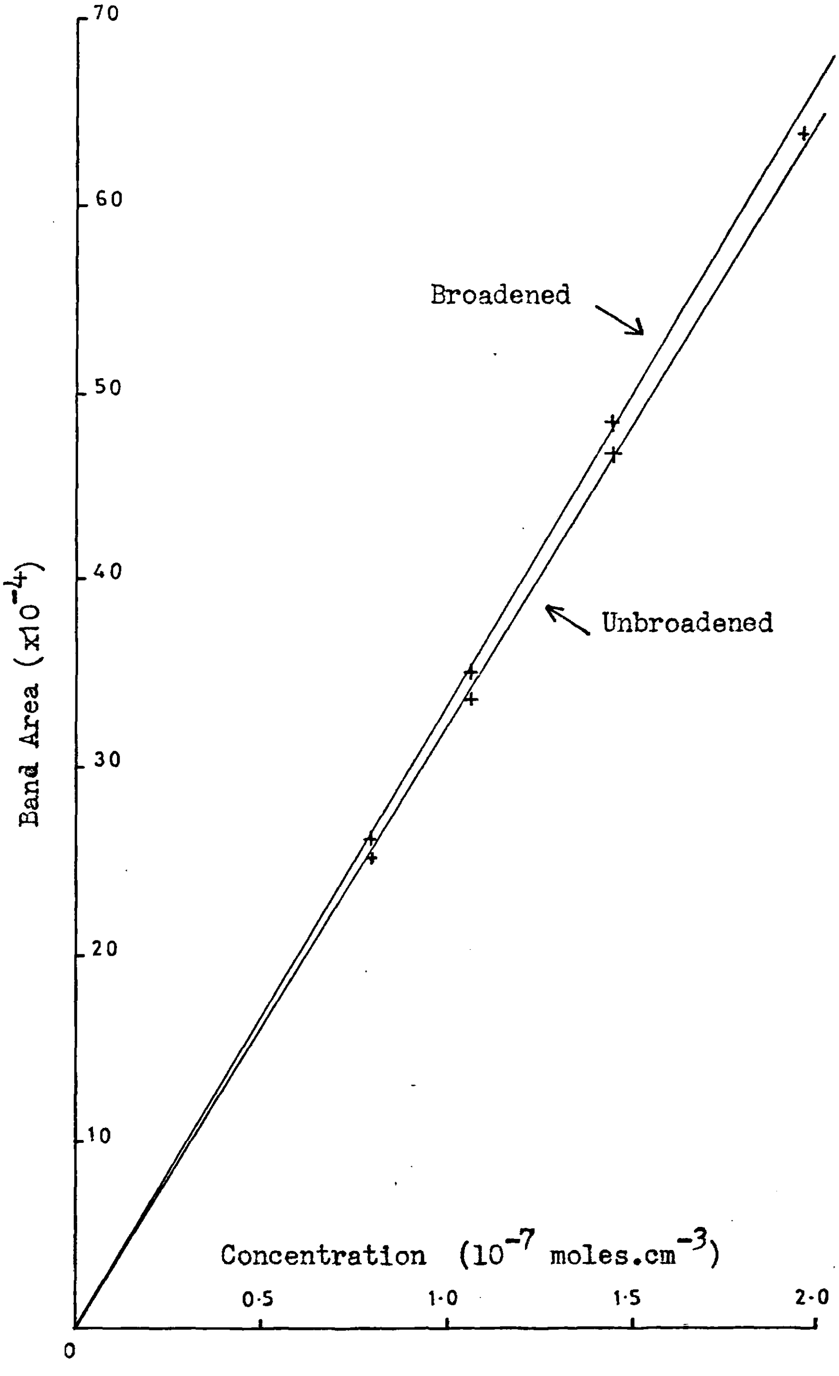


Figure 6.9 Beer's Law Plots for the 847.6 Band

The Absolute Infrared Intensity of the 847.6 cm^{-1} Band
(Unbroadened)

CONCENTRATION	AREA
1.954	63.925
1.4365	46.814
1.061	33.650
0.793	25.539
$x10^{-7}$	$x10^{-4}$

$\Gamma l=(32.491\pm.203)x2.3026x10^{3}$

$l=9.35$ cm

$\Gamma=8001\pm50$ $mole^{-1}cm^{2}$

Table 6.5

The Absolute Infrared Intensity of the 847.6 cm^{-1} Band
(Nitrogen Broadened)

CONCENTRATION	AREA
1.4365	48.520
1.061	35.127
0.793	26.088
$x10^{-7}$	$x10^{-4}$

$\Gamma l=(33.434\pm.267)x2.3026x10^{3}$

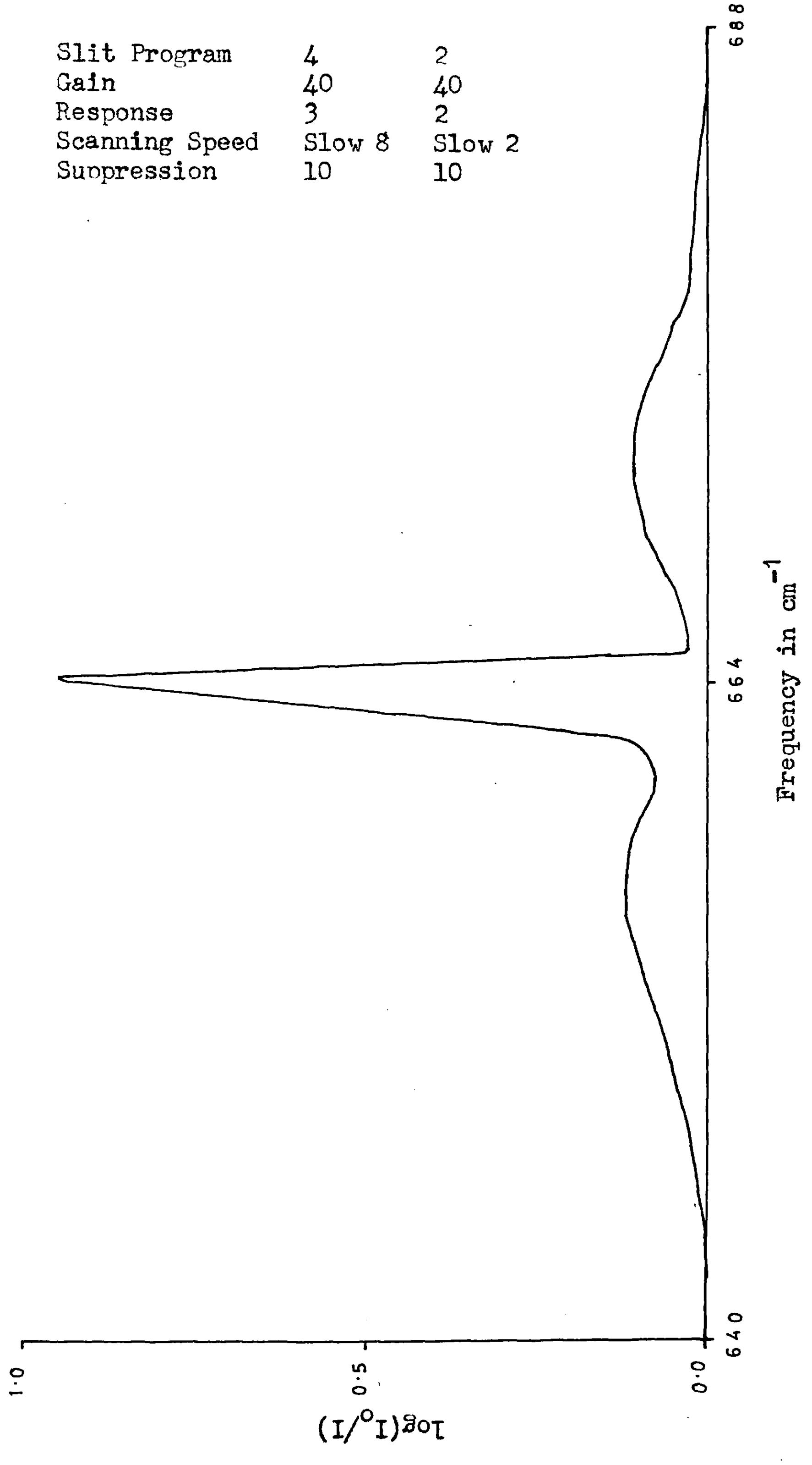
$l=9.35$ cm

$\Gamma=8234\pm66$ $mole^{-1}cm^{2}$

Table 6.6

Figure 6.10 Band Shape of 664.1 Band

Slit Program	4	2
Gain	40	40
Response	3	2
Scanning Speed	Slow 8	Slow 2
Suppression	10	10



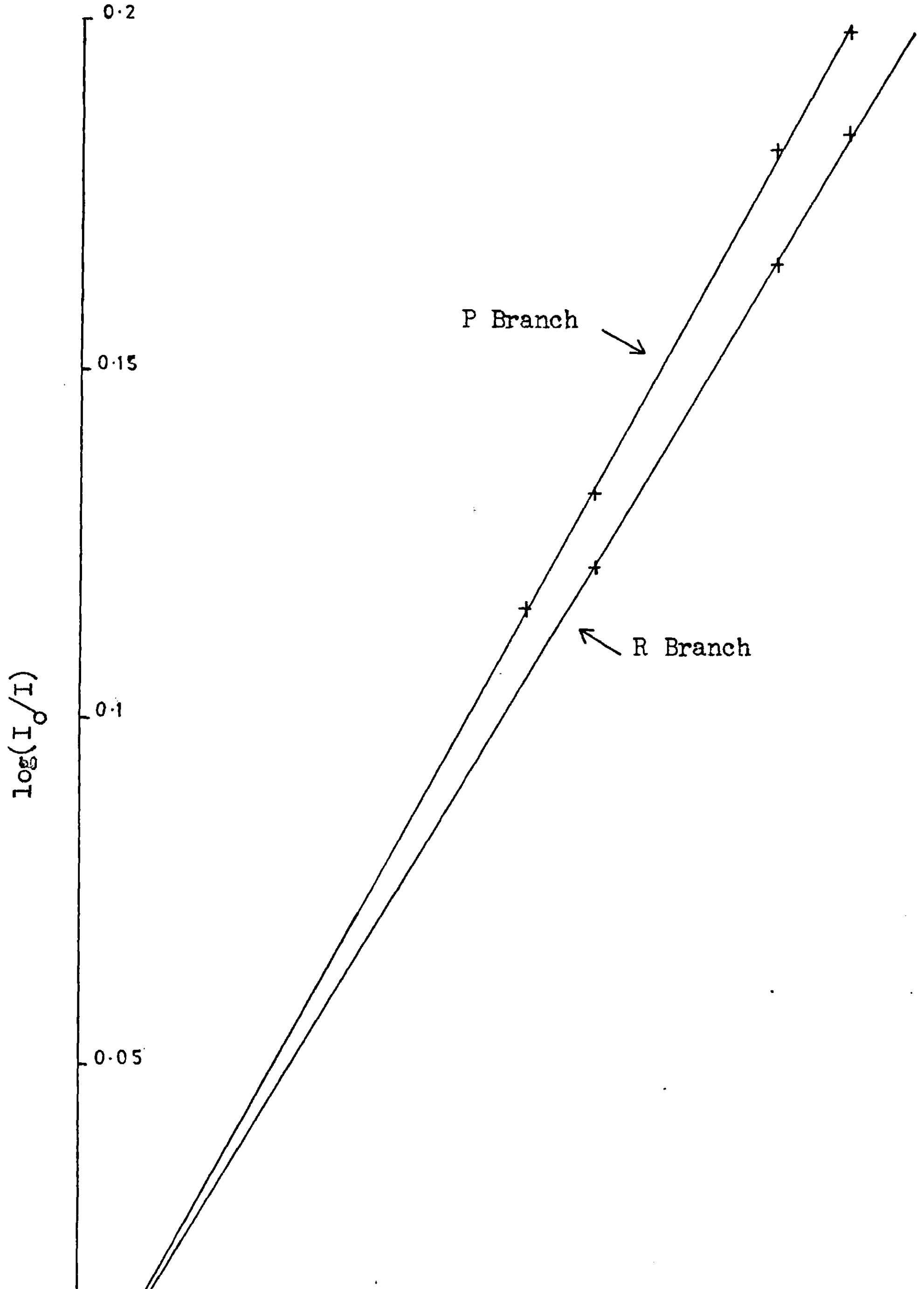


Figure 6.11 Beer's Law Plots for the P and R Branch Maxima for the 664.1 Band

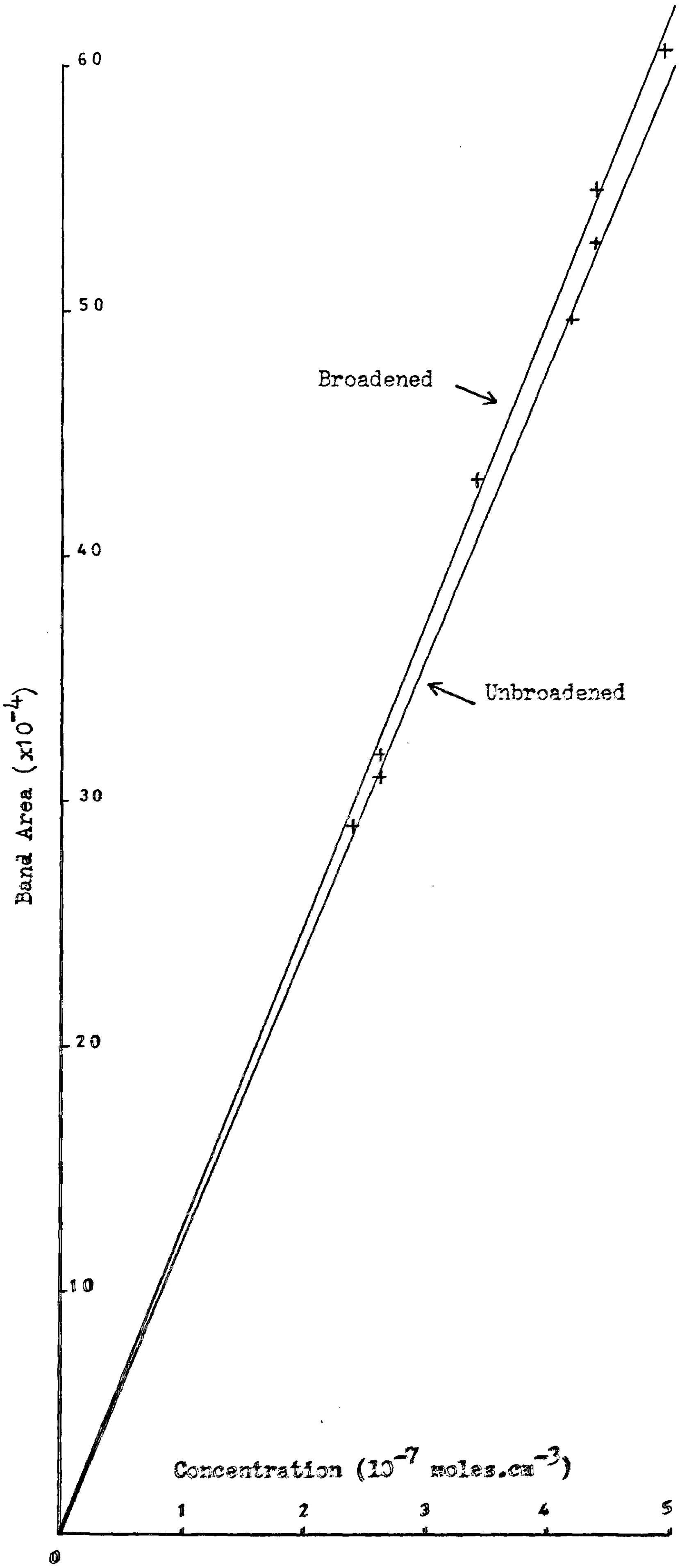


Figure 6.12 Beer's Law Plots for the 664.1 Band

The Absolute Infrared Intensity of the 664.1 cm^{-1} Band (Unbroadened)

CONCENTRATION	AREA
4.361	52.818
4.1575	49.728
2.6015	31.068
2.396	29.021
$x10^{-7}$	$x10^{-4}$

$\Gamma l=(12.034\pm.044)x2.3026x10^{3}$

$l=9.35$ cm

$\Gamma=2964\pm11$ $mole^{-1}cm^{2}$

Table 6.7

The Absolute Infrared Intensity of the 664.1 cm^{-1} Band (Nitrogen Broadened)

CONCENTRATION	AREA
4.914	60.876
4.367	55.117
3.401	43.024
2.6015	31.988
$x10^{-7}$	$x10^{-4}$

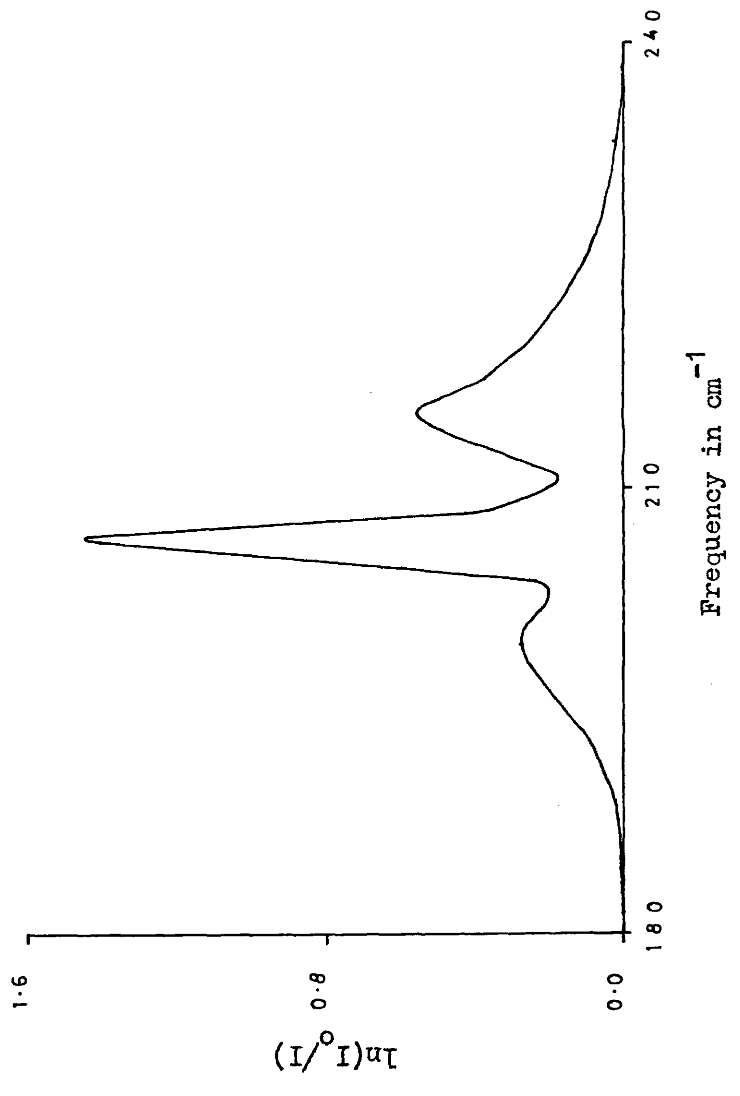
$\Gamma l=(12.499\pm.078)x2.3026x10^{3}$

$l=9.35$ cm

$\Gamma=3078\pm19$ $mole^{-1}cm^{2}$

Table 6.8

Figure 6.13 Band Shape of 205.6 Band



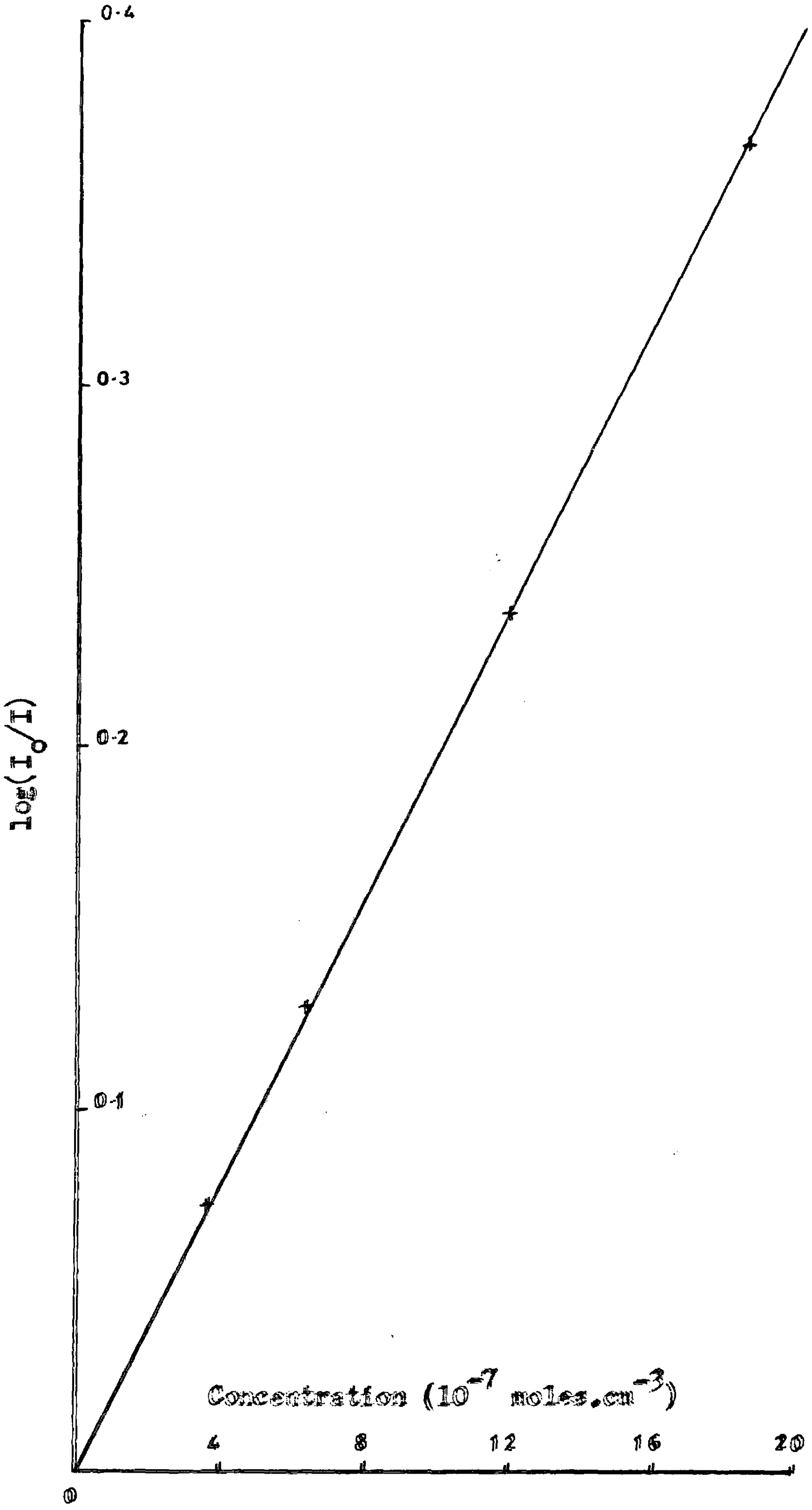


Figure 6.14 Beer's Law Plot for the R Branch Maxima for the 205.6 Band

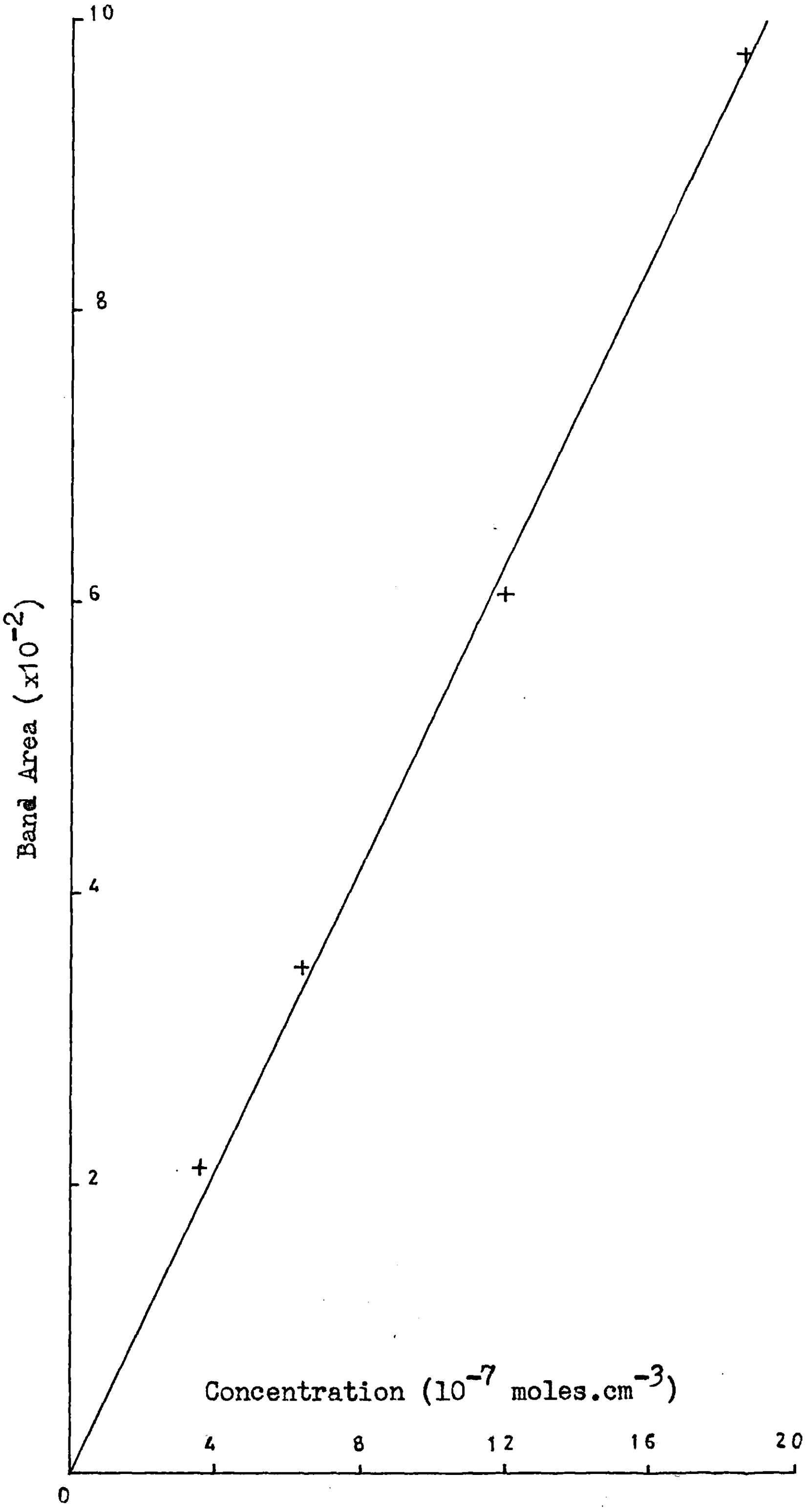


Figure 6.15 Beer's Law Plot for the 205.6 Band

The Absolute Infrared Intensity of the 205.6 cm^{-1} Band (Unbroadened)

CONCENTRATION	AREA
18.543	9.765
11.902	6.043
6.332	3.481
3.606	2.106
$\times 10^{-7}$	$\times 10^{-2}$
$\Gamma l = (0.525 \pm .008) \times 10^{5}$ $l = 107.0$ cm $\Gamma = 490 \pm 8$ mole^{-1}cm^{2}	

Table 6.9

The absolute infra red intensities and the dipole moment derivatives of the a_2'' vibrations of 1,3,5 trifluoro Benzene are given in Table 6.10.

BAND (cm^{-1})	($mole^{-1}cm^2$)	$\pm\partial\mu/\partial Q$ ($amu^{-\frac{1}{2}}D.A.^{-1}$)
847.6	8234	1.285
664.1	3078	.695
205.6	490	.154

Table 6.10

No other experimental values for the dipole moment derivatives of 1,3,5 trifluoro Benzene exist in the literature. However, these values can be checked using the band maximum technique (see Section 6.4).

Again, no error values are given in Table 6.10 and remarks, similar to those given for 1,4 difluoro Benzene, apply here.

<u>SECTION 6.4</u> Calculation of Intensity by Band Maximum technique.

The method of calculating the band shapes of non-degenerate vibrations of symmetric tops has been developed by Gerhard and Dennison (147). Edgell and Moynihan extended the method to include degenerate vibrations (148) and suggested that the dipole moment derivates of both degenerate and non-degenerate vibrations can be calculated by a comparison of calculated and experimental intensities at certain points on the band under consideration (149). Steele and Wheatley (50, 150) applied the method to Benzene and Hexafluoro Benzene, comparing the intensities at the P and R branch maxima. 1,3,5 trifluoro Benzene is an oblate symmetric top (i.e. the moments of inertia A and B are equal and are smaller than C, the moment of inertia about the axis perpendicular to the plane of the molecule) and the method is applied to the A_2'' bands (or parallel bands since the oscillating dipole is parallel to the unique C axis) to check on the experimental intensities.

The absorption coefficient at frequency v, a(v) arising from a given rotational-vibrational transition of energy hv is given by the Honl-London expression (151) and (152), p.421,

$$a(v) = \bar{C}\ v_{JK}A_{JK}g_{JK}\exp(-F_{JK}hc/kT).I^2 \qquad 5$$

where J and K are the rotational quantum numbers,

v_{JK} is the rovibrational transition frequency,

A_{JK} is a term proportional to the square of the transition moment summed over all orientations of J,

g_{JK} is the statistical weight factor of the lower state,

F_{JK} is the rotational term value of the lower state,

$\bar{C}$ is a normalization factor,

and I is the transition integral discussed in section 5.2.

The selection rules for the parallel bands of symmetric tops are,

if $K \neq 0$ $\quad \Delta K = 0$ and $\Delta J = 0, \pm 1$

if $K = 0$ $\quad \Delta K = 0$ and $\Delta J = \pm 1$

In the rigid-rotor harmonic-oscillator approximation, the transition frequencies are given by,

$\Delta J = +1$ (R branch) $\quad v^R = v_o + 2\underline{B}(J + 1)$

$\Delta J = 0$ (Q branch) $\quad v^Q = v_o$

$\Delta J = -1$ (P branch) $\quad v^P = v_o - 2\underline{B}J$

where v_o is the frequency of the band centre (i.e. fundamental frequency).

The terms A_{JK} are given by,

for $\Delta J = +1$ $\quad A_{JK} = \dfrac{(J + 1)^2 - K^2}{(J + 1)(2J + 1)}$

for $\Delta J = 0$ $\quad A_{JK} = \dfrac{K^2}{J(J + 1)}$

for $\Delta J = -1$ $\quad A_{JK} = \dfrac{J^2 - K^2}{J(2J + 1)}$

The statistical weight factor g_{JK} is given by,

for $K = 0$ $\quad 2J + 1$

for $K \neq 0$ $\quad 2(2J + 1)$

The rotational term value F_{JK} is given by

$$\underline{B}J(J + 1) + (\underline{C} - \underline{B})\, K^2$$

In all these expressions J and K are the rotational quantum numbers of the lower state and since J determines the total angular momentum and K determines a component of the angular momentum, J must be equal to or greater than K for any allowed rotational state (2), p.152.

The normalization factor $\bar{C}$ is given by (50),

$$\frac{8\pi^3 N}{3hc}\left[(hc\underline{B}/kT)^3\,\frac{(1-\underline{C}/\underline{B})}{\pi}\right]^{\frac{1}{2}} \qquad 6$$

The transition integral I is given by

$$\int \Psi^*(n'')\, \underline{\mu}\, \Psi(n')\, d\tau$$

From equation 14, section 5.2 it follows that for the 0→1 transition

$$I^2 = \frac{h}{8\pi^2 cw}\left[\frac{\partial\mu}{\partial Q}\right]^2$$

Therefore

$$a(v) = b(v)\,\frac{\bar{C}h}{8\pi^2 cw}\left[\frac{\partial\mu}{\partial Q}\right]^2 \qquad 7$$

where $b(v) = v_{JK}A_{JK}g_{JK}\exp(-F_{JK}hc/kT)$ $\qquad 8$

Provided that the rotational constants B and C are known, b(v) can be calculated. This is done using a computer, allowing K to vary from 0 to 300 and for a given value of K, J to vary from K to 300. The output values are not the individual values of b(v) but their sum b'(v) over a small frequency range dv.

Therefore $b'(v) = \sum_j b\,(v_j)$

where j varies from v + dv/2 to v - dv/2.

This is important since for heavy molecules the average absorption coefficient $\bar{a}(v)$ is related to the sum of the intensities within the frequency range dv, by (149)

$$\bar{a}(v) = \frac{\sum_j a(v_j)}{dv} \qquad 10$$

Provided that the band contour generated by the sum of the lines within this interval is smooth then

$$\bar{a}(v) = a(v)_{expt.} \qquad 11$$

for a given frequency v.

$a(v)_{expt}$ is the experimental intensity given by

$$a(v)_{expt} = \frac{1}{pl} \quad \ln \left[\frac{I_0(v)}{I(v)} \right] \qquad 12$$

Therefore substituting for $\bar{a}(v)$ using equation 10, a(v) using equation 7 and $\sum b(v)$ using equation 9, equation 11 becomes

$$a(v)_{expt} = \frac{b'(v)}{dv} \frac{\bar{C}h}{8\pi^2 cw} \left[\frac{\partial \mu}{\partial Q} \right]^2$$

Therefore $$\left[\frac{\partial\mu}{\partial Q}\right]^2 = \text{Fac} \quad \frac{w\ a(v)_{expt}\ dv}{b'(v)} \qquad 13$$

where $$\text{Fac} = \frac{8\pi^2 c}{\overline{C}h}$$

The units of: Fac are mole cm^2 sec^{-2}; w,dv and b'(v) are cm^{-1}; and $a(v)_{expt}$ mole^{-1} cm^2.

Therefore $\pm (\partial\mu/\partial Q) = x$ cm$^{3/2}$ sec^{-1}

Using arguments similar to those used in section 6.1, it follows that

$$\pm (\partial\mu/\partial Q) = x\ 10^{10}\ N^{-\frac{1}{2}}\ \text{amu}^{-\frac{1}{2}}\ D\ A^{-1}$$

It can be seen from equation 13 that to calculate the dipole moment derivative it is only necessary to compare the calculated and experimental intensities at one frequency. In practice it is more convenient to compare intensities at the P and R branch maxima rather than at specific frequencies.

<u>For 1,3,5 Trifluoro Benzene</u>,

the rotational constants $\underline{B}$ and $\underline{C}$ are given by the expressions

$$\underline{B} = \frac{h}{8\pi^2 cB} \qquad \text{and} \qquad \underline{C} = \frac{h}{8\pi^2 cC}$$

where B and C are the moments of inertia, the values of which are given in Appendix V. Therefore

$$\underline{B} = 5.88616.10^{-2}\text{cm}^{-1}$$
$$\underline{C} = 2.94308.10^{-2}\text{cm}^{-1}$$

The Normalization factor $\overline{C}$ at $T = 300^{\circ}K$ is

$$\overline{C} = 4.74375 \cdot 10^{35} \text{ mole}^{-1} \text{ erg}^{-1} \text{ cm}^{-1}$$

The values for the constants h,c,k and N are taken from Kaye and Laby (1).

The calculated values of $b'(v)$ for $dv = 0.1$ cm^{-1} and $T = 300^{\circ}K$ for the P and R branch maxima of the three a_2'' bands of 1,3,5 trifluoro Benzene are given in Table 6.11 and the experimental values of $a(v)$ (calculated from the curves in Figures 6.8, 6.11 and 6.14) are given in Table 6.12. The observed and calculated values of $\partial\mu/\partial Q$ are shown in Table 6.13.

The Dipole Moment Derivatives of 1,3,5 trifluoro Benzene
(A_2'' species)

BAND (cm^{-1})	$\pm(\partial\mu/\partial Q)_R$ (amu$^{-\frac{1}{2}}$DA^{-1})	$\pm(\partial\mu/\partial Q)_P$ (amu$^{-\frac{1}{2}}$DA^{-1})	$\pm(\partial\mu/\partial Q)_{OBS}$ (amu$^{-\frac{1}{2}}$DA^{-1})
846.7	1.19	1.14	1.29
664.1	0.62	0.67	0.70
205.6	0.16	-	0.15

Table 6.13

The agreement between observed and calculated values while not perfect is reasonable and similar to the agreement obtained by Wheatley (50) for the parallel bands of Benzene, Benzene d_6 and Hexafluoro Benzene.

b' (v) values for 1,3,5 trifluoro Benzene (A_2'' Species)

BAND	R BRANCH		P BRANCH	
(cm^{-1})	v	b' (v)	v	b' (v)
847.6	855.3	1.6700×10^6	840.1	1.5821×10^6
664.1	671.8	1.3123×10^6	656.6	1.2371×10^6
205.6	213.3	4.1647×10^5	198.1	3.7307×10^5

Table 6.11

a $(v)_{expt}$ values for 1,3,5 trifluoro Benzene (A_2'' Species

BAND	R BRANCH		P BRANCH	
(cm^{-1})	v	a (v)	v	a (v)
847.6	854.6	2.2787×10^5	839.8	1.9460×10^5
664.1	671.2	6.1271×10^4	656.2	6.6665×10^4
205.6	214.0	4.3190×10^3	-	-

Table 6.12

CHAPTER SEVEN The Rehybridization Moments

SECTION 7.1 Benzene and Hexafluoro Benzene

Benzene and Hexafluoro Benzene are both members of the D_{6h} symmetry point group and each molecule has three in plane infra red active fundamentals of the E_{1u} symmetry species and one out-of-plane infra red active fundamental of the A_{2u} symmetry species. The absolute infra red intensities of the fundamental vibrations of Benzene have been measured by Spedding and Whiffen (153) and also by Overend and Youngquist (154) and by Wheatley (50), who confirmed the earlier results of Spedding and Whiffen. Using the normal coordinates calculated by Whiffen for Benzene (12), Spedding and Whiffen (153) calculated four alternative sets of $\partial\mu/\partial S$ values for the E_{1u} fundamentals and used them to calculate intensity values for monodeutero Benzene and paradideutero Benzene. By comparing these values with the observed values, which they also measured, Spedding and Whiffen were able to deduce which was the correct set of solutions for Benzene. They also calculated intensity values for Hexadeutero Benzene, which were later measured by Dows and Pratt (155) who showed that the predictions of Spedding and Whiffen were correct. The dipole moment derivatives of the infra red active fundamentals of Benzene and Hexadeutero Benzene, together with the sign choice of Spedding and Whiffen (153) are given in Table 7.1. The changes in the dipole moments with respect to the changes in the internal coordinates ($\partial\mu/\partial R$) are given in Table 7.2. These values are taken from Steele and Wheatley (156) and were calculated from the dipole moment derivatives using the eigen vectors of Whiffen (12), as revised by Albrecht (157), and the relationships between $\partial\mu/\partial S$ and $\partial\mu/\partial R$ given by Spedding and Whiffen (153), (see also equations 28 and 30, Section 5.6). Steele and Wheatley (156) also calculated the $\partial\mu/\partial R$ values using the force fields for Benzene of Duinker and Mills (3,158) and Scherer (159) to obtain the eigen vectors and they found that the differencies between the values for the different force fields is small, especially for $\partial\mu/\partial\beta$. $\partial\mu/\partial y$ does not depend on the force field since the eigen vector for a 1 by 1 matrix is determined directly from the G matrix.

Using the bond moment hypothesis to interpret the $\partial\mu/\partial\beta$ and $\partial\mu/\partial y$ values in terms of the C - H bond moment gives the conflicting values of ± 0.32D (in plane bond moment) and ± 0.62D (out-of-plane bond moment). The inability of the bond moment hypothesis to explain results such as this is one of the reasons for its rejection. Steele and Wheatley (156) explained the difference between the $\partial\mu/\partial\beta$ and $\partial\mu/\partial y$ values as being due to

The Dipole Moment Derivatives of Benzene, Hexadeutero Benzene and Hexafluoro Benzene

MOLECULE	SYMMETRY SPECIES	BAND	$\partial\mu/\partial Q$	SIGN CHOICE
C_6H_6	E_{1u}	3080	0.843	+ -
		1486	0.393	+ or -
		1038	0.323	+ -
	A_{2u}	673	1.445	+ or -
C_6D_6	E_{1u}	2288	0.648	+ -
		1333	0.186	+ or -
		814	0.309	+ -
	A_{2u}	496	1.086	+ or -
C_6F_6	E_{1u}	1530	2.543	+ -
		1020	2.197	+ or -
		315	0.172	+ -
	A_{2u}	215	0.247	+ or -

Table 7.1

$\partial\mu/\partial R$ values for Benzene, Hexadeutero Benzene and Hexafluoro Benzene

MOLECULE	$\partial\mu/\partial\beta$ $(D.rad^{-1})$	$\partial\mu/\partial dr$ $(D.A^{-1})$	$\partial\mu/\partial dR$ $(D.A^{-1})$	$\partial\mu/\partial y$ $(D.rad^{-1})$
C_6H_6	± 0.316	± 0.465	± 0.001	± 0.617
C_6D_6	± 0.318	± 0.437	∓ 0.028	± 0.631
C_6F_6	± 0.650	∓ 5.393	∓ 0.328	± 0.351

β - C-H or C-F bond in plane bend

dr - C-H or C-F bond stretch

dR - C-C bond stretch

y - C-H or C-F bond out-of-plane bend

Table 7.2

π-electron rehybridization which is assumed to be restricted to the p_z orbitals of the carbon atom to which the moving substituent is attached. In an out-of-plane angle bend as the substituent moves out of the molecular plane, rehybridization at the carbon atom introduces some sp^3 character into the sp^2 σ - bonding orbitals of the planar molecule. If this rehybridization were complete then the fourth 'bond' in the sp^3 configuration would be a lone pair of electrons and although complete rehybridization does not occur there is some electron flow producing an increase of electron density on the opposite side of the ring to the substituent. The dipole moment or <u>rehybridization moment</u> introduced as a result acts in a direction perpendicular to the plane of the ring and opposite to the direction of electron flow.

If when a substituent is displaced from the plane of the ring, the total dipole moment due to the displaced bond is μ (in the z direction, i.e. perpendicular to the plane of the ring), the rehybridization moment is μ_{RM} and μ' is the component of the bond moment in the z direction (see Figure 7.1), then

$$\mu = \mu_{RM} + \mu' \qquad 1$$

From Section 5.6

$$\mu' = \mu_{CX}\, dy$$

defining X as the positive end of the C - X dipole.

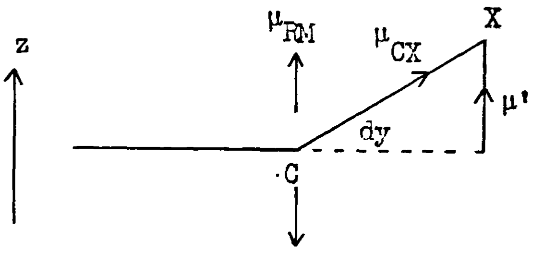


Figure 7.1 Illustration of the Electron Flow when a Substituent moves out of the Plane

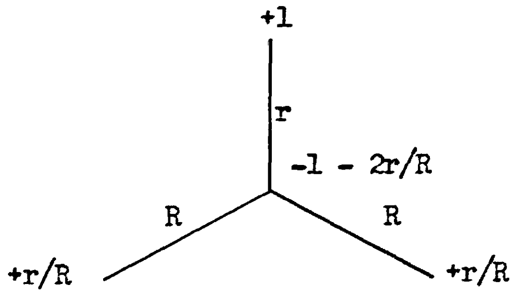


Figure 7.2 Displacements of the Atoms in an Out-of-Plane Angle Bend

Therefore $$\frac{\partial \mu}{\partial (dy)} = \frac{\partial \mu_{RM}}{\partial (dy)} + \mu_{CX} \qquad 2$$

Since $dy = y - y_e$ and y_e (the equilibrium value) is zero, it follows that $dy = y$ and therefore equation 2 becomes

$$\frac{\partial \mu}{\partial y} = \frac{\partial \mu_{RM}}{\partial y} + \mu_{CX} \qquad 3$$

If it is assumed that Hydrogen is at the positive end of the C - H dipole (for which there is considerable evidence (160,161)) and that the value of this dipole is + 0.32 D (i.e. the in plane value $\partial \mu / \partial \beta$, since a reorientation of the C - H bond cannot cause rehybridization of the p_z orbitals) then

$$\partial \mu_{RM} / \partial y = + 0.3 \text{ D.rad}^{-1}$$

if the value of $\partial \mu_z / \partial y$ is taken as + 0.62 D.rad^{-1}. Therefore, for Benzene, the difference between the $\partial \mu / \partial \beta$ and $\partial \mu / \partial y$ values can be explained by a rehybridization moment of + 0.3D.rad^{-1}.

Steele and Wheatley (156) also studied the dipole moment derivatives of the infra red active fundamentals of Hexafluoro Benzene since it is to be expected that the rehybridization moment is independent of substituent in molecules which are derivatives of Benzene. The absolute intensities of the fundamentals of Hexafluoro Benzene have been measured by Steele and Whiffen (162) (1531 and 1020-1002 cm^{-1} bands), Person et.al.(48) (1020-1002, 315 and 215 cm^{-1} bands) and Fujiyama and Crawford (51) (315 cm^{-1} bands). Steele and Wheatley (156) also measured the intensities of the 315 and 215 cm^{-1} bands and used their values together with those of Steele and Whiffen (162) to calculate the dipole moment derivatives of Hexafluoro Benzene, the values are given in Table 7.1. Using the eigen vectors of Steele and Whiffen (47) for Hexafluoro Benzene and the relationships between $\partial\mu/\partial S$ and $\partial\mu/\partial R$ of Spedding and Whiffen (153), Steele and Wheatley calculated four sets of $\partial\mu/\partial R$ values from the data for the E_{1u} symmetry species and the set they accepted as being correct is given in Table 7.2, together with the value of $\partial\mu/\partial y$ calculated from the A_{2u} fundamental. The sign choice of $\partial\mu/\partial Q$ values giving rise to these $\partial\mu/\partial R$ values is given in Table 7.1.

Using the bond moment hypothesis to interpret the $\partial\mu/\partial\beta$ and $\partial\mu/\partial y$ values in terms of the C - F bond moment again gives conflicting results of $\pm$ 0.65 D (in plane bond moment) and $\pm$ 0.35 D (out-of-plane bond moment). If it is assumed that Fluorine is at the negative end of the C - F dipole and that the value of this dipole is - 0.65 D (i.e. the in plane value) then,

$$\partial\mu_{RM}/\partial y = + 0.3 \text{ D.rad}^{-1}$$

if the value of $\partial\mu/\partial y$ is taken as - 0.35 $D.rad^{-1}$. Therefore for both Benzene and Hexafluoro Benzene the difference between the $\partial\mu/\partial\beta$ and $\partial\mu/\partial y$ values can be explained by a rehybridization moment of + 0.3 D.rad^{-1}.

Application of the theory of Gribov to the a_{2u} fundamentals of Benzene and Hexafluoro Benzene also gives equation 3 but shows that the derivation of equation 3 represents a considerable oversimplification of the problem (see Appendix). This is because it was derived for a displacement of just the substituent X, whereas an out-of-plane angle bend involves the displacement of Carbon atoms as well. For instance, the out-of-plane angle bend rdy_1 (see Figure 7.2 and Section 1.11) involves displacement of Carbon atoms 1,2 and 6 so rehybridization will occur at these Carbon atoms and also at 3 and 5 since there is a reorientation of bonds $C_2 - C_3$ and $C_5 - C_6$. Therefore $\partial\mu_{RM}/\partial y_1$ refers to the total rehybridization occurring in the molecule.

If it is assumed that rehybridization at a given Carbon atom is proportional to its displacement from the plane of the ring, then

$$\begin{aligned}\partial\mu_{RM}/\partial y_1 &= -a(-1-2\,{}^{r}/_{R}) - 2a.\,{}^{r}/_{R}\\ &= a = 0.3\ \mathrm{D.rad}^{-1}\end{aligned} \qquad 4$$

where a is a constant, it is the change in dipole moment for a unit displacement of a Carbon atom out of the plane of the Benzene ring. If, by definition, a is positive then the minus sign arises since the direction of electron flow, which is the same as the direction of motion of the Carbon atom, is in the opposite direction to the dipole moment.

In applying the theory of Gribov, the out-of-plane angle bend is, by definition, positive in the sense shown in Figure 7.2 so the sign of the ~~dipole~~ rehybridization moment is correctly predicted as being positive.

However equation 4 still represents an over simplification of the problem (for instance it does not take into account rehybridization at Carbon atoms 3 and 5) but it does show to some extent how $\partial\mu_{RM}/\partial y$ can be explained in terms of changes in dipole moment at individual atoms. A further point arising from Figure 7.2 is that since Carbon atoms 2 and 6 move there is a contribution to $\partial\mu/\partial y_1$ from the bond moments of bonds $C_2 - X_2$ and $C_6 - X_6$. This is important when the substituents are not all the same.

Jalsovszky and Orville-Thomas (170), using the CNDO method (complete neglect of differential overlap), have calculated a value of + 0.35 D for the rehybridization moment in Benzene. This value is in good agreement with that obtained by Steele and Whiffen (156).

Bruns and Person (171), also using the CNDO method, have calculated the $\partial\mu/\partial S$ values for the e_{1u} and the a_{2u} fundamentals of Benzene and Hexafluoro Benzene. By comparing the experimental and calculated $\partial\mu/\partial S$ values they made the following sign choices of $\partial\mu/\partial Q$ values: for the e_{1u} fundamentals of Benzene, + + + ; for the a_{2u} fundamentals of Benzene, + ; for the e_{1u} fundamentals of Hexafluoro Benzene, - - - ; and for the a_{2u} fundamentals of Hexafluoro Benzene, - . Not only are these sign choices in agreement with those given in Table 7.1, they also confirm the final choice between the equivalent sets of + and - solutions.

However Bruns and Person (171) do not support the idea of a rehybridization moment of 0.3 $D.rad^{-1}$. They conclude that any rehybridization moment acting at the ring Carbon atoms during an out-of-plane angle bend is much smaller than this. They calculated the following values: + 0.34 for $\partial\mu/\partial\gamma$ in Benzene (compared with + 0.61 observed); + 0.30 for $\partial\mu/\partial\beta$ in Benzene (compared with + 0.30 observed; - 1.29 for $\partial\mu/\partial\gamma$ in Hexafluoro Benzene (compared with - 0.36 observed); and - 1.38 for $\partial\mu/\partial\beta$ in Hexafluoro Benzene (compared with - 0.66 observed). Only for $\partial\mu/\partial\beta$ in Benzene are the calculated and observed values in close agreement but for both Benzene and Hexafluoro Benzene the calculated values of $\partial\mu/\partial\beta$ are almost the same as the calculated values of $\partial\mu/\partial y$, which is at variance with the experimental evidence. Therefore, it would appear that until the discrepancy between the observed values and those calculated using the CNDO method is removed no firm conclusions can be drawn from the calculations.

The introduction of a rehybridization moment has not been the only explanation offered for the conflicting $\partial\mu/\partial\beta$ and $\partial\mu/\partial y$ values in Benzene. Kovner and Snegirev (163) rejected as physically meaningless the idea of two different bond moment values and by introducing cross terms (such as $\partial\mu_i/\partial\beta_j$) calculated a value of 0.65 D. for the C - H bond moment. This value must agree with the $\partial\mu/\partial y$ value of Spedding and Whiffen (153,156) since no extra terms were introduced into the equation for the A_{2u} symmetry species. Therefore extension of the method of Kovner and Snegirev (163) to Hexafluoro Benzene would presumably result in a value of 0.35 D for the C - F bond moment. However this value is much lower than other contemporary estimates (132,164), albeit measured in aliphatic molecules, and therefore the explanation of Kovner and Snegirev (163) is not acceptable.

Also there is the possibility of explaining the anomalous results as being due to vibronic effects. Jones and Simpson (165) state that,

> It can be assumed that an important contribution to the derivative of the electric dipole with respect to the appropriate vibrational coordinate is a redistribution of the delocalized electrons as the molecule is distorted by vibration.

This idea of changes which occur in the molecule as a whole and not just in the vibrating coordinate is the generally accepted meaning of a vibronic contribution to dipole moment changes.

Brown (166) has divided the intensity expression into two components so that

$$\Gamma_i = \frac{N}{3c^2 w_i} (M_{fi} + M_{vi})^2$$

where M_{fi} is the "framework" contribution and M_{vi} is the π-electronic-vibronic contribution to the dipole moment derivative and he showed that, due to symmetry restrictions, there can be no π vibronic contribution to the a_{2u} mode of Benzene. This suggests that there can be no contribution to $\partial\mu/\partial y$ from a rehybridization moment if this is a vibronic term. However Brown (166) included in M_{fi} terms which result from the following of the nuclear motion by the electron distribution and this is made up of contributions from both σ and π bonds. If it is accepted that the rehybridization moment arises from these terms due to electron following then there can be a contribution to $\partial\mu/\partial y$ from rehybridization. Vibronic contributions to the e_{1u} modes are allowable so there is the possibility that such a contribution is incorporated in the $\partial\mu/\partial\beta$ value. This would affect the assumption that $\partial\mu/\partial\beta$ arises solely through reorientation of the C - H dipole but Brown (166) considered that the vibronic contribution to this mode would be small.

Wheatley and Linnet (167) have postulated that the p orbitals forming the π bonds in Ethylene remain perpendicular to, or "follow", the CH_2 plane during an out-of-plane vibration. Eggers (168) has calculated the contribution to the dipole moment change from this π following both for Ethylene and also for the a_{2u} vibration of Benzene (following the C - H bond). He obtained a value of 0.63 D for each C - H bond for Benzene, a value almost the same as the total dipole moment change. Coulson and Stephen (169) have pointed out that Egger's treatment (168) is not complete and also calculated quantum mechanically the changes in the dipole moment with respect to the changes in internal coordinates of Ethylene, Acetylene and the a_{2u} vibrations of Benzene. They introduced a number of variable parameters, to allow for incomplete following of the atoms forming a bond by the electrons (either σ or π) and electronegativity effects, and calculated a wide range of values for $\partial\mu/\partial y$ in Benzene. If the value of + 0.62 $D.rad^{-1}$ (the important point being that it is positive) is accepted as being correct, it indicates some degree of following of the C - H bond by the Carbon p_z orbitals.

The conclusion is that the idea of a rehybridization moment is an attractive one from the point of view of simplicity but to try to determine the exact form of the changes in the orbitals of the Carbon atoms, which give rise to this moment, would require some insight into the quantum mechanics of the problem.

Having determined that a rehybridization moment of + 0.3 $D.rad^{-1}$ is acting in both the C - H out-of-plane bending vibration of

Benzene and the C - F out-of-plane bending vibration of Hexafluoro Benzene, the next step is to investigate whether the dipole moment derivatives for the out-of-plane vibrations of molecules containing both C - H and C - F bonds can be interpreted using the idea of a rehybridization moment. It is in this extension to such molecule that the theory of Gribov is used. The two molecules studied were 1,4 difluoro Benzene and 1,3,5 trifluoro Benzene. They were chosen since both have only three infra red active out-of-plane vibrations and both are volatile, which meant that the absolute intensities could be measured in the gas phase.

SECTION 7.2 1,4 difluoro Benzene

The absolute infra red intensities of the b_{3u} fundamentals of 1,4 difluoro Benzene have been measured and the dipole moment derivatives calculated, (see Table 6.4). The $\mathbf{L}$ matrix was calculated using the 23 parameter force field for twenty Fluoro Benzenes calculated in Part I. The $\mathbf{L}$ matrix is given in Table 7.3 and the $\mathbf{L}^{-1}$ matrix in Table 7.4. The changes in the dipole moments with respect to the symmetry coordinates ($\partial\mu/\partial S$) were calculated using equation 28, Section 5.6. Since there are three fundamentals, there are eight ($= 2^3$) sets of solutions for the $\partial\mu/\partial S$ values and they are given in Table 7.5. The changes in the dipole moments with respect to the changes in the internal coordinates ($\partial\mu/\partial R$) were calculated from the $\partial\mu/\partial S$ values using equation 31, Section 5.6. The relationships between the $\partial\mu/\partial S$ and the $\partial\mu/\partial R$ values are those given in Section 5.8 between the X and $\partial\mu/\partial R$ values, with X_1 replaced by $\partial\mu/\partial S_1$, etc. (r is the C - H bond length, r' is the C - F bond length and R is the C - C bond length). The $\partial\mu/\partial R$ values are also given in Table 7.5.

Examination of Table 7.5 yields little useful information and the theory of Gribov is used to assist in the interpretation of the observed dipole moment derivatives in terms of bond moments and bond moment derivatives. The matrix T_{2q} was calculated using the method outlined in Section 4.2. The elements of the matrix T_{2q}

For the b_{3u} vibrations of 1,4 difluoro Benzene:

Eigen Vector Matrix

SYMMETRY COORDINATE	S_1	S_2	S_3
NORMAL COORDINATE			
Q_1	+0.6240	+0.6978	+0.0607
Q_2	-1.1109	+0.3283	+0.1170
Q_3	+1.1751	-0.8674	+0.4689

Table 7.3

Inverse Eigen Vector Matrix

NORMAL COORDINATE	Q_1	Q_2	Q_3
SYMMETRY COORDINATE			
S_1	+0.3898	-0.5829	+0.0930
S_2	+1.0087	+0.3428	-0.2116
S_3	+0.8706	+2.0510	+1.4767

Table 7.4

$\partial\mu/\partial S$ and $\partial\mu/\partial R$ for 1,4 difluoro Benzene

SIGN CHOICE OF $\partial\mu/\partial Q$	$\partial\mu/\partial S_1$	$\partial\mu/\partial S_2$	$\partial\mu/\partial S_3$	$\partial\mu/\partial R_1$	$\partial\mu/\partial R_2$	$\partial\mu/\partial R_3$
$\pm\ \pm\ \pm$	± 1.3531	∓ 0.0823	± 0.2919	± 1.2438	∓ 0.0446	± 0.2036
$\pm\ \pm\ \mp$	± 0.9834	∓ 0.9533	∓ 0.3352	± 0.9040	∓ 0.5167	∓ 0.2338
$\mp\ \pm\ \pm$	± 0.3563	± 1.4085	± 0.0542	± 0.3275	± 0.7634	± 0.0378
$\pm\ \mp\ \pm$	± 0.0134	∓ 0.5376	± 0.5729	± 0.0124	∓ 0.2914	± 0.3996

R_1 - y_{CF}

R_2 - y_{CH}

R_3 - ϕ_{FH}

Table 7.5

are shown in Figure 7.3 . T_{1q} is calculated from T_{2q} using the relationship

$$T_{1q} = M^{-1}T_{2q}^{t}$$

Therefore matrix X can be calculated and using the relationships given in Section 5.8 the following equations are obtained.

$$\partial\mu_{RM}/\partial y_{CF} = \partial\mu/\partial y_{CF} - 0.5\,\mu_{CH} - 0.5\,\mu_{CF} \qquad 5$$

$$\partial\mu_{RM}/\partial y_{CH} = \partial\mu/\partial y_{CH} - 0.75\,\mu_{CH} - 0.25\,\mu_{CF} \qquad 6$$

$$\partial\mu_{RM}/\partial\phi_{FH} = \partial\mu/\partial\phi_{FH} + 0.217\,(\mu_{CH} - \mu_{CF}) \qquad 7$$

where the values of $\partial\mu/\partial y_{CF}$, $\partial\mu/\partial y_{CH}$ and $\partial\mu/\partial\phi_{FH}$ are the values of $\partial\mu/\partial R$ given in Table 7.5.

According to the bond moment hypothesis (see Section 5.6) changes in the dipole moment with respect to changes in a bending coordinate are due solely to reorientation of the appropriate bond moments. This means that $\partial\mu_{RM}/\partial R = 0$ for all internal coordinates. Therefore with this condition and solving equations 5 and 6 simultaneously the following relationships are obtained.

$$\mu_{CH} = 2\partial\mu/\partial y_{CH} - \partial\mu/\partial y_{CF} \qquad 8$$

$$\mu_{CF} = 3\partial\mu/\partial y_{CF} - 2\partial\mu/\partial y_{CH} \qquad 9$$

And from equation 7

$$\mu_{CH} - \mu_{CF} = -\partial\mu/\partial\phi_{FH}\cdot 1/0.217 \qquad 10$$

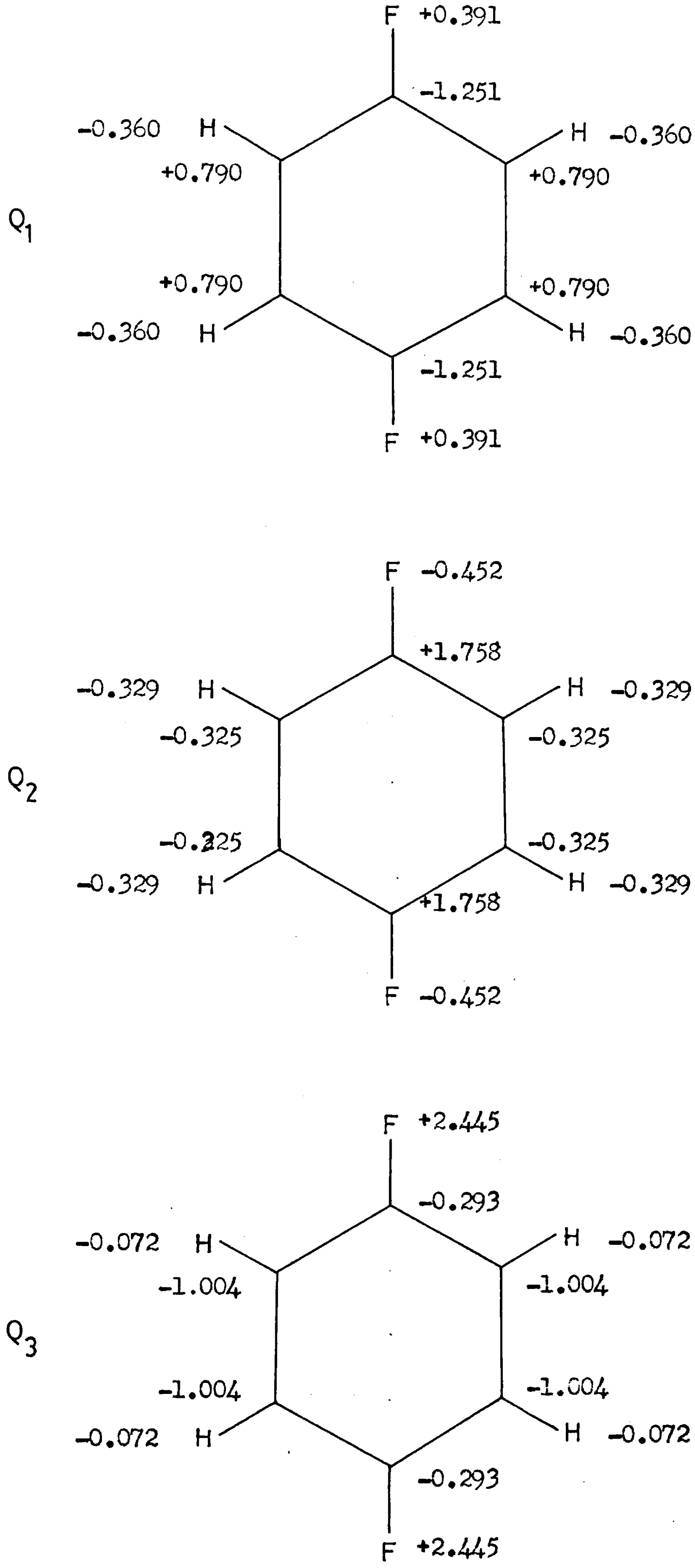


Figure 7.3 T_{2q} Matrix Elements

For the b_{3u} vibrations of 1,4 difluoro Benzene

μ_{CH} and μ_{CF} values, calculated using the Bond Moment Hypothesis

SIGN CHOICE	μ_{CH}	μ_{CF}	$\mu_{CH} - \mu_{CF}$ from $\partial\mu/\partial y$	$\mu_{CH} - \mu_{CF}$ from $\partial\mu/\partial\phi$
$\pm\ \pm\ \pm$	∓ 1.332	± 3.822	∓ 5.154	∓ 0.938
$\pm\ \pm\ \mp$	∓ 1.938	± 3.744	∓ 5.682	± 1.077
$\mp\ \pm\ \pm$	± 1.198	∓ 0.542	± 1.740	∓ 0.174
$\pm\ \mp\ \pm$	∓ 0.594	± 0.618	∓ 1.212	∓ 1.842

Table 7.6

Rehybridization Moments

$\mu_{CH} = +0.3$ D

$\mu_{CF} = -0.65$ D

SIGN CHOICE	$\partial\mu_{RM}/\partial y_{CF}$	$\partial\mu_{RM}/\partial y_{CH}$	$\partial\mu_{RM}/\partial\phi_{FH}$
+ + +	+1.419	−0.107	+0.409
+ + −	+1.079	−0.579	−0.028
+ − +	+0.187	−0.354	+0.605
− + +	+0.502	+0.701	+0.244
− − +	−0.729	+0.454	+0.440
− + −	+0.163	+0.229	−0.194
+ − −	−0.153	−0.826	+0.168
− − −	−1.069	−0.018	+0.002

Table 7.7

The values of μ_{CH} and μ_{CF} and the two sets of values of $\mu_{CH} - \mu_{CF}$ calculated using these relationships are shown in Table 7.6. The only set of solutions which is acceptable in terms of the value calculated for u_{CH} is the - + - sign choice. Also only for this sign choice are the two $\mu_{CH} - \mu_{CF}$ values in reasonable agreement.

These values still yield little useful information and are included only to show how the $\partial\mu/\partial R$ values in Table 7.5 would be interpreted using the bond moment hypothesis. The rehybridization moment has been ignored whereas the results from Benzene and Hexafluoro Benzene show it must be included. Therefore, substituting the values $\mu_{CH} = + 0.3$ and $\mu_{CF} = - 0.65$ and the $\partial\mu/\partial R$ values given in Table 7.5 in equations 5,6 and 7 gives the eight sets of values for the rehybridization moments shown in Table 7.7.

The question that now arises is which set of solutions is the correct set. Two conditions, which must be satisfied by the correct set of solutions, are proposed. They are:

Condition A, $\partial\mu_{RM}/\partial\gamma_{CH} \sim \partial\mu_{RM}/\partial y_{CF} \sim + 0.3\ \mathrm{D.rad}^{-1}$

Condition B, $\partial\mu_{RM}/\partial\phi_{FH} < 0 \quad (\sim - 0.074\ \mathrm{D.rad}^{-1})$

Condition A, which is the more important of the two, assumes that the idea of the rehybridization moment as explained in Section 7.1 can be extended to the out-of-plane vibrations of 1,4 difluoro

Benzene (and 1,3,5 trifluoro Benzene).

Condition B is obtained by applying to a special torsion the simple quantitative analysis applied to an out-of-plane angle bend in Section 7.1. The cartesian displacements of the atoms involved in the special torsion $Rd\phi_{FH}$ are given in Figure 7.4. If it is assumed that rehybridization at a given Carbon atom is proportional to its displacement from the plane of the ring, then

$$\partial\mu_{RM}/\partial\phi_{FH} = -\frac{2a}{3^{\frac{1}{2}}} \; R \; \frac{r' - r}{r'r}$$

$$= -0.074 \text{ D.rad}^{-1}$$

when the value + 0.3 D.rad^{-1} is substituted for a. (The bond lengths are given in Section 2.4).

Examination of Table 7.7 shows that the two sets of solution which most nearly satisfy Condition A are those for the - + + and the - + - sign choices. Of these two only the - + - sign choice satisfies Condition B as well. However these solutions are rather restricted in the choice of values for μ_{CH} and μ_{CF} (especially the μ_{CF} value which is rather low). Therefore assuming that

$$\partial\mu_{RM}/\partial y = \partial\mu_{RM}/\partial y_{ch} = \partial\mu_{RM}/\partial y_{CF} \qquad 11$$

the following relationships are obtained from equations 5 and 6

$$\mu_{CH} - \mu_{CF} = 4(\partial\mu/\partial y_{CH} - \partial\mu/\partial y_{CF}) \qquad 12$$

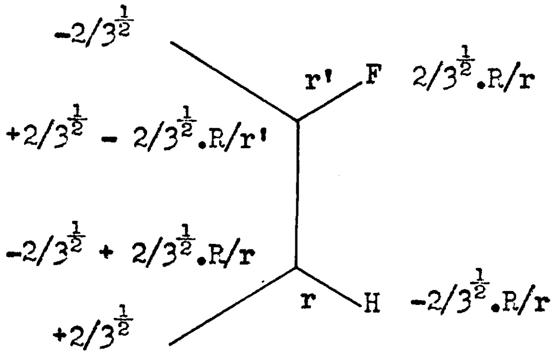
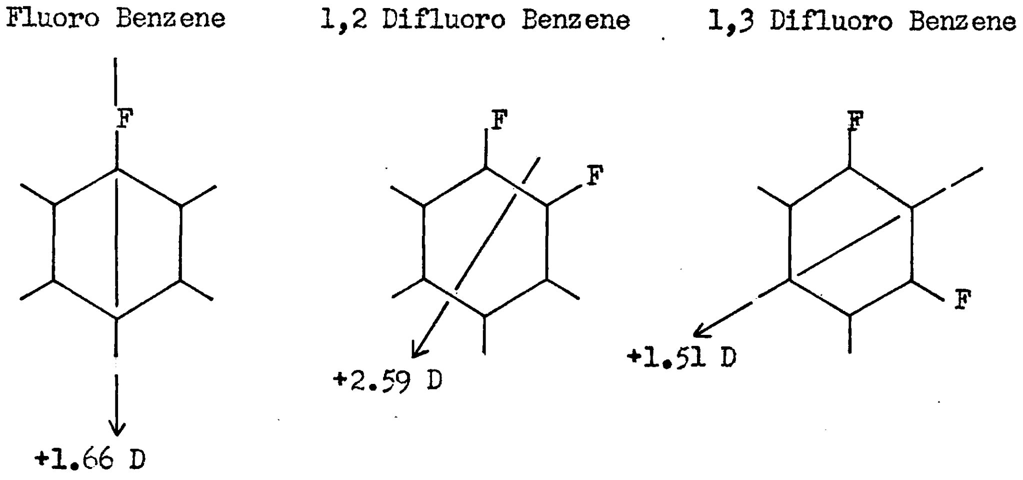


Figure 7.4 Displacements of the Atoms in a Special Torsion



$\mu_{CH} + \mu_{CF} = 1.66$

$(\mu_{CH} + \mu_{CF}) \times 2\cos 30 = 2.59$

$\mu_{CH} + \mu_{CF} = 1.50$

$(\mu_{CH} + \mu_{CF}) \times 2\cos 60 = 1.51$

$\mu_{CH} + \mu_{CF} = 1.51$

Figure 7.5 Dipole Moments of Fluorobenzene, 1,2 difluoro Benzene and 1,3 difluoro Benzene

$$\partial \mu_{RM}/\partial y = 3\partial \mu/\partial y_{CF} - 2\,\partial \mu/\partial y_{CH} - \mu_{CF} \qquad 13$$

$$= -\partial \mu/\partial y_{CF} + 2\,\partial \mu/\partial y_{CH} - \mu_{CH} \qquad 14$$

The value of $\mu_{CH} - \mu_{CF}$ calculated using equation 12 is independent of the value of $\partial \mu_{RM}/\partial y$ and is the same as that calculated from the $\partial \mu/\partial y$ values assuming $\partial \mu_{RM}/\partial y$ is zero (see Table 7.6). It is therefore necessary to decide what is a reasonable value of $\mu_{CH} - \mu_{CF}$.

Due to symmetry restrictions both 1,4 difluoro Benzene and 1,3,5 trifluoro Benzene have an overall dipole moment of zero so they provide no information about the $\mu_{CH} - \mu_{CF}$ value. However the dipole moments of Fluoro Benzene, 1,2 difluoro Benzene and 1,3 trifluoro Benzene are known (60). Assuming vectorial addition of bond moments the dipole moments of the two difluoro Benzene molecules are consistent with a $\mu_{CH} - \mu_{CF}$ value of 1.50 D and the dipole moment of Fluoro Benzene with a $\mu_{CH} - \mu_{CF}$ value of 1.66 D (see Figure 7.5). (It must be remembered that by definition C → X is the positive direction for a CX dipole so that $-\mu_{CF}$ has a positive value).

Therefore a third condition is proposed. It is

Condition C, $\mu_{CH} - \mu_{CF} \sim + 1.5$ D

The two solutions which are consistent with this condition are again those for the - + + sign choice (+ 1.740 D) and the - + - sign choice (+ 1.212 D).

Therefore substituting these values for $\mu_{CH} - \mu_{CF}$ in equation 7 and the appropriate values for $\partial\mu/\partial y_{CH}$ and $\partial\mu/\partial y_{CF}$ in equations 13 and 14 gives the following relationships.

− + − sign choice	− + + sign choice
$\mu_{CH} - \mu_{CF} = + 1.212$ D	$\mu_{CH} - \mu_{CF} = + 1.740$ D
$\partial\mu_{RM}/\partial y = 0.594 - \mu_{CH}$	$\partial\mu_{RM}/\partial y = 1.199 - \mu_{CH}$
$= - 0.618 - \mu_{CF}$	$= - 0.545 - \mu_{CF}$
$\partial\mu_{RM}/\partial\phi_{FH} = - 0.137$ D.rad^{-1}	$\partial\mu_{RM}/\partial\phi_{FH} = + 0.416$ D.rad^{-1}
For $\partial\mu_{RM}/\partial y = + 0.3$ D.rad^{-1}	
$\mu_{CH} = 0.294$ D	$\mu_{CH} = + 0.899$ D
$\mu_{CF} = - 0.918$ D	$\mu_{CF} = - 0.945$ D

For the − + + sign choice the value of $\partial\mu_{RM}/\partial\phi_{FH}$ is not in agreement with condition B and the value of the C − H bond moment is higher than the usual estimates (132,133), so this solution is rejected.

For the − + − sign choice the value of $\partial\mu_{RM}/\partial\phi_{FH}$ is consistent with condition B and this solution is therefore accepted as being the correct one. It is discussed further, with particular reference to the values of μ_{CH} and μ_{CF}, in Section 7.4.

SECTION 7.3 1,3,5 trifluoro Benzene

The absolute infra red intensities of the a_2'' fundamentals of 1,3,5 trifluoro Benzene have been measured and the dipole moment derivatives calculated (see Table 6.10). The analysis of these results is carried out in much the same way as that for the 1,4 difluoro Benzene results (see Section 7.2).

The L matrix, calculated using the 23 parameter force field for set Z (see Chapter Three), is given in Table 7.8 and the L^{-1} matrix in Table 7.9. The eight sets of values calculated for $\partial\mu/\partial S$ and $\partial\mu/\partial R$ are given in Table 7.10. They are calculated using the relationships given in Section 5.8.

The elements of the matrix T_{2q} are shown in Figure 7.6. Therefore matrix T_{1q} and then matrix X can be calculated and the following relationships are obtained.

$$\partial\mu_{RM}/\partial y_{CF} = \partial\mu/\partial y_{CF} - 0.333\ \mu_{CH} - 0.667\ \mu_{CF} \qquad 15$$

$$\partial\mu_{RM}/\partial y_{CH} = \partial\mu/\partial y_{CH} - 0.667\ \mu_{CH} - 0.333\ \mu_{CF} \qquad 16$$

$$\partial\mu_{RM}/\partial\phi_{FH} = \partial\mu/\partial\phi_{FH} + 0.145\ (\mu_{CH} - \mu_{CF}) \qquad 17$$

where the values of $\partial\mu/\partial y_{CF}$, $\partial\mu/\partial y_{CH}$ and $\partial\mu/\partial\phi_{FH}$ are the values of $\partial\mu/\partial R$ given in Table 7.10.

Using the bond moment hypothesis to interpret the results (i.e. assuming $\partial\mu_{RM}/\partial y = 0$) and solving equations 15 and 16 simultaneously the following relationships are obtained.

For the a_2'' vibrations of 1,3,5 trifluoro Benzene:

Eigen Vector Matrix

SYMMETRY COORDINATE NORMAL COORDINATE	S_1	S_2	S_3
Q_1	+0.6240	+0.6978	+0.0607
Q_2	-1.1109	+0.3283	+0.1170
Q_3	+1.1751	-0.8674	+0.4789

Table 7.8

Inverse Eigen Vector Matrix

NORMAL COORDINATE SYMMETRY COORDINATE	Q_1	Q_2	Q_3
S_1	+0.3898	-0.5829	+0.0930
S_2	+1.0087	+0.3428	-0.2116
S_3	+0.8706	+2.0510	+1.4767

Table 7.9

$\partial\mu/\partial S$ and $\partial\mu/\partial R$ for 1,3,5 trifluoro Benzene

SIGN CHOICE OF $\partial\mu/\partial Q$	$\partial\mu/\partial S_1$	$\partial\mu/\partial S_2$	$\partial\mu/\partial S_3$	$\partial\mu/\partial R_1$	$\partial\mu/\partial R_2$	$\partial\mu/\partial R_3$
± ± ±	∓0.5449	±0.9013	±0.2211	∓0.4090	±0.5640	±0.1259
± ± ∓	∓1.1076	±0.3781	∓0.2963	∓0.8304	±0.2367	∓0.1688
∓ ± ±	±0.3425	∓0.3717	±0.4887	±0.2570	∓0.2327	±0.2783
± ∓ ±	±0.2202	±0.8949	∓0.2380	±0.1653	±0.5601	∓0.1355

R_1 - y_{CF}

R_2 - y_{CH}

R_3 - ϕ_{FH}

Table 7.10

$$\mu_{CH} = 2\,\partial\mu/\partial y_{CH} - \partial\mu/\partial y_{CF} \qquad 18$$

$$\mu_{CF} = 2\,\partial\mu/\partial y_{CF} - \partial\mu/\partial y_{CH} \qquad 19$$

And from equation 17

$$\mu_{CH} - \mu_{CF} = -\,\partial\mu/\partial\phi_{FH}\cdot 1/0.145 \qquad 20$$

The values of μ_{CH} and μ_{CF} and the two sets of values of $\mu_{CH} - \mu_{CF}$ calculated using these relationships are shown in Table 7.11. In view of the high values of μ_{CH} no set of solutions is acceptable.

Substituting the values $\mu_{CH} = +\,0.3$ D and $\mu_{CF} = -\,0.65$ D in equations 15, 16 and 17 gives the eight sets of values for the rehybridization moments shown in Table 7.12. The only sets of solutions which satisfy Conditions A and B are those for the + − + and the + − − sign choices.

Assuming $\partial\mu_{RM}/\partial y_{CH} = \partial\mu_{RM}/\partial y_{CF}$ the following relationships are obtained from equations 15 and 16.

$$\mu_{CH} - \mu_{CF} = 3\,\partial\mu/\partial y_{CH} - 3\,\partial\mu/\partial y_{CF} \qquad 21$$

$$\partial\mu_{RM}/\partial y = 2\,\partial\mu/\partial y_{CF} - \partial\mu/\partial y_{CH} - \mu_{CF} \qquad 22$$

$$= 2\partial\mu/\partial y_{CH} - \partial\mu/\partial y_{CF} - \mu_{CH} \qquad 23$$

The only solutions which give a value $\mu_{CH} - \mu_{CF}$ (see Table 7.11) consistent with Condition C are again those for the + − + (+ 1.185D) and the + − − (+ 1.470 D) sign choices.

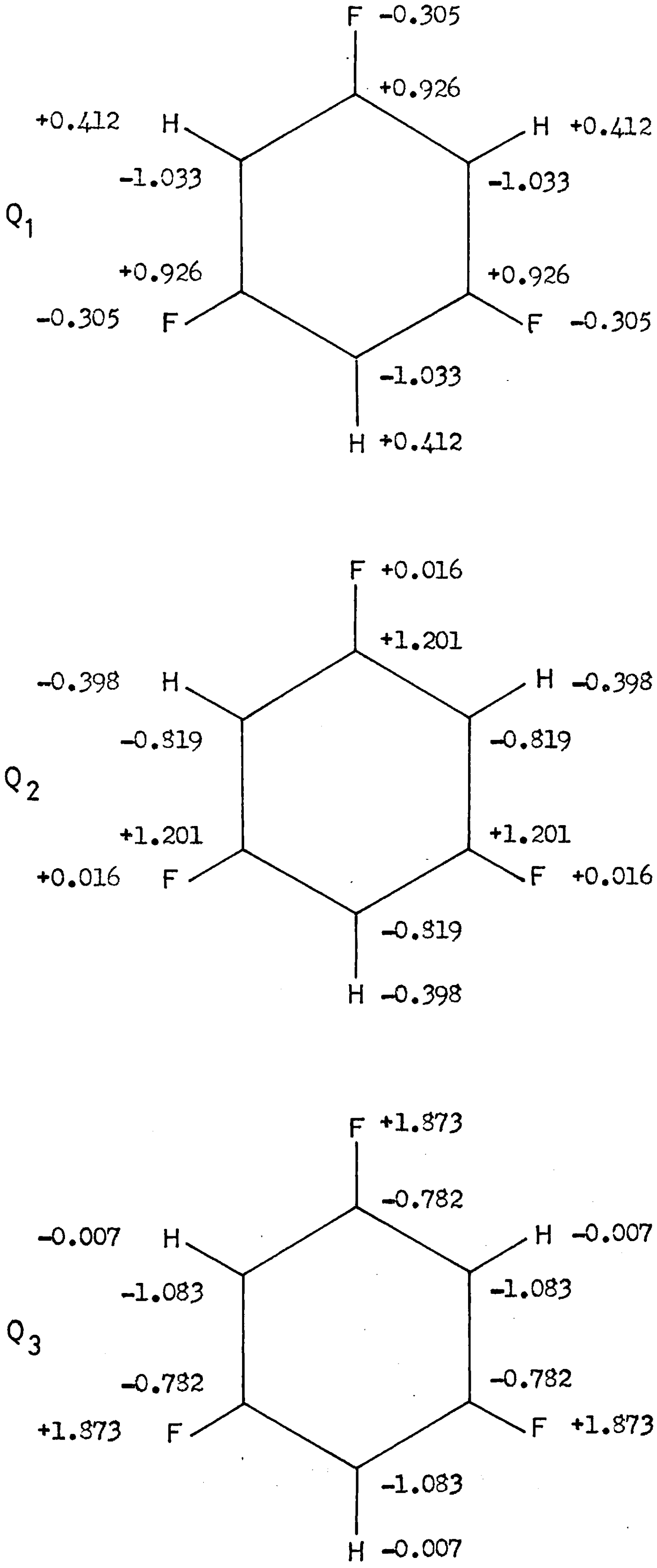


Figure 7.6 T_{2q} Matrix Elements

For the a_2'' vibrations of 1,3,5 trifluoro Benzene

μ_{CH} and μ_{CF} values, calculated using the Bond Moment Hypothesis

SIGN CHOICE	μ_{CH}	μ_{CF}	$\mu_{CH} - \mu_{CF}$ from $\partial\mu/\partial y$	$\mu_{CH} - \mu_{CF}$ from $\partial\mu/\partial\phi$
$\pm$ $\pm$ $\pm$	± 1.537	∓ 1.382	± 2.919	∓ 0.868
$\pm$ $\pm$ $\mp$	± 1.304	∓ 1.897	± 3.201	± 1.164
$\mp$ $\pm$ $\pm$	∓ 0.723	± 0.747	∓ 1.470	∓ 1.919
$\pm$ $\mp$ $\pm$	± 0.955	∓ 0.230	± 1.185	± 0.934

Table 7.11

Rehybridization Moments

$\mu_{CH} = +0.3$ D

$\mu_{CF} = -0.65$ D

SIGN CHOICE	$\partial\mu_{RM}/\partial y_{CF}$	$\partial\mu_{RM}/\partial y_{CH}$	$\partial\mu_{RM}/\partial\phi_{FH}$
+ + +	−0.076	+0.581	+0.263
+ + −	−0.498	+0.253	+0.120
+ − +	+0.498	+0.577	+0.002
− + +	+0.590	−0.216	+0.416
− − +	+1.164	−0.220	+0.154
− + −	+0.167	−0.543	+0.273
+ − −	+0.076	+0.249	−0.141
− − −	+0.742	−0.547	+0.011

Table 7.12

Therefore substituting these values for $\mu_{CH} - \mu_{CF}$ in equation 17 and the appropriate values for $\partial\mu/\partial y_{CH}$ and $\partial\mu/\partial y_{CF}$ in equations 22 and 23 gives the following relationships.

+ − − Sign Choice	+ − + Sign Choice
$\mu_{CH} - \mu_{CF} = +1.470$ D	$\mu_{CH} - \mu_{CF} = +1.185$ D
$\partial\mu_{RM}/\partial y = 0.723 - \mu_{CH}$	$\partial\mu_{RM}/\partial y = +0.955 - \mu_{CH}$
$= -0.747 - \mu_{CF}$	$= -0.230 - \mu_{CF}$

For $\partial\mu_{RM}/\partial y = +0.3$ D.rad^{-1}

$\mu_{CH} = +0.423$ D	$\mu_{CH} = +0.655$ D
$\mu_{CF} = -1.047$ D	$\mu_{CF} = -0.530$ D

For the + − + sign choice the value of μ_{CH} is larger than the absolute value of μ_{CF} and $\partial\mu_{RM}/\partial\phi_{FH}$ is positive and therefore not consistent with Condition B, (though the value is very small and therefore this might just be due to errors in the measurements and calculation).

However, for the + − − sign choice the value of $\partial\mu_{RM}/\partial\phi_{FH}$ is in very good agreement with the theoretical value suggested in Condition B, (though in view of the simple theory used to calculate it this is probably somewhat fortuitous). Also the value of $\mu_{CH} - \mu_{CF}$ is in closer agreement with Condition C, so this solution is preferred. It is discussed further, with particular reference to the values of μ_{CH} and μ_{CF}, in Section 7.4.

SECTION 7.4 Conclusions

The values of μ_{CH} and μ_{CF} calculated for the four molecules, Benzene, 1,4 difluoro Benzene, 1,3,5 trifluoro Benzene and Hexafluoro Benzene, assuming that $\partial\mu_{RM}/\partial y = +0.3$ D.rad^{-1} and is independent of the moving substituent, are summarized in Table 7.13.

	μ_{CH}	μ_{CF}	$\mu_{CH}-\mu_{CF}$
Benzene	+ 0.32		
1,4 difluoro Benzene	+ 0.29	- 0.92	+ 1.21
1,3,5 trifluoro Benzene	+ 0.42	- 1.05	+ 1.47
Hexafluoro Benzene		- 0.65	

All values are in Debye units.

Table 7.13.

The three values derived here for μ_{CH} are in reasonable agreement with each other and also with other estimates of the value of this bond moment (132,133). The values of μ_{CF} for 1,4 difluoro Benzene and 1,3,5 trifluoro Benzene are in reasonable agreement with each other and the values of $\mu_{CH} - \mu_{CF}$ for these molecules are in reasonable agreement with those measured for 1,2 and 1,3 difluoro Benzene (60). The value of μ_{CF} calculated for Hexafluoro

Benzene is lower than the other two values. This is possibly due to the fact that in Hexafluoro Benzene there are six highly electronegative Fluorine atoms competing with each other for electrons and the C - F bond moment is smaller than that of the other molecules where there are fewer Fluorine atoms. Literature estimates of the value of μ_{CF} vary over quite a wide range. Hornig and McKean (132) give a value in the region of - 1.5 D, which is slightly higher than that derived here.

These results show that the dipole moment derivatives of the out-of-plane vibrations of Benzene, 1,4 difluoro Benzene, 1,3,5 trifluoro Benzene, and Hexafluoro Benzene can be explained satisfactorily in terms of a theory which divides changes in the dipole moments with respect to changes in the internal coordinates into two parts: a contribution from the bond moments u_{CH} and u_{CF} due to reorientation of the relevant bonds; and a contribution from the rehybridization moments $\partial\mu_{RM}/\partial y$ and $\partial\mu_{RM}/\partial\phi_{FH}$ due to electron flow when the atoms move out of the plane of the ring. To some extent these parameters are transferable between the molecules.

Bruns and Person (171) have criticised the assumption that $\partial\mu/\partial\beta$, the change in dipole moment with respect to the change in an inplane angle bend, is due solely to the reorientation of the appropriate bond moments. However no values of $\partial\mu/\partial\beta$ have been calculated for 1,4 difluoro Benzene and 1,3,5 trifluoro Benzene and by using the theory of Gribov to analyse the results it is not necessary to make this assumption. All that is required is that u_{CH} and u_{CF} have realistic values.

One of the problems associated with the interpretation of dipole moment derivatives in terms of bond parameters is the question of errors. As mentioned in Section 6.2, to obtain a true estimate of the errors in the values of $\partial\mu/\partial S$ or $\partial\mu/\partial R$ requires an exhaustive statistical analysis as explained by Russell et.al.(146). Bruns and Person (171), using a method similar to that of Russell (146), calculated errors of ± 0.03 in the $\partial\mu/\partial S$ values for the a_{2u} vibrations of Benzene and Hexafluoro Benzene. Errors of this magnitude will not affect the interpretation of the results. There are two main sources of error: the $\partial\mu/\partial Q$ values; and the L matrix. As pointed out in Sections 6.2 and 6.3 the errors in the $\partial\mu/\partial Q$ values for 1,4 difluoro Benzene and 1,3,5 trifluoro Benzene are small. Also, for both these molecules the agreement between the observed frequencies and those calculated using the 23 parameter force field is good (see Section 2.3) and since this field is fitted to a large number of frequencies the errors associated with the L matrices would not be expected to be large. Therefore any errors should not affect the conclusions though they might affect the actual values given in Table 7.13.

Another source of error which would affect these conclusions is the question of which sign choice of $\partial\mu/\partial Q$ values is the correct one. If the wrong sign choice is made then the conclusions will not be consistent with physical reality. For the a_{2u} vibrations of Benzene and Hexafluoro Benzene, the choices of + 0.32 and - 0.65, respectively, for the $\partial\mu/\partial y$ values are confirmed by the CNDO calculations of Bruns and Person (171). For both the b_{3u} vibrations of 1,4 difluoro Benzene and the a_2'' vibrations of 1,3,5 trifluoro Benzene there are eight sets of solutions any of which could be the correct set. The choice of solutions was made on the basis of three conditions (see Section 7.2), two of which assumed that the idea of a rehybridization is correct and the third that bond moments are additive. To confirm that these solutions are the correct ones (or show if they are not), two further investigations should be made.

1. Intensities of Deuterated Molecules. The measurement of the absolute infra red intensities and hence the dipole moment derivatives of the b_{3u} vibrations of 1,4 difluoro Tetradeutero Benzene and the a_2'' vibrations of 1,3,5 trifluoro Trideutero Benzene and the interpretation of these results in terms of $\partial\mu/\partial S$ values. Comparison of these results with those of the original molecules should show which sign choices of

$\partial\mu/\partial Q$ values give rise to the correct set of solutions.

2. CNDO calculations. The calculation of the $\partial\mu/\partial S$ values for the b_{3u} vibrations of 1,4 difluoro Benzene and the a_2'' vibrations of 1,3,5 trifluoro Benzene. Comparison of these results with the experimental results should also show which sign choices of $\partial\mu/\partial Q$ values give rise to the correct set of solutions.

APPENDICES

Appendix I Matrix Algebra and Notation

It is not intended to describe in detail matrix algebra and notation but simply to mention a few points relevant to its use here.

A matrix is an array of numbers.

If a_{ij} is the i,j th element of the rectangular matrix A, dimension l by m, where i is the row number and j the column number of the element;

b_{ik} is the i,k th element of the matrix B, dimension m by n;

and c_{kj} is the k,j th element of the matrix C, dimension n by l;

and if the product of the two matrices B and C is A, then

$$A = BC$$

and $$a_{ij} = \sum_k b_{ik} c_{kj}$$

where the summation k is over all elements of the i th row of B and the j th column of C.

If X_i is the i th element of the column (or one dimensional) matrix X, dimension l;

and Y_j is the j th element of the column matrix Y, dimension m;

and if the product of the matrices A and Y is X, then

$$X = AY$$

and $$X_i = \sum_j a_{ij} Y_j$$

An important point to note is that, if

$$\frac{X_i}{Y_j} = a_{ij}$$

then $X_i = \sum_j a_{ij} Y_j$ as given above

and NOT $X_i = a_{ij} Y_j$

The notation used here is that usually followed, i.e. small (or lower case) letters for the elements of a two dimensional matrix and capital (or upper case) letters for the elements of a one dimensional matrix.

A square matrix is one for which the number of rows equal the number of columns.

A diagonal matrix is one for which only the diagonal elements are non-zero. Only a square matrix can be diagonal.

The unit or identity matrix E is a diagonal matrix in which all the diagonal elements have the value one.

The transpose of a matrix is one in which the row and column descriptions of the original are exchanged. Therefore, if B^t is the transpose of matrix B, then

$$(b^t)_{ij} = b_{ji}$$

If $$a_{ij} = \sum_k b_{ik}\, b_{jk}$$
$$= \sum_k b_{ik}\, (b^t)_{kj}$$

Therefore $$A = BB^t$$

and in this case A must be square.

If $$A = BC$$

then $$A^t = C^t B^t$$

The transpose of a column matrix X is a row matrix X^t.

A symmetric matrix is one whose transpose equals itself. Therefore

$$A = A^t$$

and $$a_{ij} = a_{ji}$$

A symmetric matrix must be square.

A diagonal matrix must be symmetric.

A unitary matrix is one for which

$$AA^t = E$$

Only a square matrix can have an inverse.

If $\qquad A = BC$

then $\qquad A^{-1} = C^{-1}B^{-1}$

provided A, B and C are all square.

If matrix A is a diagonal matrix, then matrix A^{-1} is also diagonal and if the i th diagonal element of A is a_i, then the i th diagonal element of A^{-1} is $1/a_i$.

In books on physical chemistry, matrices expressed in symmetry coordinates are printed in italics to distinguish them from matrices expressed in internal coordinates. In this thesis matrices expressed in symmetry coordinates are overprinted with an upper left to lower right diagonal line (or heraldic bend). Therefore,

$$\bcancel{G} = UGU^t$$

$$\bcancel{F} = UFU^t$$

$$\bcancel{Z} = UZU^t$$

$$\bcancel{L} = UL$$

Finally, the summation instruction

$$\Sigma^2_{i,j} = \Sigma_i \Sigma_j$$

Appendix II Calculation of the Symmetry Coordinates of 1,4 difluoro Benzene

Step 1. The symmetry elements of the molecule are determined and hence the symmetry point group.

The symmetry elements of 1,4 difluoro Benzene are:

a. Identity E

b. Planes of Symmetry $\sigma_h(yz)$ - the molecular plane
$\sigma_v(xy)$
$\sigma_v(xz)$

c. Axes of Symmetry $C_2(x)$
$C_2(y)$
$C_2(z)$

d. Centre of Symmetry i

These symmetry elements are shown in Appendix IV. From them it follows that 1,4 difluoro Benzene is a member of the D_{2h} ($=V_h$) symmetry point group, for which the character table is given in Wilson, Decius and Cross (8), Appendix X, p.327.

Step 2. The Reducible Representation of the transformations of the cartesian coordinates is calculated and divided into its Irreducible Representations.

As only the traces of the transformation matrices are required, only the transformations of the coordinates of those atoms which are coincident with the symmetry operation under consideration are considered.

The reducible representation is

E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma_v(xy)$	$\sigma_v(xz)$	$\sigma_h(yz)$
36	-4	0	0	0	0	4	12

The irreducible representations are obtained from the reducible representation by use of equation 73, Section 1.12.

$$a_i = 1/g \sum X(RR)\, X_i(IR)$$

Therefore the irreducible representations of the transformations of the cartesian coordinates are:

A_g	$(36 - 4 + 4 + 12)/8 = 6$
B_{1g}	$(36 - 4 - 4 - 12)/8 = 2$
B_{2g}	$(36 - 4 + 4 - 12)/8 = 4$
B_{3g}	$(36 + 4 - 4 + 12)/8 = 6$
A_u	$(36 + 4 - 4 - 12)/8 = 3$
B_{1u}	$(36 - 4 + 4 + 12)/8 = 6$
B_{2u}	$(36 + 4 - 4 + 12)/8 = 6$
B_{3u}	$(36 + 4 + 4 - 12)/8 = 4$

The irreducible representations of the translations and rotations are:

T_x	B_{3u}	R_x	B_{3g}
T_y	B_{2u}	R_y	B_{2g}
T_z	B_{1u}	R_z	B_{1g}

Therefore the symmetry species of the 3n-6 normal modes have been calculated. Since 1,4 difluoro Benzene is a planar molecule, the normal modes can be further subdivided into in and out-of-plane vibrations. An out-of-plane vibration is one for which the character of σ (yz) is -1, (yz being the molecular plane).

Therefore

Γ (in plane normal modes) = $6A_g + 5B_{3g} + 5B_{1u} + 5B_{2u}$

Γ (out-of-plane normal modes) = $B_{1g} + 3B_{2g} + 2A_u + 3B_{3u}$

Step 3. The Symmetry Coordinates are constructed

The internal coordinates are also into in and out-of-plane and only the out-of-plane coordinates y and ϕ are considered. The numbering of the coordinates is shown in Figure 2.1.

Internal Coordinate Sets		Representative Internal Coordinate
y_{CF}	i.e. y_1, y_4	y_1
y_{CH}	i.e. y_2, y_3, y_5, y_6	y_2
ϕ_{HH}	i.e. ϕ_2, ϕ_5	ϕ_2
ϕ_{HF}	i.e. ϕ_1, ϕ_3, ϕ_4, ϕ_6	ϕ_1

For each symmetry operator, OR (the internal coordinate generated by operating on the representative internal coordinate R with the symmetry operator O) is determined. They are

O	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma_v(xy)$	$\sigma_v(xz)$	$\sigma_h(yz)$
R								
y_1	y_1	$-y_1$	$-y_4$	y_4	$-y_4$	y_4	y_1	$-y_1$
y_2	y_2	$-y_6$	$-y_3$	y_5	$-y_5$	y_3	y_6	$-y_2$
ϕ_2	ϕ_2	ϕ_5	ϕ_2	ϕ_5	$-\phi_5$	$-\phi_2$	$-\phi_5$	$-\phi_2$
ϕ_1	ϕ_1	ϕ_6	ϕ_3	ϕ_4	$-\phi_4$	$-\phi_3$	$-\phi_6$	$-\phi_1$

The symmetry coordinates are calculated using equation 86, Section 1.12.

$$S^r = N \sum_O \chi_O^r \, OR$$

The internal coordinates OR are given above and the values of χ_O^r are taken from the character table for the D_{2h} symmetry point group.

Therefore, the linear combinations of internal coordinates which make up the symmetry coordinates for the out-of-plane vibrations of 1,4 difluoro Benzene, according to the symmetry species under which they transform, are:

B_{1g} : $y_2 + y_3 - y_5 - y_6$
$\phi_1 - \phi_3 - \phi_4 + \phi_6$
B_{2g} : $y_1 - y_4$
$y_2 - y_3 - y_5 + y_6$
$\phi_1 + \phi_3 - \phi_4 - \phi_6$
$\phi_2 - \phi_5$
A_u : $y_2 - y_3 + y_5 - y_6$
$\phi_1 + \phi_3 + \phi_4 + \phi_6$
$\phi_2 + \phi_5$
B_{3u} : $y_1 + y_4$
$y_2 + y_3 + y_5 + y_6$
$\phi_1 - \phi_3 + \phi_4 - \phi_6$

Therefore, Γ (out-of-plane symmetry coordinates) =

$$2B_{1g} + 4B_{2g} + 3A_u + 3B_{3u}$$

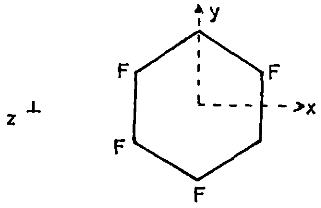
and one redundancy exists in each of the B_{1g}, B_{2g}, A_u symmetry coordinates.

The actual U matrix, together with the normalizing factors N, is shown in Table 2.10, Appendix IV.

Appendix III Calculation of the Principal Axes of 1,2,3,5 Tetrafluoro Benzene

Step 1. The Coordinates of the Centre of Mass and the Moment of Inertia Tensor are calculated.

The labelling of the substituents and the orientation of the arbitrary cartesian axes x, y and z is shown below.



The coordinates of the centre of mass are

$$C_x = -0.28 \text{ A}$$

$$C_y = -0.16 \text{ A}$$

$$C_z = 0.0$$

The moment of inertia tensor is

$$T = \begin{vmatrix} 315 & -50 & 0 \\ -50 & 373 & 0 \\ 0 & 0 & 689 \end{vmatrix}$$

These values are in amu.A^2

Step 2. The Principal Moments of Inertia and the orientation of the Principal Axes are calculated.

The moment of inertia tensor T is diagonalized, so that

$$TR = RI$$

Therefore

$$I = \begin{vmatrix} 286 & 0 & 0 \\ 0 & 402 & 0 \\ 0 & 0 & 689 \end{vmatrix}$$

and

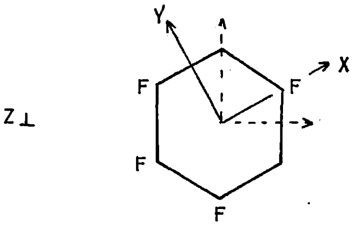
$$R = \begin{vmatrix} 3^{\frac{1}{2}}/2 & -1/2 & 0 \\ 1/2 & 3^{\frac{1}{2}}/2 & 0 \\ 0 & 0 & 1 \end{vmatrix}$$

where R is the principal axis transformation. Therefore

$\cos \theta = 3^{\frac{1}{2}}/2$, $\sin \theta = 1/2$, so $\theta = 30^{\circ}$

$\sin \phi = 1/2$, $\cos \phi = 3^{\frac{1}{2}}/2$, so $\phi = 30^{\circ}$

The orientation of the Principal Axes is, therefore, shown below:



With each principal axis is associated a principal moment and the axes are relabelled so that the axis with the smallest moment is A, etc. Therefore,

$I_X = 286$ amu.A^2 X → A

$I_Y = 402$ amu.A^2 Y → B

$I_Z = 689$ amu.A^2 Z → C

Step 3. The Principal Axes are assigned to their Symmetry Species.

1,2,3,5 tetrafluoro Benzene is a member of the C_{2v} Symmetry Point Group, of which the character table is given in Wilson Decius and Cross (8), Appendix X, p. 325. The orientation of the symmetry axes is determined using Mulliken's Rules (15).

For a planar C_{2v} molecule, they are that,

the z axis is the C_2 axis,

the x axis is perpendicular to the molecular plane,

the y axis is the remaining axis.

These symmetry axes belong to the same symmetry species as their corresponding translations T_x, T_y, and T_z, for which the symmetry species are given in the Character Table.

Symmetry Axis	Translation	Symmetry Species
x	T_x	B_1
y	T_y	B_2
z	T_z	A_1

Each of the symmetry axes is coincident with a principal axis of the molecule. Therefore,

Principal Axis A is coincident with Symmetry Axis z,

.. B .. .. y,

.. C .. .. x,

and for 1,2,3,5 tetrafluoro Benzene,

Type A Bands belong to the A_1 Symmetry Species,

.. B .. B_2 .. ,

.. C .. B_1 .. .

Appendix IV The U Matrices

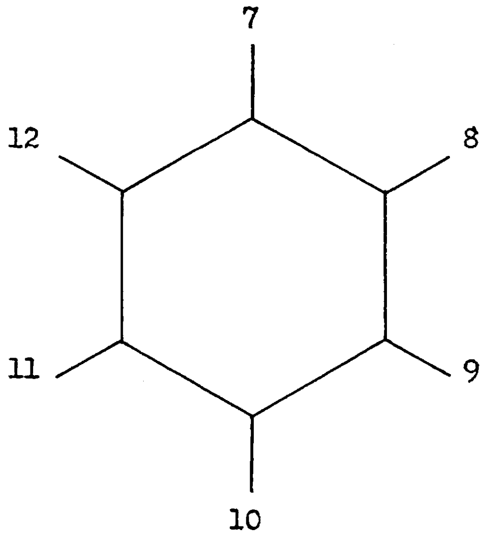
In the following 18 pages, the symmetry point groups, the symmetry elements and the U matrices for the molecules considered here are given.

The molecules are grouped as follows.

Symmetry Point Group	Molecule	Pages
C_s	1,2,4 trifluoro Benzene	397 & 398
C_{2v}	Fluoro Benzene Fluoro Pentadeutero Benzene Pentafluoro Benzene Pentafluoro Deutero Benzene	399 & 400
C_{2v}	1,2 difluoro Benzene 1,2,3,4 tetrafluoro Benzene	401 & 402
C_{2v}	1,3 difluoro Benzene 1,2,3,5 tetrafluoro Benzene	403 & 404
C_{2v}	1,2,3 trifluoro Benzene	405 & 406
C_{2v}	1,3,5 trifluoro Monodeutero Benzene 1,3,5 trifluoro Dideutero Benzene	407 & 408
D_{2h}	1,4 difluoro Benzene 1,4 difluoro Tetradeutero Benzene 1,2,4,5 tetrafluoro Benzene	409 & 410
D_{3h}	1,3,5 trifluoro Benzene 1,3,5 trifluoro Trideutero Benzene	411 & 412
D_{6h}	Benzene Hexadeutero Benzene Hexafluoro Benzene	413 & 414

C_s Symmetry Point Group

1,2,4 trifluoro Benzene



σ_h - Molecular Plane

	Atoms						Bond Lengths	
Molecule	7	8	9	10	11	12	r'	r
1,2,4 trifluoro Benzene	F	F	H	F	H	H	CF	CH

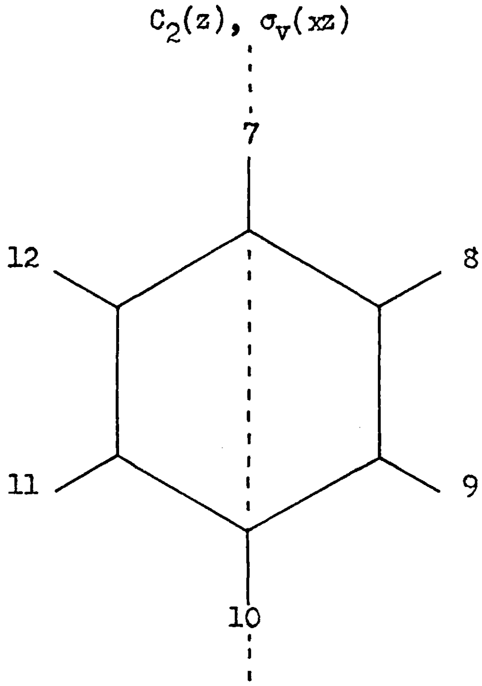
U Matrix - C_s Symmetry

SYMMETRY		COEFFICIENTS FOR i =						N	INTERNAL
SPECIES	COORD.	1	2	3	4	5	6	FACTOR	COORDINATE
A''	S_1	+1						1	$r'dy_i$
	S_2		+1					1	$r'dy_i$
	S_3			+1				1	$r\ dy_i$
	S_4				+1			1	$r'dy_i$
	S_5					+1		1	$r\ dy_i$
	S_6						+1	1	$r\ dy_i$
	S_7	+1						1	$R\ d\phi_i$
	S_8		+1					1	$R\ d\phi_i$
	S_9			+1				1	$R\ d\phi_i$
	S_{10}				+1			1	$R\ d\phi_i$
	S_{11}					+1		1	$R\ d\phi_i$
	S_{12}						+1	1	$R\ d\phi_i$

Table 2.4

C_{2v} Symmetry Point Group

Fluoro Benzene
Fluoro Pentadeutero Benzene
Pentafluoro Benzene
Pentafluoro Deutero Benzene



$\sigma_v(yz)$ - Molecular Plane

	Atoms						Bond Lengths	
Molecule	7	8	9	10	11	12	r'	r
Fluoro Benzene	F	H	H	H	H	H	CF	CH
Fluoro Pentadeutero Benzene	F	D	D	D	D	D	CF	CH
Pentafluoro Benzene	H	F	F	F	F	F	CH	CF
Pentafluoro Deutero Benzene	D	F	F	F	F	F	CH	CF

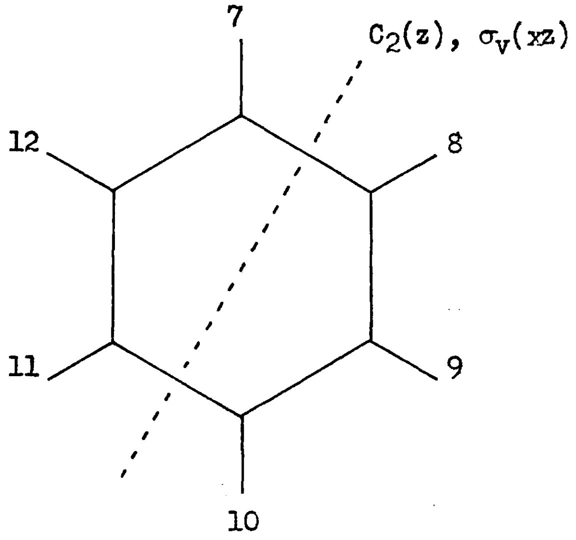
U Matrix - C_{2v} Symmetry

SYMMETRY		COEFFICIENTS FOR i =						N	INTERNAL
SPECIES	COORD.	1	2	3	4	5	6	FACTOR	COORDINATE
A_2	S_1		+1				-1	$2^{-\frac{1}{2}}$	$r\ dy_i$
	S_2			+1		-1		$2^{-\frac{1}{2}}$	$r\ dy_i$
	S_3	+1					+1	$2^{-\frac{1}{2}}$	$R\ d\phi_i$
	S_4		+1			+1		$2^{-\frac{1}{2}}$	$R\ d\phi_i$
	S_5			+1	+1			$2^{-\frac{1}{2}}$	$R\ d\phi_i$
B_1	S_1	+1						1	$r'dy_i$
	S_2				+1			1	$r\ dy_i$
	S_3		+1				+1	$2^{-\frac{1}{2}}$	$r\ dy_i$
	S_4			+1		+1		$2^{-\frac{1}{2}}$	$r\ dy_i$
	S_5	+1					-1	$2^{-\frac{1}{2}}$	$R\ d\phi_i$
	S_6		+1			-1		$2^{-\frac{1}{2}}$	$R\ d\phi_i$
	S_7			+1	-1			$2^{-\frac{1}{2}}$	$R\ d\phi_i$

Table 2.5

C_{2v} Symmetry Point Group

1,2 difluoro Benzene
1,2,3,4 tetrafluoro Benzene



$\sigma_v(yz)$ - Molecular Plane

	Atoms						Bond Lengths	
Molecule	7	8	9	10	11	12	r'	r
1,2 difluoro Benzene	F	H	F	H	H	H	CF	CH
1,2,3,4 tetrafluoro Benzene	H	F	H	F	F	F	CH	CF

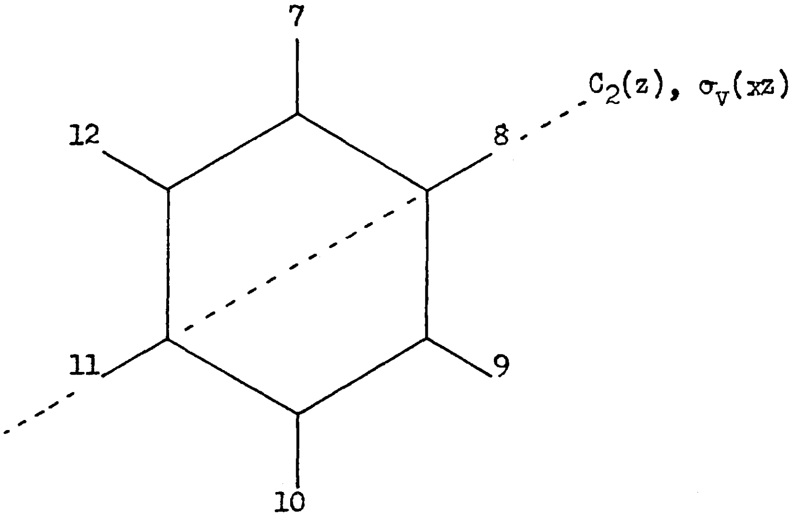
U Matrix - C_{2v} Symmetry

SYMMETRY		COEFFICIENTS FOR i =						N	INTERNAL
SPECIES	COORD.	1	2	3	4	5	6	FACTOR	COORDINATE
	S_1	-1	+1					$2^{-\frac{1}{2}}$	$r' dy_i$
	S_2			+1			-1	$2^{-\frac{1}{2}}$	$r\ dy_i$
	S_3				+1	-1		$2^{-\frac{1}{2}}$	$r\ dy_i$
A_2	S_4	+1						1	$R\ d\phi_i$
	S_5				+1			1	$R\ d\phi_i$
	S_6		+1				+1	$2^{-\frac{1}{2}}$	$R\ d\phi_i$
	S_7			+1		+1		$2^{-\frac{1}{2}}$	$R\ d\phi_i$
	S_1	+1	+1					$2^{-\frac{1}{2}}$	$r' dy_i$
	S_2			+1			+1	$2^{-\frac{1}{2}}$	$r\ dy_i$
B_1	S_3				+1	+1		$2^{-\frac{1}{2}}$	$r\ dy_i$
	S_4		+1				-1	$2^{-\frac{1}{2}}$	$R\ d\phi_i$
	S_5			+1	-1			$2^{-\frac{1}{2}}$	$R\ d\phi_i$

Table 2.6

C_{2v} Symmetry Point Group

1,3 difluoro Benzene
1,2,3,5 tetrafluoro Benzene



$\sigma_v(yz)$ - Molecular Plane

	Atoms						Bond Lengths	
Molecule	7	8	9	10	11	12	r'	r
1,3 difluoro Benzene	F	H	F	H	H	H	CF	CH
1,2,3,5 tetrafluoro Benzene	H	F	H	F	F	F	CH	CF

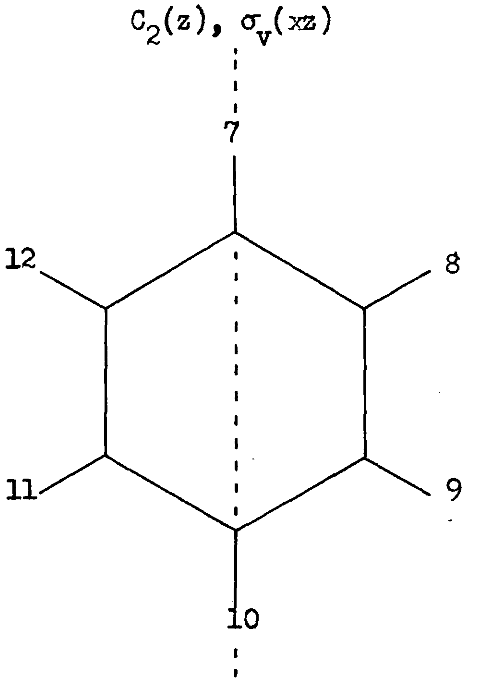
U Matrix - C_{2v} Symmetry

SYMMETRY		COEFFICIENTS FOR i =						N	INTERNAL
SPECIES	COORD.	1	2	3	4	5	6	FACTOR	COORDINATE
A_2	S_1	-1		+1				$2^{-\frac{1}{2}}$	$r' dy_i$
	S_2				+1		-1	$2^{-\frac{1}{2}}$	$r\ dy_i$
	S_3	+1	+1					$2^{-\frac{1}{2}}$	$R\ d\phi_i$
	S_4			+1			+1	$2^{-\frac{1}{2}}$	$R\ d\phi_i$
	S_5				+1	+1		$2^{-\frac{1}{2}}$	$R\ d\phi_i$
B_1	S_1	+1		+1				$2^{-\frac{1}{2}}$	$r' dy_i$
	S_2				+1		+1	$2^{-\frac{1}{2}}$	$r\ dy_i$
	S_3		+1					1	$r\ dy_i$
	S_4					+1		1	$r\ dy_i$
	S_5	-1	+1					$2^{-\frac{1}{2}}$	$R\ d\phi_i$
	S_6			+1			-1	$2^{-\frac{1}{2}}$	$R\ d\phi_i$
	S_7				+1	-1		$2^{-\frac{1}{2}}$	$R\ d\phi_i$

Table 2.7

C_{2v} Symmetry Point Group

1,2,3 trifluoro Benzene



$\sigma_h(yz)$ - Molecular Plane

	Atoms						Bond Lengths	
Molecule	7	8	9	10	11	12	r'	r
1,2,3 trifluoro Benzene	F	F	H	H	H	F	CF	CH

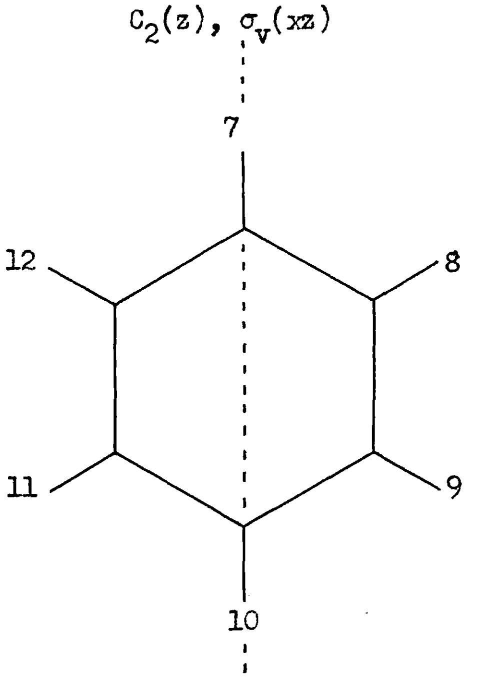
U Matrix - C_{2v} Symmetry

SYMMETRY		COEFFICIENTS FOR i =						N FACTOR	INTERNAL COORDINATE
SPECIES	COORD.	1	2	3	4	5	6		
A_2	S_1		+1				-1	$2^{-\frac{1}{2}}$	$r'dy_i$
	S_2			+1		-1		$2^{-\frac{1}{2}}$	$r\ dy_i$
	S_3	+1					+1	$2^{-\frac{1}{2}}$	$R\ d\phi_i$
	S_4		+1			+1		$2^{-\frac{1}{2}}$	$R\ d\phi_i$
	S_5			+1	+1			$2^{-\frac{1}{2}}$	$R\ d\phi_i$
B_1	S_1	+1						1	$r'dy_i$
	S_2				+1			1	$r\ dy_i$
	S_3		+1				+1	$2^{-\frac{1}{2}}$	$r'dy_i$
	S_4			+1		+1		$2^{-\frac{1}{2}}$	$r\ dy_i$
	S_5	+1					-1	$2^{-\frac{1}{2}}$	$R\ d\phi_i$
	S_6		+1			-1		$2^{-\frac{1}{2}}$	$R\ d\phi_i$
	S_7			+1	-1			$2^{-\frac{1}{2}}$	$R\ d\phi_i$

Table 2.8

C_{2v} Symmetry Point Group

1,3,5 trifluoro Monodeutero Benzene
1,3,5 trifluoro Dideutero Benzene



$\sigma_h(yz)$ - Molecular Plane

Molecule	Atoms 7	8	9	10	11	12	Bond Lengths r'	r
1,3,5 trifluoro Monodeutero Benzene	F	H	F	D	F	H	CF	CH
1,3,5 trifluoro Dideutero Benzene	F	D	F	H	F	D	CF	CH

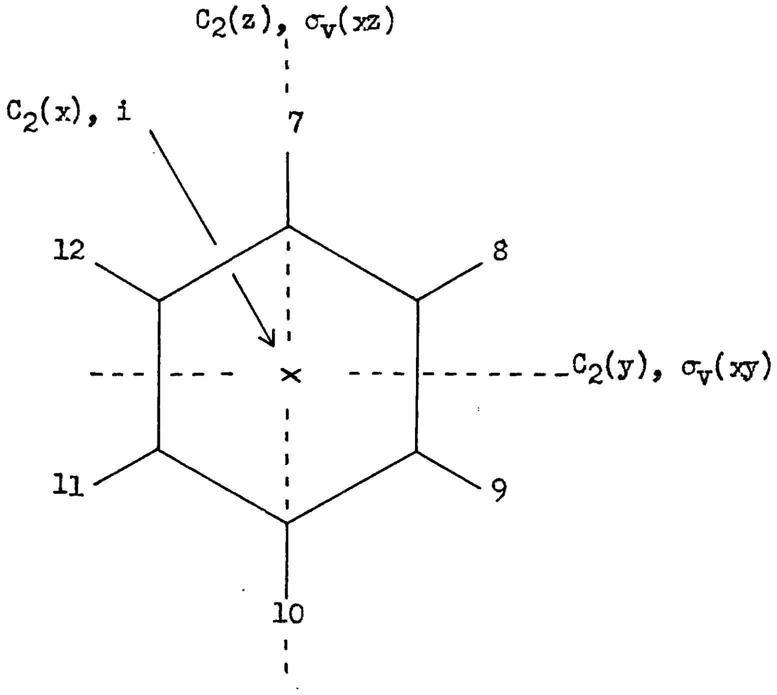
U Matrix - C_{2v} Symmetry

SYMMETRY		COEFFICIENTS FOR i =						N	INTERNAL
SPECIES	COORD.	1	2	3	4	5	6	FACTOR	COORDINATE
A_2	S_1		+1				-1	$2^{-\frac{1}{2}}$	$r\ dy_i$
	S_2			+1		-1		$2^{-\frac{1}{2}}$	$r' dy_i$
	S_3	+1					+1	$2^{-\frac{1}{2}}$	$R\ d\phi_i$
	S_4		+1			+1		$2^{-\frac{1}{2}}$	$R\ d\phi_i$
	S_5			+1	+1			$2^{-\frac{1}{2}}$	$R\ d\phi_i$
B_1	S_1	+1						1	$r' dy_i$
	S_2				+1			1	$r\ dy_i$
	S_3		+1				+1	$2^{-\frac{1}{2}}$	$r\ dy_i$
	S_4			+1		+1		$2^{-\frac{1}{2}}$	$r' dy_i$
	S_5	+1					-1	$2^{-\frac{1}{2}}$	$R\ d\phi_i$
	S_6		+1			-1		$2^{-\frac{1}{2}}$	$R\ d\phi_i$
	S_7			+1	-1			$2^{-\frac{1}{2}}$	$R\ d\phi_i$

Table 2.9

D_{2h} Symmetry Point Group

1,4 difluoro Benzene
1,4 difluoro Tetradeutero Benzene
1,2,4,5 tetrafluoro Benzene



$\sigma_h(yz)$ - Molecular Plane

Molecule	Atoms						Bond Lengths	
	7	8	9	10	11	12	r'	r
1,4 difluoro Benzene	F	H	H	F	H	H	CF	CH
1,4 difluoro Tetradeutero Benzene	F	D	D	F	D	D	CF	CH
1,2,4,5 tetrafluoro Benzene	H	F	F	H	F	F	CH	CF

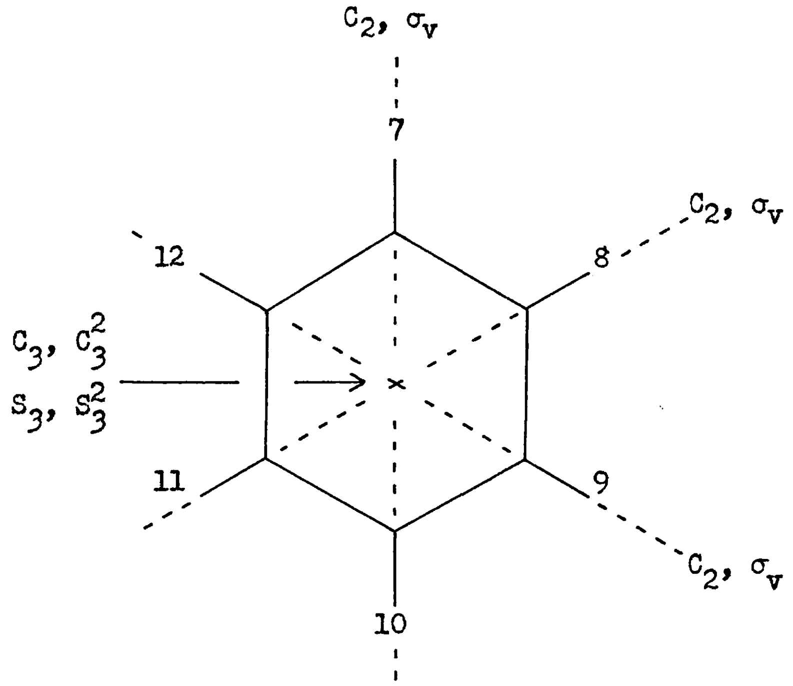
U Matrix - D_{2h} Symmetry

SYMMETRY		COEFFICIENTS FOR i =						N	INTERNAL
SPECIES	COORD.	1	2	3	4	5	6	**FACTOR**	COORDINATE
B_{1g}	S_1		+1	+1		-1	-1	2^{-1}	$r\ dy_i$
	S_2	+1		-1	-1		+1	2^{-1}	$R\ d\phi_i$
B_{2g}	S_1	+1			-1			$2^{-\frac{1}{2}}$	$r'dy_i$
	S_2		+1	-1		-1	+1	2^{-1}	$r\ dy_i$
	S_3		+1			-1		$2^{-\frac{1}{2}}$	$R\ d\phi_i$
	S_4	+1		+1	-1		-1	2^{-1}	$R\ d\phi_i$
A_u	S_1		+1	-1		+1	-1	2^{-1}	$r\ dy_i$
	S_2		+1			+1		$2^{-\frac{1}{2}}$	$R\ d\phi_i$
	S_3	+1		+1	+1		+1	2^{-1}	$R\ d\phi_i$
B_{3u}	S_1	+1			+1			$2^{-\frac{1}{2}}$	$r'dy_i$
	S_2		+1	+1		+1	+1	2^{-1}	$r\ dy_i$
	S_3	+1		-1	+1		-1	2^{-1}	$R\ d\phi_i$

Table 2.10

D_{3h} Symmetry Point Group

1,3,5 trifluoro Benzene
1,3,5 trifluoro Trideutero Benzene



σ_h - Molecular Plane

	Atoms						Bond Lengths	
Molecule	7	8	9	10	11	12	r'	r
1,3,5 trifluoro Benzene	F	H	F	H	F	H	CF	CH
1,3,5 trifluoro Trideutero Benzene	F	D	F	D	F	D	CF	CH

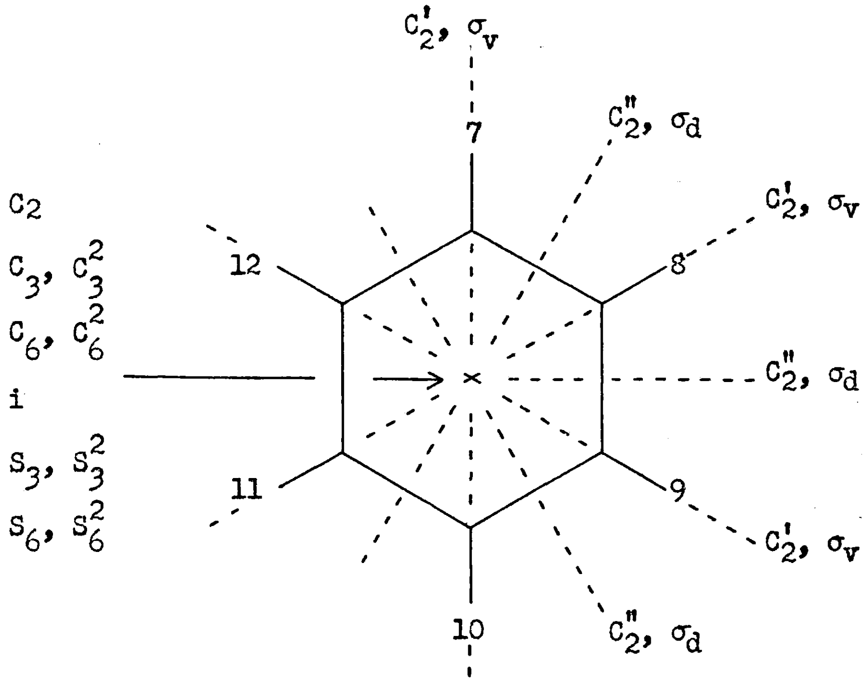
U Matrix - D_{3h} Symmetry

SYMMETRY		COEFFICIENTS FOR i =						N	INTERNAL
SPECIES	COORD.	1	2	3	4	5	6	FACTOR	COORDINATE
A_2''	S_1	+1		+1		+1		$3^{-\frac{1}{2}}$	$r' dy_i$
	S_2		+1		+1		+1	$3^{-\frac{1}{2}}$	$r\ dy_i$
	S_3	+1	-1	+1	-1	+1	-1	$3^{-\frac{1}{2}}$	$R\ d\phi_i$
E''	S_{1a}	+2		-1		-1		$6^{-\frac{1}{2}}$	$r' dy_i$
	S_{1b}			+1		-1		$2^{-\frac{1}{2}}$	$r' dy_i$
	S_{2a}		-1		+2		-1	$6^{-\frac{1}{2}}$	$r\ dy_i$
	S_{2b}		-1				+1	$2^{-\frac{1}{2}}$	$r\ dy_i$
	S_{3a}	+1	+2	+1	-1	-2	-1	$12^{-\frac{1}{2}}$	$R\ d\phi_i$
	S_{3b}	-1		+1	+1		-1	2^{-1}	$R\ d\phi_i$
	S_{4a}	+1		-1	+1		-1	2^{-1}	$R\ d\phi_i$
	S_{4b}	+1	-2	+1	+1	-2	+1	$12^{-\frac{1}{2}}$	$R\ d\phi_i$

Table 2.11

D_{6h} Symmetry Point Group

Benzene
Hexadeutero Benzene
Hexafluoro Benzene



σ_h - Molecular Plane

	Atoms						Bond Lengths	
Molecule	7	8	9	10	11	12	r'	r
Benzene	H	H	H	H	H	H		CH
Hexadeutero Benzene	D	D	D	D	D	D		CH
Hexafluoro Benzene	F	F	F	F	F	F		CF

U Matrix - D_{6h} Symmetry

SYMMETRY		COEFFICIENTS FOR i =						N	INTERNAL
SPECIES	COORD.	1	2	3	4	5	6	FACTOR	COORDINATE
B_{2g}	S_1	+1	-1	+1	-1	+1	-1	$6^{-\frac{1}{2}}$	$r\ dy_i$
	S_2	-1	+1	-1	+1	-1	+1	$6^{-\frac{1}{2}}$	$R\ d\phi_i$
E_{1g}	S_{1a}	+2	+1	-1	-2	-1	+1	$12^{-\frac{1}{2}}$	$r\ dy_i$
	S_{1b}		+1	+1		-1	-1	2^{-1}	$r\ dy_i$
	S_{2a}	+1	+2	+1	-1	-2	-1	$12^{-\frac{1}{2}}$	$R\ d\phi_i$
	S_{2b}	-1		+1	+1		-1	2^{-1}	$R\ d\phi_i$
A_{2u}	S_1	+1	+1	+1	+1	+1	+1	$6^{-\frac{1}{2}}$	$r\ dy_i$
E_{2u}	S_{1a}	+2	-1	-1	+2	-1	-1	$12^{-\frac{1}{2}}$	$r\ dy_i$
	S_{1b}		-1	+1		-1	+1	2^{-1}	$r\ dy_i$
	S_{2a}	-1		+1	-1		+1	2^{-1}	$R\ d\phi_i$
	S_{2b}	-1	+2	-1	-1	+2	-1	$12^{-\frac{1}{2}}$	$R\ d\phi_i$

Table 2.12

Appendix V Band Types

Band Types and Moments of Inertia of Symmetric Top Molecules

Molecule	Moment	Symmetry Species	Band Type
Benzene	148	E_{1u}	perp.
	296	A_{2u}	para.
1,3,5 trifluoro Benzene	476	E'	perp.
	951	A_2''	para.
Hexafluoro Benzene	807	E_{1u}	perp.
	1614	A_{2u}	para.

The Moments of Inertia are in 10^{-40} g.cm^2

perp. - Perpendicular

para. - Parallel

Band Types of Asymmetric Top Molecules

Molecule	Band Type	Symmetry Species
Fluoro Benzene	A	A_1
	B	B_2
	C	B_1
1,2 difluoro Benzene	A	A_1
	B	B_2
	C	B_1
1,3 difluoro Benzene	A	B_2
	B	A_1
	C	B_1
1,4 difluoro Benzene	A	B_{1u}
	B	B_{2u}
	C	B_{3u}
1,2,3 trifluoro Benzene	A	B_2
	B	A_1
	C	B_1
1,2,4 trifluoro Benzene	A	A'
	B	
	C	A''
1,2,3,4 tetrafluoro Benzene	A	B_2
	B	A_1
	C	B_1
1,2,3,5 tetrafluoro Benzene	A	A_1
	B	B_2
	C	B_1
1,2,4,5 tetrafluoro Benzene	A	B_{2u}
	B	B_{1u}
	C	B_{3u}
Pentafluoro Benzene	A	B_2
	B	A_1
	C	B_1

Appendix VI Application of the theory of Gribov to Benzene

The equation to be solved is equation 45, section 5.8.

$$\left[|\partial \mu / \partial Q| - |\mu| S^{-1} \Delta T_{1q} \right] \mathcal{L}^{-1} U = |e| \, |\partial \mu / \partial R|$$

Since there is only one vibration in the A_{2u} symmetry species of Benzene, G and L are both one by one matrices with single elements g and a respectively. Therefore, from equation 32, Section 1.5

$$g = a^2$$

Also $$g = 1/m_H + 1/m_C$$

This is the form given by Miller and Crawford (116) and can also be obtained by expansion of the relevant equations in Chapter One, using the B, M^{-1} and U matrices given below.

$|\mu|$ is a six by one matrix with identical elements μ_{CH} - the C-H bond moment (It is assumed that μ_{CC} is zero).

S^{-1} is a six by six matrix with diagonal elements $1/r$, where r is the C-H bond length.

Δ is a six by twelve matrix, the first row of which is

Atoms	H_1	H_2	H_3	H_4	H_5	H_6	C_1	C_2	C_3	C_4	C_5	C_6
	1	0	0	0	0	0	-1	0	0	0	0	0

For bond 2, $H_2 = 1$, $C_2 = -1$, etc.

From equation 44, Section 5.8

$$T_{1q} = M^{-1} B_q^t U^t \mathcal{G}^{-1} \mathcal{L}$$

M^{-1} is a twelve by twelve matrix, the first six diagonal elements of which are $1/m_H$ and the next six are $1/m_C$.

B is a twelve by six matrix, the first column of which is

Atoms	Internal Coordinate rdy_1
H_1	+1
H_2	0
H_3	0
H_4	0
H_5	0
H_6	0
C_1	$-1-2r/R$
C_2	r/R
C_3	0
C_4	0
C_5	0
C_6	r/R

where R is the C–C bond length.

For internal coordinate rdy_2, $H_2 = +1$, $C_2 = -1-2r/R$, etc.

U^t is a six by one matrix, such that the symmetry coordinate is

$$S = 6^{-\frac{1}{2}} (rdy_1 + rdy_2 + rdy_3 + rdy_4 + rdy_5 + rdy_6)$$

(See Appendix IV).

Therefore, by expansion it can be shown that

$$|\mu| S^{-1} \Delta T_{1q} = 6^{\frac{1}{2}} \mu_{CH}/r \;.\; a$$

and $$X = \partial\mu/\partial Q \;.\; a^{-1} - 6^{\frac{1}{2}} \mu_{CH}/r$$

where X is defined by equation 46, Section 5.8, and in this case is a one by one matrix.

The first element of XU is, therefore,

$$(XU)_1 = \partial\mu/\partial Q \;.\; a^{-1}\, 6^{-\frac{1}{2}} - \mu_{CH}/r$$

The first element of $|e||\partial\mu/\partial R|$ is $\partial\mu_{RM}/\partial R_1$, (see Section 5.8)

Also $R_1 = rdy_1$ and since $dy = y - ye$ and ye (the equilibrium value) is zero, $dy = y$.

Therefore, $\partial\mu_{RM}/\partial y_1 = \partial\mu/\partial y_1 - \mu_{CH}$

where $\partial\mu/\partial y_1 = \partial\mu/\partial Q \,.\, a^{-1}\, 6^{-\frac{1}{2}}\, r$

and this is the value calculated for the bond moment derivative, using the bond moment hypothesis (153, 156).

All the elements of XU and $|e||\partial\mu/\partial R|$ are the same since all the internal coordinates rdy_1 to rdy_6 are the same. Therefore

$$\partial\mu_{RM}/\partial y_{CH} = \partial\mu/\partial y_{CH} - \mu_{CH}$$

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