

CHAPTER I

INTRODUCTION

Various methods of evaluating intramolecular force constants are discussed with a brief account of important types of force fields. The parameter approach to force fields has been described. Procedures for calculating force constants using additional experimental data are also summarised.

1. Introduction

An immense amount of experimental data has been accumulated from investigations of infrared absorption spectra and of the Raman effect in polyatomic molecules. Only an extremely small fraction of this material has been subjected to analysis, although the theoretical tools for such analysis are quite well developed and the results which could be obtained are of considerable interest. One reason for this situation is the amount of labour required to unravel the spectrum of a complex molecule. In attempting to account for the observed infrared and Raman spectra of molecules, a certain simplified model for such molecules is adopted and then the spectra which this model would exhibit are calculated. One of the best representations for the normal state of the molecule is provided by the potential energy function for the molecule which is a representation of the forces that arise when the atoms are displaced from their equilibrium positions. This leads to a determination of the various force constants for the bonds in a molecule.

A molecule may be regarded as a group of atoms bound together by certain forces. Acting between the atoms, these forces tend to keep the molecule in squili-

brium. Small oscillations of atoms about their equilibrium positions in the molecule cause the appearance of the so called vibrational infrared and Raman spectra.

In a polyatomic molecule the number of force constants usually exceeds the number of normal vibrations. In such cases certain approximations are made and considerable amount of work has been done in the determination of molecular force fields. However upto now the determination of exact force constants has been restricted mainly to molecules with two vibrations in a single species. In the present work the force constants of some molecules having two or three vibrations in a single species is attempted with the aid of new approximation methods. A brief review of the theory of normal vibrations, different types of force fields described in literature and methods for evaluating them is presented in the following pages.

2. Theory of Normal Vibrations and Normal Co-ordinate Analysis.

In diatomic molecules, the vibration of the nuclei occurs only along the line connecting two nuclei. In polyatomic molecules however the situation is much more complicated because all the nuclei perform their own harmonic oscillations. It can be shown that any of these

extremely complicated vibrations of the molecule may be represented as a superposition of a number of normal vibrations corresponding to the harmonic frequencies.

The mathematical analysis of molecular vibrations requires as the first step the formulation of expressions for kinetic and potential energies of the molecule in any convenient set of co-ordinates (1-4). In the course of a vibration, the change in the equilibrium configuration of a molecule may be represented by a set of cartesian displacement co-ordinates q_i ($i = 1, 2, \dots, n$) where $n = 3N$ for an N -atomic molecule. For small displacements, the potential energy V of the molecule, which depends only on the internal configuration of the molecule is a homogeneous quadratic function of the displacements of the atoms about their equilibrium positions. This constitutes the well known harmonic approximation in the theory of small vibrations. The potential energy is accordingly written in the form

$$V = \frac{1}{2} \sum_{ij}^{3N} b_{ij} q_i q_j \quad (1.1)$$

where b_{ij} are the force constants. The kinetic energy T of the molecule may be written as a quadratic function of the time derivatives of the displacement co-ordinates.

$$T = \gamma_2 \sum_1^{3N} \dot{q}_1^2 \quad (1.2)$$

The cross terms in the potential energy expressions can be eliminated by a linear transformation of the displacement co-ordinates q_1 to a set of "normal co-ordinates" Q_1 through the relation

$$q_k = \sum_1 B_{ki} Q_i \quad (1.3)$$

By an appropriate choice of the coefficients B_{ki} , both the potential and the kinetic energies can be expressed as

$$T = \gamma_2 \sum_1 \dot{Q}_1^2 \quad (1.4)$$

$$V = \gamma_2 \sum_1 \lambda_1 Q_1^2 \quad (1.5)$$

without any cross products.

Substitution of these expressions in the Lagrange equations of motion results in the set of equations of motion

$$\ddot{Q}_k + \lambda_k Q_k = 0 \quad (1.6)$$

It can hence be shown that λ 's are the eigenvalues of the b_{ij} matrix and are given by the roots of the deter-

secular equation

$$\begin{vmatrix} b_{11}-\lambda & b_{12} & b_{13} & - & - \\ b_{21} & b_{22}-\lambda & b_{23} & - & - \\ b_{31} & b_{32} & b_{33}-\lambda & - & - \\ - & - & - & - & - \\ - & - & - & - & - \end{vmatrix} = 0$$

(1.7)

The order of this secular equation is equal to the number of normal vibrations. Each normal co-ordinate Q_k corresponds to an independent mode of vibration of the molecule and has a characteristic parameter λ_k called the frequency parameter which is related to the vibrational frequency ν_k by

$$\lambda_k = 4\pi^2 \nu_k^2 \quad (1.8)$$

On solving the secular equation we get in general $3N-6$ nonzero real roots, ($3N-5$ for linear molecules), equal in number to the vibrational degree of freedom. The zero roots of the secular equation represent the translational and rotational modes of the molecule. In practice using experimentally observed fundamental vibrational frequencies, the secular equation is

solved for the force constants and normal modes. The programme of evaluating force constants and normal co-ordinates of a molecule is known as normal co-ordinates analysis.

The force constants may be calculated using Wilson's FG matrix method (5, 6). The essential merit of this method is that by exploiting molecular symmetry, the vibrational secular equation can be factored into lower orders. To apply the FG matrix method, first the number of genuine vibrations belonging to each irreducible representation of the point group of the molecule is found by group-theoretical considerations (1, 4). A set of internal co-ordinates which are changes in bond length and bond angle is chosen since the potential and kinetic energies expressed in terms of internal co-ordinates do not involve translational and rotational motion of the molecule as a whole.

Using the internal co-ordinate 'r' the expression for potential energy is written as

$$2V = \sum f r \quad (1.9)$$

where f is the force constant matrix. The internal co-ordinates r are transferred into an orthogonal set of symmetry co-ordinates which are linear combinations

of the internal co-ordinates and are constructed in such a way that they transform according to the character of the vibrational type of the point group to which they belong. The symmetry co-ordinates are defined by the transformation

$$S = Ux \quad (1.10)$$

where U is an orthogonal matrix.

In symmetry co-ordinates the expression for the potential energy is

$$2V = \tilde{S} F S \quad (1.11)$$

where F is the matrix of symmetry force constants.

F is related to f by the equation

$$F = U f \tilde{U} \quad (1.12)$$

The corresponding expression for the kinetic energy of the molecule is

$$2T = \tilde{\dot{x}} g^{-1} \dot{x} \quad (1.13)$$

$$= \tilde{\dot{S}} G^{-1} \dot{S} \quad (1.14)$$

where $G = U g \tilde{U}$

The kinetic energy matrix G^{-1} is determined by the atomic masses and molecular geometry. The method

for calculating elements of the G matrix is reported in the literature (7-11). The G_{ij} elements for a non-degenerate species are given by

$$G_{ij} = \sum_p \mu_p g_p \vec{s}_i^t \cdot \vec{s}_j^t \quad (1.15)$$

and for a degenerate species

$$G_{ij} = \frac{1}{d} \sum_p \mu_p g_p (\vec{s}_{ia}^t \cdot \vec{s}_{ja}^t + \vec{s}_{ib}^t \cdot \vec{s}_{jb}^t + \dots) \quad (1.16)$$

where P refers to a set of equivalent atoms, t a typical atom, μ_p the reciprocal mass of the atom, g_p the number of equivalent atoms in the P^{th} set and d is the degree of degeneracy.

The \vec{s} vectors in the above expressions are given by

$$\vec{s}_i^t = \sum_k U_{ik} \vec{s}_{kt} \quad (1.17)$$

where i represents the i^{th} symmetry co-ordinate and U_{ik} the coefficient of the k^{th} internal co-ordinate in it. Expressions for the \vec{s}_{kt} vectors are given by Wilson, Decius and Cross (4) and by Meister and Cleveland (9).

In terms of the symmetry force constant matrix F and inverse kinetic energy matrix G , the secular

equation may be written as

$$|F - G^{-1}\lambda| = 0 \quad (1.18)$$

or

$$|GF - E\lambda| = 0 \quad (1.19)$$

where E is a unit matrix. λ is related to the observed harmonic vibrational frequency ω

$$\lambda = 4\pi^2 c^2 \omega^2 \quad (1.20)$$

ω is in cm^{-1} and c is the velocity of light.

Usually the number of force constants to be determined far exceeds the number of normal frequencies and a unique solution is not possible using the vibrational frequencies alone. Hence the interpretation of the molecular potential function is based on some simplified model employing an approximate force field so as to reduce the number of unknown force constants. The ideas underlying some of these approximation methods are discussed below.

3. Approximate Force Fields

Several approximate force fields such as central force field (CFF), valence force field (VFF), modified valence force field (MVFF), orbital valence force

field (OVFF), Urey-Bradley force field (UBFF), and general valence force field (GVFF) have been proposed and widely used in literature. In the CFF approximation the forces in the molecule are assumed to be acting along the lines joining the atoms, irrespective of whether they are connected by a valence bond or not (12, 13). The number of force constants under this assumption is smaller than the number of frequencies. But the assumption holds only if the molecules are held by ionic interactions. Also the frequencies predicted on the basis of the central force field often do not agree with the observed ones.

According to the VFF postulated by Bjerrum (12) the restoring forces oppose the changes in valence coordinates like bond lengths and interbond angles. Here also the number of force constants is less than that of the vibrational frequencies. However the interactions between stretching and bending of different bonds in the molecule are not considered. A combination of central and valence type force fields has been postulated by Mecke (14) for XY_2 type molecules. Taking into account Pauling's idea that the stability of a molecule is due to the overlap of the orbitals of the bonded atoms, Wilson and Howard formulated a modified valence force field (MVFF) for XY_3 type molecules (15). In the UVFF introduced by Linnert and Heath (16-18) the electron density in

each bond is represented by localized molecular orbitals. In this theory no interactions between bond-stretching and bond-bending co-ordinates are included. But the properties of bonds in a molecule are well related to the inter-bond angles (19, 20). The hybrid bond force field (HBFF), a modification of OVFF based on the correlation of bond strength with bond angle, is successfully applied to ammonia molecule (21).

The UBFF (22) is another widely used model which takes into account the valence forces between bonded atoms and also the central forces between non-bonded atoms. This model satisfactorily reproduces the vibrational frequencies. Shimenouchi (23-24) has demonstrated the general validity of the UBFF. The number of force constants is not too many. But the UBFF does not account properly for the interaction between different internal valence co-ordinates. Several modifications have been suggested for the UBFF introducing different concepts like bond flexibility, trans interaction and trans and gauche interactions (25, 26, 27). One such modification, accounting for the presence of lone pair of electrons in the molecule has been shown to yield a useful force field model (28).

A more complete picture of the intramolecular force field is presented by the GVFF, which includes, in addition to the valence force constants, all possible

interactions between stretching and stretching, bending and bending and stretching and bending and altogether there are $\frac{1}{2} n (n + 1)$ force constants for an n^{th} order vibrational species. The GVFF furnishes the most general and physically meaningful model and many a normal co-ordinate analysis has been carried out using this picture. In the present investigation the general valence force field is employed. In the GVFF the determination of $\frac{1}{2} n (n + 1)$ force constants using n vibrational frequencies is often difficult. Here some approximation methods have to be used and in the following pages a brief review of the several approximation methods used for the force field will be given.

4. Approximation Procedures in a GVFF Framework

Many attempts have been made, in recent years, to develop a method, based on some mathematical constraint to determine an approximate force field from the vibrational frequencies alone. An excellent survey of approximation methods in general is made by Alix et.al. (29), and also an analysis of "Parameter Methods for Molecular Force Fields" is given by Ananthakrishnan et.al.(30).

4.1 Parameter Method

The parameter method is applied to the evaluation of molecular force fields throughout this work and hence a detailed review of this method will be given here.

The normal co-ordinates Q are related to the symmetry co-ordinates S through the transformation matrix L as

$$S = LQ \quad (1.21)$$

The L matrix is known as the normal co-ordinate transformation matrix. Wilson (5) has given a norm on the choice of the proper L matrix such that

$$L \tilde{L} = G \quad (1.22)$$

The matrices G , F and L together serve to determine the vibrational frequency ω_i through the equation

$$GFL = L \Lambda \quad (1.23)$$

where Λ is a diagonal matrix of elements $\lambda_i =$

$$4 \pi^2 c^2 \omega_i^2$$

The force constant matrix F is given by

$$F = (\tilde{L})^{-1} \Lambda L^{-1} \quad (1.24)$$

In the parametric approach to the vibrational problem, the L matrix is split into two factors in a more easily visualizable manner. Though this splitting is in no way unique, generally we can write

$$L = L_0 \Lambda \quad (1.25)$$

The only condition imposed on L_0 is that $L_0 \tilde{L}_0 = G$. Since L_0 is normed by Wilson's condition, it follows that A is an orthogonal matrix (31).

Even though there are several choices for L_0 , there exist two methods whereby it is constructed. They are the rotation and shear methods, whose geometrical significance in the S and Q space has been illustrated by Person and Crawford (32). Employing the currently used notation

$$L_0 = V \Gamma^{1/2} \quad (\text{in the rotation method}) \quad (1.26)$$

$$L_0 = T \quad (\text{in the shear method}) \quad (1.27)$$

Here V and Γ are respectively the eigen-vector and the eigen-value matrices of G . T is a triangular matrix which can be written in two alternative forms, viz. $T_{ij} = 0$ with $i < j$ or with $i > j$. The former one is preferable if the normal co-ordinates are nearly pure and if the ordering of frequencies is such that

$$\lambda_1 > \lambda_2 > \dots > \lambda_n \quad (32, 33).$$

The matrix A can be expressed as a function of $1/2 n (n - 1)$ parameters. Among the different ways of writing the A matrix the following three representations are useful (34).

(a) Angle parameters

$$A(\phi) = \prod_{i=1}^{n-1} \prod_{j=i+1}^n A_{ij}(\phi_{ij}) \quad (1.28)$$

Here A_{ij} is an elementary rotation matrix in the ij plane, the ii^{th} and jj^{th} elements are $\cos \phi_{ij}$, the ij^{th} element is $-\sin \phi_{ij}$ and the ji^{th} element is $\sin \phi_{ij}$. All other diagonal elements are unity and the off-diagonal elements are zero.

(b) Antisymmetric parameter matrix

$$A = (E - K)(E + K)^{-1} = 2(E + K)^{-1} - E \quad (1.29)$$

Here E is a unit matrix and the elements of the antisymmetric matrix K are the parameters α_{ij}

$$K = \gamma_2 \begin{bmatrix} 0 & \alpha_{12} & \alpha_{13} & \dots & \alpha_{1n} \\ -\alpha_{12} & 0 & \alpha_{23} & \dots & \alpha_{2n} \\ -\alpha_{13} & -\alpha_{23} & 0 & \dots & \alpha_{3n} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ -\alpha_{1n} & -\alpha_{2n} & -\alpha_{3n} & \dots & 0 \end{bmatrix} \quad (1.30)$$

(c) Exponential parameter matrix

$$A = e^K \quad (1.31)$$

where K has the same meaning as in (b). The first two types are quite often used, rather than the last one.

Other forms of L_0 matrix have also been suggested (35-37). But among the different representations for L_0 , the one in the triangular form appears superior to all others.

Making use of equation (1.25) in eq. (1.24) we get

$$(\tilde{L}_0)^{-1} A \Lambda \tilde{K} L_0^{-1} = F \quad (1.32)$$

This result was first obtained by Taylor (38) in 1950 and later by Török and Püley in a more general form (31). The same result has been arrived at or subjected to discussion by several authors during recent years (39-48).

Arbitrary A matrices constitute a representation of the n dimensional real orthogonal group $O(n)$, and such representations generate possible solutions of F .

Equation (1.32) is of basic importance and furnishes a systematic approach to the study of the complete set of mathematically possible solutions. This equation enables one to express the $1/2 n(n+1)$ elements of F_{ij} as a function of $1/2 n(n-1)$ parameters in a vibrational problem of order n . The second order problem is particularly interesting in this respect, since there is only one variable parameter, and one can always

look for the variation of the F_{ij} elements with this single parameter. Expressions for the elements F_{11} , F_{12} and F_{22} have been given as a function of a single parameter in such second order cases (47-49). Graphs showing the variation of the force constant elements with respect to an angle parameter have been drawn by Pfeiffer (35) and Strey (47). Similar graphs are presented for some pyramidal XY_3 type molecules in Chapter II.

For a vibrational problem of order $n = 3$, there will be 3 parameters and a four dimensional space is required to express each of the F_{ij} elements as a function of these parameters. A modification of this method using only 2 parameters for a third order vibrational problem has been developed in Chapter IV. Another approximation for the mapping of F_{ij} elements is by limiting the F_{ij} values to a certain maximum or minimum (47, 50). If we know the probable limits of at least a few of the F_{ij} elements then the possible range of the others can be computed from the F_{ij} mappings. While mapping the possible force fields for a certain assignment it is sufficient to scan the parameter space of ϕ_{ij} between the limits $-\pi/4 < \phi_{ij} < \pi/4$, because ϕ_{ij} occurs only in cosine and sine functions.

4.2 Iterative Methods

In this approach, one starts with an approximate

inverse kinetic energy matrix G_0 and a force constant matrix F_0 . The transformation from F_0 to the true F matrix which reproduces the experimental frequencies is achieved by an iterative procedure. In the method proposed by Fadini and Sawodny (51-53) the choice of the initial set of force constants corresponds to a complete neglect of the kinematic coupling of the vibrational modes. The true G matrix without the off-diagonal elements is taken as the initial G_0 matrix and the corresponding F_0 matrix is given by

$$G_0 = \Lambda_{\text{exp}} G_0^{-1} \quad (1.33)$$

The final true force constant matrix F is determined by a stepwise introduction of the off-diagonal elements of G matrix. At each step a correction ΔF to the force constant matrix is calculated by solving a system of equations based on the Cayley-Hamilton theorem.

Starting with the same initial set of matrices, Becher and Mattes (54) also suggested a stepwise coupling method, in which the final F matrix is calculated by a simple matrix multiplication process. The iteration is made possible by the successive application of the relation

$$F = \tau^{-1} \Lambda L^{-1} \quad (1.33)$$

The approximate F matrix at each step is used to formulate the eigenvector matrix L of the next

step. For the k^{th} step L_k is calculated from the secular equation

$$G_k F_{k-1} L_k = L_k \Delta_k \quad (1.34)$$

Taking into account the different symmetry representations and the possible interdependence of force constants, Chacon and Metzke (55) formulated a modified approach for the transformation to the final set.

In these stepwise coupling methods, the final result depends on the choice of the initial set of F_0 and G_0 matrices and on the method of introducing the off-diagonal elements of G (56-59). These methods impose no restrictions or conditions on the choice of the coordinate system. As such one can use a coordinate system in which the complete G matrix is diagonal. In this case the stepwise transition from G_0 to G is of little meaning (60).

Based on the same principle of stepwise coupling and transferability of the eigenvectors from an approximate solution to the exact solution of the secular equation, Alix et al. presented the matrix polynomial expansion method (56-58). In this approach a commutation relation of the form

$$[G_k F_{k-1}, G_k \Delta F_k] = 0 \quad (1.35)$$

exists between the solutions of the K^{th} and $(K-1)^{\text{th}}$ steps. With the use of the Cayley-Hamilton theorem this commutation relation yields a unique solution of the correction term ΔF_k .

4.3 Non-iterative Methods

In the F -trace approach (61-63) the eigenvector matrix L is considered in the parametric form

$$L = V \Gamma^{1/2} X \quad (1.36)$$

where V is the eigenvector matrix of G , Γ the diagonal matrix containing the eigenvalues of G and X an arbitrary orthogonal matrix containing $1/2 n(n-1)$ parameters. The corresponding parametrized F -matrix reads

$$F = V \Gamma^{1/2} X \Lambda \bar{X} \Gamma^{-1/2} \bar{V} \quad (1.37)$$

This approximation is based on the assumption that the same orthogonal matrix diagonalises the matrices F and G . The proper orthogonal matrix corresponds to the extremal values of the sum of the diagonal force constants. Using Lagrangian multipliers the stationary value of $\text{tr } F$ is reduced to the form

$$\text{tr } F^0 = \sum_i \Gamma_i^{-1} \lambda_i^0 \quad (1.38)$$

The value of $\text{tr } F$ is a minimum on choosing the eigen-

values in the increasing sequence and τ_i in the decreasing sequence. For the reverse ordering $\text{tr } F$ should be a maximum.

By a graphical method Stray (47) has investigated the external properties of force constants, in $n = 2$ cases, varying the angle parameter ϕ systematically over the range $0 \leq \phi \leq 2\pi$. According to Stray, the constraint that the force constant function is a maximum with respect to ϕ gives good force fields for hydrides. For many other types of molecules the condition f_{∞} minimum represents a satisfactory force field.

According to the L-trace approach the proper L matrix is one with maximum trace and smaller off-diagonal elements. The corresponding orthogonal matrix X is shown to be \tilde{V} . For problems of small mass-coupling the method is found to be successful. According to Pulay and Török (40, 41) the characteristic matrix L must be such that the sum of the difference between the co-ordinates Q_i and S_i is minimum. On imposing this condition

$$\sum_{i=1}^n |Q_i - S_i| \min = n + \text{tr } G - 2 [\text{tr } L]_{\max} \quad (1.39)$$

The proper L matrix is then shown to be $G^{1/2}$ defined as

$$G^{1/2} = V \Gamma^{1/2} \tilde{V}$$

The F trace and L trace approaches do not possess the property of invariance under scaling (40, 63-65).

Müller et al. (66-70) developed the L matrix approximation method, imposing the condition.

$\alpha_{ij} = 0, i < j$. The method is equivalent to Terkington's (71-72) approximation

$$(GF)_{ij} = 0, i < j \quad (1.40)$$

If the vibrations are characteristic, the approach yields reasonable force constants (66-70). The method has been successfully applied to $n = 3$ cases (70) and widely investigated in second order problems (66-70, 73-76).

According to the approximation method formulated by Redington and Alibury (77), the constraints are made directly on the restoring forces acting on a molecule in any displaced position and not on the force constant matrix. The basic assumption of this method rests on considerations of minimum potential energy. The parametrized restoring force F_k is assumed to be parallel to the corresponding internal co-ordinates. It is also assumed that the restoring force exerted by the

molecule for each internal co-ordinate is as large as possible. The condition to maximise the restoring forces for all displacements simultaneously is achieved through the virial theorem. The method is found to be suitable for obtaining reliable sets of force constants for species with no redundant symmetry coordinates.

4.4 Pseudo-Exact Methods

The force constants derived using the "relative Raman intensities" and "high-low frequency separation method" (HLFS) fall under the category of "pseudo-exact force constants". These methods are mainly important for ions and complexes where in general not as many additional data exist as for molecules in the gas phase (78).

Using the bond polarizability theory, (79) it has been demonstrated that one can calculate the force constants for XY_4 (T_d) type molecules (80-83). This procedure was later utilized by Müller et al (84) for some XY_4 (T_d) type molecules when $m_x \gg m_y$. The available results indicate that the application of the bond polarizability theory leads to a physically meaningful set of force constants for XY_4 (T_d) type molecules and XY_3 (D_{3h}) type molecules and ions. However the major problem with this procedure is the occurrence of multiple solutions for the force constants consistent with the observed relative Raman intensities.

The high-low frequency separation method (4, 85) is based on the separability of characteristic high or low group frequencies and hence a reduction of the order of the secular equation. This procedure is particularly advantageous for $n = 3$ cases, where one has the frequencies of a normal and isotopically substituted molecule, provided the coupling between the frequency to be factored out and the other two vibrations is negligible. Though for the solution of the complete secular equation, the 3 isotopic shifts are not sufficient, one can get the force constants corresponding to the (2×2) block using this method. However this method is successful only if the isotopically substituted atoms are essentially involved in at least one vibration of the truncated secular equation (85). The application of HLF5 method to many XY_3Z (C_{3v}) and XY_2Z (C_{2v}) and XYZ (C_s) type molecules suggests that this procedure is in most cases useful for determining the force constants. The Coriolis coupling constants can also be used to solve the truncated problem if sufficient data are not known.

5. Exact Determination of Force Constants Using Additional Data

The inadequacy of the frequency data alone in solving the secular determinant for $\frac{1}{2}n(n+1)$ force constants using 'n' frequencies for a symmetry species

constitutes the main problem of normal co-ordinate analysis. In such cases additional experimental data like isotopic frequencies, Coriolis coupling constants, mean amplitudes of vibration and centrifugal distortion constants are very useful. The normal co-ordinate transformation matrix L plays an important role in the theory of these constants.

5.1 Isotopic frequencies: Under the Born-Oppenheimer approximation the molecular force field is unaltered by isotopic substitution, as the force field is a function of the electronic structure of the molecule. But due to the change in atomic masses, the inverse kinetic energy matrix G and hence the secular equation are altered. An extra set of equations connecting the same force constants to the observed isotopic frequencies is obtained. Hence for an isotopic pair using the parameter eq. (1.32) it can be written as

$$(\tilde{L}_0)^{-1} \Lambda \Lambda (L_0)^{-1} = (\tilde{L}_0^*)^{-1} \Lambda^* \Lambda^* \tilde{\Lambda}^* (L_0^*)^{-1} \quad (1.41)$$

Here * denotes the case after isotopic substitution.

For a second order vibrational problem the three F_{ij} elements can be expressed as quadratic functions of a single parameter for the molecule and its substituent

(49). A search is then made for points in the parameter space where all the three equations hold. Such parameter plots yield two intersection points for the curves representing the three equalities and hence yield two sets of force fields, fitting the frequencies of the normal molecule and an isotopic substituent. Thus we arrive at an interesting result that, despite the application of isotopic frequencies there are two sets of force fields that fit these data in the $n = 2$ case, extremely well. Hence further experimental data are needed to eliminate the anomalous set. The use of mean amplitudes of vibration for this purpose has been proposed (49).

The graphical method of locating interactions cannot be extended to higher orders since even in the $n = 3$ case, one would require a six dimensional parameter space. Török (87) has suggested a simple method for mapping the F matrix by changing the values of $\frac{1}{2}(n-1)$ $(n-2)$ parameters in some systematic fashion.

5.2 Coriolis coupling constants: The coriolis coupling constants ζ^{α} depend upon the interaction between the rotation and vibration of a molecule (88) and can be experimentally obtained from the analysis of vibrational bands. A method to calculate these constants has been put forward by Meal and Polo (89)

$$\zeta^\alpha = L^{-1} C^\alpha (\tilde{L})^{-1} \quad (1.42)$$

The C^α matrices can be calculated from the geometry and atomic masses of the molecule (90-92). Duncan (93) has suggested a graphical method of incorporating the experimental ζ values into the vibrational problem of order two. Parametric approaches in this direction have been formulated by several authors. (31, 76, 94, 95). Substitution of eq. (1.25) into eq. (1.42) yields

$$\zeta = \tilde{\lambda} (L_0)^{-1} C^\alpha (\tilde{L}_0)^{-1} \Lambda \quad (1.43)$$

Equation (1.43) provides a method of mapping ζ^α values for systematic variation of parameter in Λ . It can be shown (95) that this equation may be expressed as

$$\zeta^\alpha = \tilde{\lambda} J \Lambda \quad (1.44)$$

where $J = T^{-1} C^\alpha (\tilde{T})^{-1}$ with T matrix in the lower triangular form.

Expanding eq. (1.44) in terms of the angular parameter ϕ for the second order vibrational problem and then solving for ϕ one gets

$$\tan \phi = \frac{-J_{12} \pm \sqrt{J_{12}^2 - (J_{11} - \zeta_{11})(J_{22} - \zeta_{11})}}{(J_{22} - \zeta_{11})}$$

$$+ J_{12} \pm \frac{\sqrt{J_{12}^2 - (J_{11} - J_{22})(J_{22} - J_{33})}}{(J_{11} - J_{22})}$$

(1.45)

Equation (1.45) is extremely useful in evaluating Φ and hence the F_{ij} elements for molecules of type XY_3 (C_{3v}), XY_3 (D_{3h}) and XY_4 (T_d) (95).

5.3 Mean amplitudes of vibration: These constants are generally considered insensitive as additional data in fixing the force field. However, a recent parametric approach (96) indicates that the mean amplitude of vibration corresponding to the nonbonded atom pair does serve well to fix the force fields in molecules of types XY_2 (C_{2v}), XY_3 (D_{3h}) and XY_4 (T_d). Attempts to parameterise the vibrational amplitudes have also been made by Alix et.al (97) and Török et.al (98).

Expressions for the mean amplitude of vibration $\bar{q}(X-Y)$ and $\bar{q}(Y \dots Y)$ in terms of the elements of the symmetrised mean square amplitude matrix Σ have been tabulated by Cyvin (90) for some molecules. The Σ matrix is related to L matrix and the vibrational frequencies ω_i as (90)

$$L \Delta \bar{L} = \Sigma \quad (1.46)$$

where Δ is a diagonal matrix of elements

$$\Delta_i = \frac{h}{8 \pi^2 \omega_i} \coth \frac{h \omega_i}{2 k T} \quad (1.47)$$

Expansion of eq. (1.46) for \sum_{ij} elements using eq. (1.25) enables one to write the \sum_{ij} elements as a function of a single parameter in the vibrational species of order two. Substituting these into the expressions for $\mathfrak{J}(X - Y)$ and $\mathfrak{J}(Y \dots Y)$, parametric expressions for vibrational amplitudes can be written. Incorporation of experimental values of $\mathfrak{J}(X - Y)$ and $\mathfrak{J}(Y \dots Y)$ into these equations can lead to the evaluation of the parameter and hence the molecular force field. It has been noted that there are two solutions for the parameter, if $\mathfrak{J}(X - Y)$ or $\mathfrak{J}(Y \dots Y)$ alone is used as additional data, however both data together serve to eliminate the anomalous solution (96).

5.4 Centrifugal distortion constants: The original theory of the centrifugal distortion constants $\mathfrak{F}_{\alpha\beta\gamma\delta}$ was developed by Kivelson and Wilson (99). The $\mathfrak{F}_{\alpha\beta\gamma\delta}$ are related to quantities $\mathfrak{t}_{\alpha\beta\gamma\delta}$ through the equation

$$\mathfrak{t}_{\alpha\beta\gamma\delta} = -2I_{\alpha\alpha}^c I_{\beta\beta}^c I_{\gamma\gamma}^c I_{\delta\delta}^c \mathfrak{F}_{\alpha\beta\gamma\delta} \quad (1.48)$$

where $\alpha, \beta, \gamma, \delta = x, y$ or z and $I_{xx}^e, I_{yy}^e, I_{zz}^e$ are the principal moments of inertia at equilibrium state. The Kivelson-Wilson theory has been further simplified by Cyvin et.al (100) by introducing a new matrix T_s which can be calculated from the geometry of the molecule. Then the $t_{\alpha\beta\gamma\delta}$ elements are given by the matrix relation

$$t = \tilde{T}_s G^{-1} F^{-1} G^{-1} T_s \quad (1.49)$$

Substituting for G and F from eqs. (1.22) and (1.32) the parametric form of eq. (1.49) can be written as

$$t = \tilde{B} A \Lambda^{-1} \tilde{A} B \quad (1.50)$$

The matrix B is given by

$$B = (L_0)^{-1} T_s \quad (1.51)$$

which depends only on the molecular geometry and masses of the atoms constituting the molecule. Eq. (1.50) can be effectively employed (101) to evaluate A and hence the force field in molecules with vibrational species of order $n = 2$.

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