MOLECULAR INTERNAL MECHANICS

STUDIES ON MOLECULAR STRUCTURE AND PROPERTIES USING MICROWAVE AND INFRARED SPECTRAL DATA

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CERTIFICATE

This is to certify that this thesis is a record of bonafide research carried out by Shri.Paul C.M., part-time research scholar, during the period 1977-'82 in the Department of Physics, Cochin University under my guidance.

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DECLARATION

This is to certify that this thesis has not previously formed the basis for the award of any degree, diploma, associateship, fellowship or other similar title or recognition.

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PREFACE

The investigations presented in this thesis have been carried out in the Department of Physics, Cochin University, where the author has been working as a part-time research scholar during the period 1977-'82.

The major objective of the thesis is essentially to evolve and apply certain computational procedures to evaluate the structure and properties of some simple polyatomic molecules making use of spectroscopic data available from the literature. It must be said that though there is dwindling interest in recent times in such analyses, there exists tremendous scope and utility for attempting such calculations as the precision and reliability of experimental techniques in spectroscopy have increased vastly due to enormous sophistication of the instruments used for these measurements. In the present thesis an attempt is made to extract maximum amount of information regarding the geometrical structure and interatomic forces of simple molecules from the experimental data on microwave and infrared spectra of these molecules.

A notable feature of the present thesis is the use of centrifugal distortion constants for the first time to determine the geometry of symmetric top molecules (Chapter V). The method developed here shows that reliable estimation of the molecular geometry can be carried out even when the microwave spectroscopic data on isotopic molecule are unavailable. The thesis contains seven chapters in all. The first two chapters are of an introductory nature and the basic background required for the calculation of centrifugal distortion constants is developed here. In the third chapter theory of parametrisation of centrifugal distortion constants in XY_2 bent symmetric molecules is discussed in detail. In addition to difining the limits of $\tau_{\alpha\beta\gamma\delta}$ elements, this approach helps to fix uniquely the force fields of molecules belonging to the above type. It is also shown that the prediction of fundamental vibrational frequencies is possible from a knowledge of the experimental values of $\tau_{\alpha\beta\gamma\delta}$ elements in these molecules. An exhaustive discussion of the parametrised form of D_J, D_{JK} for pyramidal XY_3 molecule is given in Chapter IV. Certain natural approximation formulas for D_J, D_{JK} and D_K are developed and the use of these formulas is demonstrated in Chapter V. The interatomic distances and interbond angles of PF_3, AsF_3 and OPF_3 molecules for which no complete isotopic data are available have been calculated making use of centrifugal distortion constants along with rotational constants and fundamental vibrational frequencies. Excellent agreement with results from electron diffraction studies assures the reliability of the method presented here.

Chapter VI contains a simple formula for the vibrational mixing parameter for XY_2 bent symmetric molecules. It also shows how the interbond angle in these molecules can be estimated from the pair of frequencies of the symmetric vibrations. In the last chapter an attempt is made to solve a third order vibrational problem using pseudo-exact parameter method. The set of force constant elements obtained in the case of CH_3F making use of this method is found to agrees very well with the results from more elaborate calculations.

Most of the calculations presented in this thesis have been carried out using the computor facilities available at the Cochin University Computor Centre. A sample programme (BASIC) used for the calculation of the centrifugal distortion constants in XY_3 symmetric top molecules is given as an Appendix.

Part of the investigations presented in this thesis has been published in the form of following papers.

1) Use of D_J, D_{JK} constants for the unique fixing of intramolecular forces in XY_3 pyramidal molecules.
Ananthakrishnan T.R., Paul C.M. and
Girijavallabhan C.P. 1977 Pramana 9 329

2) Molecular geometry using centrifugal distortion constants.
Paul C.M. and Girijavallabhan C.P.
1979 Nat. Acad. Sci. Letters 2 237

3) A note on obtaining vibrational mixing parameter from average bending energy criterion.
Girijavallabhan C.P. and Paul C.M.
1981 Pramana <u>17</u> 193

4) Molecular geometry of XY_3Z type molecules using centrifugal distortion constant.
Paul C.M. and Girijavallabhan C.P.
Paper presented at the fifty-first annual session of The National Academy of Sciences, India,
Cochin 1981 Paper No.122 (Physical Science Section)

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CHAPTER I

INTRODUCTION

Abstract

A general introduction to earlier work such as normal coordinate analysis, importance of L matrix, parametric approach, model force fields, kinetic models of molecules, approximation techniques and molecular structure determination from microwave data. The parameter representation of vibrational normal modes is stressed throughout.

1-1 Introduction:

The studies of structure and properties of molecules have acquired a renewed vigour in the past two decades mainly on account of the great strides made during these periods in the design and fabrication of technical equipment for spectroscopic measurements. The fact that the advent of laser has revolutionised the field of molecular spectroscopy is a well known one. Coupled with the microprocessor revolution which yields virtually unlimited computational capability, these recent developments have given the spectroscopists unprecedented power, precision and possibility to gain new insight into the atomic and molecular processes.

Even after the classic attempt by Wilson, Decious and Cross[2] a great deal remains to be done to organise and to assimilate the experimental data that have accumulated in the recent past. The body of knowledge of the vibrational infrared and Raman spectra of molecules and of rotational spectral data from microwave and high resolution infrared and Raman spectral studies of low pressure gases and vapours is so immense that the above objective is a major task which is likely to remain unfinished for ever. In the present thesis a humble effort is made to obtain some useful informations on the structure and properties of some poly atomic molecules making use of the experimental data on vibrational and rotational frequencies of the molecules reported earlier in the literature. The work heavily exploits many of the recently introduced unifying pictures of molecular vibration and interatomic force field. The following sections in this chapter give a systematic and concise description of the different aspects of vibration and rotation of polyatomic molecules.

1-2 Normal coordinate analysis:

According to the theory of small vibrations in the harmonic approximation, any actual vibration of the molecule can be represented as a linear superposition of a number of normal vibrations[1-10] at the characteristic frequencies of the molecule. Eliminating the six coordinates required to describe the translational and rotational motion of the molecule as a whole, there are (3 N - 6) normal modes of vibration for a molecule consisting of N atoms. Since no rotational freedom exists around the molecular axis a linear molecule has only (3 N - 5) normal modes.

The frequency of a normal vibration is determined by the kinetic and potential energy of the system. The kinetic energy depends on the masses of the individual atoms and their geometrical arrangement within the molecule, while the potential energy arises from interaction between the atoms and is described in terms of a set of force constants. The programme of evaluating force constants and normal coordinates of the molecule is known as normal coordinate analysis. Force constants may be conveniently calculated using Wilson's GF matrix method.[10] The essential merit of this method lies in the fact that it leads to a break up of the vibrational secular equation according to the symmetry species of the molecule. To apply the GF 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 [2, 7]. A set of internal coordinates which are changes in bondlength and bond angle is chosen. From the internal coordinates, orthonormalised linear combinations called symmetry coordinates are constructed such that they tranform according to the characters of the symmetry species to which they belong.

Let R denotes the column matrix of any symmetric coordinates r_i and S the column matrix of any symmetry coordinates S_i and Q the column matrix of normal coordinates. These are connected by

$$S = L\,Q = U\,R \qquad (1.1)$$

Here U is an orthogonal matrix and L is called the normal coordinate tranformation matrix[10]. The potential energy of the molecule is given by the expression

$$2\,V = \sum_{i,j} f_{ij}\; r_i\, r_j \qquad (1.2)$$

in which $f_{ij} = f_{ji}$ is the force constant corresponding to the interaction pair of internal coordinates r_i, r_j. In matrix form this is expressed as

$$2\,V = \tilde{R}\; f\; R \qquad (1.3)$$

Here $\sim$ denotes the tranpose of the column matrix R. The potential energy is not changed by the tranformation to symmetry coordinates. Hence

$$2\,V = \tilde{S}\; F\; S \qquad (1.4)$$

Where F is the force constant matrix in symmetry coordinates. It can be seen that

$$F = U\; f\; \tilde{U} \qquad (1.5)$$

The kinetic energy can also be expressed in matrix form as

$$2\,T = \tilde{\dot{S}}\;G^{-1}\;\dot{S} \tag{1.6}$$

Here G represents the inverse kinetic energy matrix which satisfies the normalising condition

$$G = L\,\tilde{L} \tag{1.7}$$

The G elements for a non degenerate species are given by the relation

$$G_{ij} = \sum_p \mu_p \; g_p \; (\vec{S}_{it} \cdot \vec{S}_{jt}) \tag{1.8}$$

Here i and j refer to the symmetry coordinates S_i and S_j respectively, p the set of equivalent atoms, a typical set being t, μ_p the reciprocal mass of an atom and g_p the number of equivalent atoms in the p^{th} set. The summation in eq.(1.8) extents over all the sets of equivalent atoms in the molecule. For a degenerate species

$$G_{ij} = (1/d) \sum_p \mu_p \; g_p \; (\vec{S}_{ia,t} \cdot \vec{S}_{ja,t}) \tag{1.9}$$

Here d denotes the degree of degeneracy of the species. The vectors appearing in both the above expressions (1.8) and (1.9) are known as S vectors and are obtained from the " s_{kt} vectors" according to the equation

$$S_{it} = \sum_k U_{ik} \; \vec{s}_{kt} \tag{1.10}$$

U_k being the coefficient of the internal coordinates r_k in the symmetry coordinates S_i. Wilson, Decius and Cross[2] have given expression for the s_{kt} vectors refering to different types of internal coordinates. Ferigle and Meister[5] have developed methods for writing down these vectors in the case of linear molecules.

The matrices G, F and L together serve to determine the vibrational frequencies Λ_i through[1-10] the equation

$$G F L = L \Lambda \qquad (1.11)$$

Here Λ is a diagonal matrix of elements $\lambda_i = 4\pi^2 c^2 \omega_i^2$. The condition for self consistancy of eq.(1.11) can be expressed as

$$| G F - E \Lambda | = 0 \qquad (1.12)$$

The elements λ_i can be calculated by solving this secular equation provided G and F are accurately known.

However in practice the eq.(1.12) is utilised for determining the F_{ij} elements since

i) direct relationship available for the force constants are only approximate[11,12,13]

ii) the vibrational frequencies can be obtained from infrared and Raman experiments with very high accuracy[8].

But under this formalism a vibrational species of order n would involve (1/2) n (n-1) force constant elements and their evaluation with the n experimentaly available λ_i values is an indeterminate problem. (in all cases except when n = 1). Any attempt to render the problem determinate should be based on either 1) the reduction of the number of F_{ij} elements by evolving restrictive models for force fields or 2) the increase of experimental results which can be used as additional input data. While the former method is not unique, the latter one sounds more physically satisfactory. Force constant evaluation during these years utilizes either of the two or both methods together.

1-3 Importance of L matrix :

Recent trends in the evaluation of molecular force constants are directed through the normal coordinate tranformation matrix L and employ the equation

$$F = \tilde{L}^{-1} \Lambda \quad L^{-1} \qquad (1.13)$$

obtained by substitution of eq.(1.7) into (1.11). Equation (1.13) throws light on the signefecance of matrix L in the analysis of molecular force fields. In addition to force constants[14], the mean ampletude of vibration, the Coriolis coupling constants[6], centrifugal distortion constants[15], the molecular dipole moments[16,17] and the polarizability tensors are all basically governed by the L_{ij} elements. In short the L matrix governs the characterstic vectors representing the vibrational forms of the molecule and bears the key for the whole molecular dynamics. The geometrical visualization of these normal coordinate tranformation matrices has been illustrated by Person and Crawford[19].

1-4 Paramatric approach :

In the parametric approach to the vibrational problem the normal coordinate tranformation L is split up into two parts in a more visualizable manner. Thus the splitting is in no way unique, generaly we can write

$$L = L_o \ C \qquad (1.14)$$

The only condition imposed on L_o is that $L_o \tilde{L}_o = G$. Since L is normalised by Wilson's condition, eq.(1.7), one can expect C to be an orthogonal matrix. A rigorous proof for this condition on C has been given by Torok and Pulay[20].

Though one can have several models for L_o, mainly two methods are being used. They are the shear method, whose geometrical significance in the S and Q space have been illustrated by Person and Crawford. Employing the most currently used terminology

$$L_0 = V \Upsilon^{1/2} \qquad (1.15)$$

In the rotation method and

$$L_o = T \qquad (1.16)$$

In the shear method. Here V and Υ are the eigen vector and eigen values of G respectively. T is a triangular matrix which can be written in the form, viz. $T_{ij} = 0$ with $i < j$ or with $j < i$. The former one corresponds to a lower triangular matrix. However if the order of frequencies is such that $\lambda_1 > \lambda_2 \ldots . > \lambda_m$ and if the normal coordinate is nearly pure, the lower triangular matrix is preferrable.[19,21]

The matrix C can be expressed as a function of (1/2) n (n-1) parameters. Among the different ways of writing the C matrix, the following three representations are useful[22]

a) Angle parameters

$$C(\phi) = \prod_{i=1}^{n-1} \prod_{j=i+1}^{n} A_{ij} (\phi_{ij}) \qquad (1.16a)$$

Here the A_{ij}'s are elementary rotation matrices in the ij plane

$$A_{ij}(\phi_{ij}) = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & U & 0 & 0 & 0 & -V & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & V & 0 & 0 & 0 & U & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

Where $U = \cos \phi_{ij}$ and $V = \sin \phi_{ij}$

In A_{ij} the iith and jjth element is $\cos\phi_{ij}$, the ijth element is $-\sin\phi_{ij}$ and the jith element is $\sin\phi_{ij}$. All the other diagonal elements are unity and off-diagonal elements are zero.

b) Antisymmetric parameters

$$C = (E - K)(E + K)^{-1} = 2\ (E + K)^{-1} - E \qquad (1.16b)$$

Here E is a unit matrix and the elements of the antisymmetric matrix K are the parameters

$$K = 2^{-1} \begin{bmatrix} 0 & \alpha_{12} & \alpha_{13} & \cdots\cdots & \alpha_{1n} \\ -\alpha_{12} & 0 & \alpha_{23} & \cdots\cdots & \alpha_{2n} \\ -\alpha_{13} & -\alpha_{23} & 0 & \cdots\cdots & \alpha_{3n} \\ \cdot & \cdot & \cdot & \cdots\cdots & \cdot \\ \cdot & \cdot & \cdot & \cdots\cdots & \cdot \\ -\alpha_{1n} & -\alpha_{2n} & -\alpha_{3n} & \cdots\cdots & 0 \end{bmatrix}$$

e) Exponential parameters

$$C = e^{K}$$

Here K has the same meaning as in eq.(1.16b). Thus the first two types are quite often used, rather than the last one.

It should be mentioned that neither the L_0's nor the C's are the same in the two formalism arising out of substitution of eq.(1.15) and (1.16) in eq.(1.14), though they may be related by the constraint that L must be the same in both cases. Thus

$$V \Upsilon^{1/2} C_R = T C_S \qquad (1.17)$$

This can be written as

$$C_R \tilde{C}_S = \Upsilon^{-1/2} \tilde{V} T \qquad (1.18)$$

Here C_R and C_S represents the C matrices in the rotation and shear methods respectively. Thus for n = 2, C_R and C_S matrices contains only one angle parameter in each which we will call ϕ_R and ϕ_S respectively and one gets a relation[21]

$$\phi_R = \phi_S + \delta + 2n\pi \qquad (1.19)$$

Here ϕ is the angle parameter, of the rotation matrix $Y = \Upsilon^{-1/2} \tilde{V} T$. Other form of L_0 matrices have also been[23,24,25] suggested but these forms are often applicable to n = 2 cases only[25] and are reducible to one of the two types discussed above, though equations analogous to eq.(1.17). Among these different representations for L_0, the one in the triangular form appears superior by virtue of

i) easy computability[19,21], especialy for higher order problems

ii) the progressive rigidity picture[26-34], it presents among the different modes of vibration

iii) the ease with which any particular mode of vibration can be treated as uncoupled[21] and

iv) its invariant nature to the scaling changes.

substituting eq.(1.14) into eq.(1.13) we get

$$F = \tilde{L}_0^{-1} \quad C \wedge \tilde{C} \quad L_0^{-1} \tag{1.20}$$

This result was first obtained by Taylor[35] in 1950 and later by Torok and Pulay in a more general form[20]. The above equation is basically important and provides a systematic approach to the study of the complete set of mathematically possible solutions. This equation has been succesfully applied to studies of problems in infrared and N.M.R. spectroscopy as well[36]

1-5 Model force fields:

The inadequacy of frequency data in determining all the (1/2) n (n+1) force constants for a symmetric species of order n constitutes the main problem of normal coordinate analysis. The problem in general is indeterminate unless additional data made use of or some extra assumptions are made which reduce the the number of force constants. In the absence of additional data, one can generate an infinite set of force fields as given in eq.(1.13) as

$$F = \tilde{L}^{-1} \quad \Lambda \quad L^{-1} \quad \text{with } L = L_0 C .$$

As a solution to this multiplicity, various approximate force fields have been suggested which imply one or other assumption of a physical or mathematical nature.

One such approximation leads to the central force field of Dennison[46] which postulates only forces along lines joining pairs of atoms. The number of force constants in this model is less than that of the frequencies. However, this assumption is strictly valid only if the molecule is held by ionic intractions and this is not in the case of general.

The simple valence force field (S.V.F.F), first introduced by Bjerrum[47], postulates a strong restoring force in the line of each valence bond whenever the distance between two bonded atoms changes. In addition, there is a resistive force opposing a change of angle between any two bonds.

The most general form of force field called the general valance force field (G.V.F.F) is defined by eq.(1.2), the f_{ij} are the general valance force constants. Various intractions between stretching and bending and stretching and stretching deformations are taken into account in this model. The number of interaction force constants that can be included in the potential energy function is always much larger than that of the observed frequencies from which they have to be evaluated. Then it becomes necessary to neglect some of the interaction force constants. The general valance force field presents a near complete picture of the internuclear forces and has been widely used in the investigation of force fields. If there are n_j vibrations of a given species j, the total number of independent force constants for a molecule in the general valance force field is given by $(1/2) \sum n_j (n_j + 1)$.

The concept of directed valance[48] has been applied by Heath and Linnet[49-52] to the function of a force field called the orbital valance force field (O.V.F.F), which eliminates the difficulty of introducing separate angle bending constants for out-of-plane vibrations. O.V.F.F accounts in a better way for the vibrational frequencies of certain molecules than does the simple valance force field. This however differs from the latter only in the treatment of the angular displacements. This O.V.F.F criterion for minimum potential energy is maximum overlap between the bonding orbitals of bonded atoms. O.V.F.F. breaks down in the case of molecules containing heavier atoms, and further, its treatment of bending vibrations is essentially artificial. But O.V.F.F. is only an approximation of the G.V.F.F., since the former takes into account a limited number of force constants. The hybrid bond force field (H.B.F.F), a modification of O.V.F.F.based on the correlation of bond strength with bond angle,is successfully applied to NH_3 molecule[66].

In the Urey Bradly[67] force field (U.B.F.F) in addition to main force constants which represents stretching or bending, repulsion force constants between non-bonded atoms are of the Vander Waals type. The main advantage of U.B.F.F. is that it contains a smaller number of force constants than the G.V.F.F.

does, and Shimonanochi[68,69,70] has demonstrated the general validity of the U.B.F.F.

Several modifications have been suggested for the conventional U.B.F.F by various workers[70-77]. From a comparative study of the U.B.F.F. and the G.V.F.F. in some tetrahedral, pyramidal and trigonal planar molecules, Duncan[78] has concluded that for the Urey Bradly model to be successful, the non-bonded repulsion force constant must explain both bond-bond and bond-angle interactions at one and the same time. However, this restriction breaks down when the atomic repulsions are not all in one plane and in these cases the Urey Bradly model fails to give a true picture.

1-6 Kinetic models for molecules:

Despite the indeterminate nature of vibrational problem when the frequencies are the experimental data, many attempts have been made to find mathematical conditions which at least approximate the correct physical situation. By putting C = E in eq.(1.20) we get a certain F matrix which depends only on the inverse kinetic energy matrix G. C = E means vibrations are purely governed by kinetic coupling between internal coordinates. Ideas along these lines of kinetically defined normal coordinates have been suggested mainly in the three different patterns.

i) the method of Billes potential[53,54]

ii) the method of charaterstic set of coordinates[24,37,40,41,55]

iii) the method of progressive rigidity[19, 26-34]

The method of progressive rigidity has been enjoying wider use in the recent years[26-34]. Here L = T is the lower triangular matrix. The validity of this approximation in calculating the force constants has been investigated by Muller[34] et al in detail. This method has the advantage that the potential is independent of the normalisation of the internal coordinates. This property known as scaling invariance makes the model of progressive rigidity more satisfactory than the two other models. Freeman[30] has given a comparison between the three kinematic models.

1-7 Approximation techniques :

The kinetic models mentioned earlier often lead to approximate force fields near the exact ones. But this method is basicaly unreliable since C = E means that the vibrations are purely governed by kinematic couplings between the internal coordinates. When these couplings are large, physically unacceptable off-diagonal elements appear in F. Moreover, the force field obtained in most cases fails to reproduce some of the sensitive additional data. These facts suggest small non zero values for the off-diagonal elements in C.

Many methods have been suggested during the last few years to obtain C matrices, that would correspond to the real physical situation in a better manner. Few of such methods appear to give the same picture given by the kinetic models, but some recent ones approach to true physical situation in a more satisfactory manner. They are Strey's method[44,21,23,32], method of Becher and Ballien[23,44,56,57], L matrix approximation by

Muller[32-34,58-61] and Reddingtons method[65]. Out of all these different methods, L matrix approximation technique developed mainly by Muller and collaberators is a more convenient one when compared to other methods and hence it is given below.

The L matrix plays a vital role of bringing in mixing between the symmetry coordinates and the normal coordinates. The validity of certain L matrix approximation has been analysed by Muller et al. Accordingly the frequencies ν and δ are assigned to the stretching and bending modes in a molecule. ν is grater than δ in most second order vibrational species and this type of problem may be called a $\nu\delta$ case. Following the same convention other cases viz. $\nu\nu$, $\delta\delta$ and $\nu\delta$ are also rarely possible. The approximation suggested by Muller are

$L_{12} = 0$ for $\nu\delta$ case

$L_{21} = 0$ for $\delta\nu$ case

$L_{12} = L_{21}$ for $\nu\nu$ or $\delta\delta$ case

$L_{12} = L_{21} = 0$ when the frequencies are well separated.

The approximation $L_{12} = 0$ is equivalent to the progressive rigidity model as well as to Streys' F_{22} minimisation condition as already mentioned. The method $L_{12} = 0$ is especially excellent in the evaluation of vibrational amplitudes. Muller has further noted that F_{22} will be more accurate than F_{11} under this approximation. Expressions for F_{ij} elements under the approximation

$L_{12} = 0$ and $L_{21} = 0$ are included in Table 1. The $L_{12} = 0$ approximation actually leads to a complete characteristic vibration for the mode corresponding to frequency δ[34,57,60]. This is quite obvious since under this condition, one is able to write an equation $G_{22} F_{22} = \lambda_2$. Supplementing to this idea it may be said that $L_{21} = 0$ approximation should lead to a complete characteristic vibration for the frequency ν , since under this condition one is able to write an equation $G_{11} F_{11} = \lambda_1$. The approximation $L_{12} = L_{21} = 0$ originates from the characteristic set of coordinate picture and is valid only in the limiting case of $G_{12} \approx 0$.

A rationalisation of the properties of L matrix for n = 3 is possible by considering the n = 3 problem to be made up of three n = 2 cases. Thus in a $\nu\nu\delta$ case one expects $L_{13} \approx L_{23} \approx 0$ ($\nu\delta$ case) and $L_{12} \approx L_{21}$ ($\nu\nu$ case) as has been suggested by Muller. Though there are eight different cases associated with the three frequencies, only $\nu\nu\delta$ and $\nu\delta\delta$ are the common ones. The approximation $L_{12} = L_{13} = L_{23} = 0$ for $\nu\nu\delta$ case have been found to be quite valid for the bent X Y Z molecules, with the frequencies in the decreasing order. The examples analysed are NSF, NSCl, ONF, ONCl and ONBr[34]. The expressions for the F_{ij} elements in terms of the λ and G elements are given in Table 2. The approximation $L_{12} = L_{13} = L_{23} =$ (corresponds to the progressive rigidity model. It can be noted that under this model the F_{ij} elements for n = 2 can be obtained from the F_{ij} elements for n = 2 by putting $\lambda_3 = 0$.

A general feature of the three approximation methods discussed so far is that the L matrix elements in all these are determined by mechanical couplings rather than by any chemical binding couplings.[34,63] Muller[63] has shown that the different approximation methods for the n = 2 case, discussed so far coincide in the case of very small mass couplings, ie. when $G_{12} << G_{11}$ and G_{22}. This means that any approximation method should be better checked with molecules having large mass couplings. Results of such attempts indicate that the $L_{12} = 0$ model gives better force fields generally[30,61]. Quite recently the criterion of minimum average bending energy has been found to give very satisfactory results in the case of small molecules[79,80].

1-8 Molecular structure determination from microwave data :

Determination of molecular geometry from spectral data has been a major endeavor of the experimental microwave spectroscopist. Spectroscopy in the microwave region is concerned with the study of rotating molecules. The rotation of a three dimensional body is quite complex and it is convenient to resolve it into rotational components about three mutually perpendicular directions through the centre of gravity - ie. along the principle axes of rotation. Then a body has three principal moments of inertia, one about each axis, usually designated I_A, I_B and I_C. Molecules are classified into groups according to their relative values of their three principal moments of inertia

i) Linear molecules for which $I_B = I_C$, $I_A = 0$

ii) Symmetric top molecules for which $I_B = I_C \neq I_A$

iii) Spherical top molecules for which $I_B = I_C = I_A$

iv) Asymmetric top molecules for which $I_B \neq I_C \neq I_A$

The structural information concerning bondlength and bond angles in a particular molecule is contained in the principal moments of inertia, which are inversely propotional to the rotational constants A, B, and C derived from the microwave spectrum. The effective bondlength derived from B_0 for the general ground vibrational state is designated as r_0 and the associated structure is called r_0 structure.

Solving Schrodinger equation, the rotational energy levels allowed to a rigid diatomic molecule are given by the expression

$$E_J = (h^2/8\pi^2 I)\ J(J+1) \tag{1.21}$$

Where J = 0, 1, 2, 3, ... In this expression h is Planck's constant, I is the moment of inertia either I_B or I_C, since both are equal. J is the rotational quantum number. For a diatomic molecule if m_1 and m_2 are the masses separated by a distance r_0 then moment of inertia

$$I = m_1 m_2 (m_1 + m_2)^{-1} r_e^2 = \mu r_0^2 \tag{1.22}$$

In the rotational region, spectra are usually discussed in terms of wave number, so eq.(1.21) can be expressed as

$$\epsilon_J = (E_J/hc) = B\ J\ (J+1) \quad cm^{-1} \tag{1.23}$$

Where c is the velocity of light in cm s^{-1} and B is the rotational constant given by

$$B = (h/8\pi^2 I_B\ c) \tag{1.24}$$

Consider the molecule in $J = 0$ state. By absorbing radiation it is raised to $J = 1$ state. The energy absorbed will be

$$\epsilon_{J=1} - \epsilon_{J=0} = 2\ B\ \text{cm}^{-1}$$

Hence an absorption line will appear at $2\ B\ \text{cm}^{-1}$. In general to raise a molecule from J to (J+1) state we would have

$$\epsilon_J \rightarrow \epsilon_{J+1} = 2\ B\ (J+1)\ \text{cm}^{-1} \qquad (1.25)$$

The step-wise raising of the rotational energy results in an absorption spectrum consisting of lines at 2 B, 4 B, ... cm^{-1}. Once 2 B is known from the measurement of the separation between the absorption lines, the bondlength of the diatomic molecule can be obtained using eq.(1.22) and (1.24).

On studying closely the spacing between the spectral lines we can find that separation slightly decreases for higher values of J. This is caused by the centrifugal stretching of the bonds, which indicates that the bonds are not rigid. In the upper rotational levels the molecule rotates faster and the bond is elongated slightly resulting in a decrease in the spacing between levels due to a slight increase in the moment of inertia.

The Schrodinger equation may be set up for a non-rigid molecule and the rotational energy levels are found to be

$$\epsilon_J = B\ J(J+1) - D\ J^2\ (J+1)^2\ \text{cm}^{-1} \qquad (1.26)$$

Where D is the centrifugal distortion constant given by

$$D = (h^3/32\pi^4\ I^2\ r^2\ K\ c)\ \ \text{cm}^{-1} \qquad (1.27)$$

K is the elasticity or force constant of the bond, and if the motion is S.H.M.

$$K = 4 \pi^2 \bar{\omega}^2 \mu c^2 \tag{1.28}$$

$\bar{\omega}$ is the vibrational frequency in cm^{-1} and μ is the reduced mass. For diatomic molecule $\mu = m_1 m_2 (m_1 + m_2)^{-1}$. If the force field is anharmonic eq.(1.26) becomes

$$\epsilon_J = B J (J+1) - D J^2 (J+1)^2 + H J^3 (J+1)^3 + K J^4 (J+1)^4 + \ldots\ldots cm^{-1} \tag{1.29}$$

where H, K etc. are small constants dependent upon the geometry of the molecule. They are however negligible compared with D. Considering the selection rule $\Delta J = \pm 1$ the energy levels of a non rigid molecule can be expressed as

$$\epsilon_{J+1} - \epsilon_J = 2 B (J+1) - 4 D (J+1)^3 \; cm^{-1} \tag{1.30}$$

Symmetric top molecules:

The rotational energy equation for symmetric top molecules involve two different moments of inertia and two quantum numbers, namely J, characterizing the total angular momentum of the molecule and K, the angular momentum about the major axis. The energy levels of non rigid symmetric top can be expressed as

$$\epsilon_{J,K} = B J (J+1) + (A - B) K^2 - D_J J^2 (J+1)^2 - D_{JK} J (J+1) K^2 - D_K K^4 \; cm^{-1} \tag{1.31}$$

Where $B = (h/8\pi^2 I_B c)$ and $A = (h/8\pi^2 I_A c)$. The energy depends on K^2 so that it is immaterial whether the molecule spins in clockwise or anticlockwise, the energy is the same for a given J. For all $K > 0$, the energy levels are double degenerate. The selection rule is $\Delta J = 0, \pm 1$ and $\Delta K = 0$. D_J, D_{JK} and D_K are the small corrections for the non rigidity.

$$\epsilon_{J+1,K} - \epsilon_{J,K} = 2\,B(J+1) - 4\,D_J(J+1)^3 - 2\,D_{JK}\,J(J+1)\,K^2\ \mathrm{cm}^{-1} \qquad (1.33)$$

The spectrum is basically that of a linear molecule including centrifugal stretching, with additional term which depends on K^2.

Due to the selection rules, the analysis of the microwave spectrum of symmetric top molecules yields only information about the rotational constant B. In symmetric top molecules the structural parameters to be evaluated is grater than the available rotational constants.Hence in these type of molecules the molecular geometry is obtained by studying the microwave spectrum of its isotopic substituents. The terms D_J, D_{JK} and D_K which are the corrections for the non rigidity of the molecule, are functions of molecular geometry and force field of the molecule. The details regarding the calculation of centrifugal distortion constants for polyatomic molecules are discussed in chapter II.

TABLE 1

Expressions for F matrix elements under different approximations[63] for second order vibrational species

Approximation	F_{11}	F_{12}	F_{22}	Remarks	Reference
$L_{21} = 0$	$\frac{\lambda_1 G_{22}}{\lvert G \rvert}$	$-\lambda_1 G_{12} \lvert G \rvert^{-1}$	$\frac{\lambda_2}{G_{22}} + \frac{\lambda_1 G_{12}^2}{G_{22}} \lvert G \rvert^{-1}$	corresponds to F_{11} maximation.	21,23,32,44
$L_{12} = 0$	$\lambda_1 G_{11}^{-1} + 2 G_{12}^2 G_{11}^{-1} \lvert G \rvert^{-1}$	$-\lambda_2 G_{12} \lvert G \rvert^{-1}$	$\lambda_2 G_{11} G^{-1}$	corresponds to F_{22} minimisation and the progressive rigidity model	21,23,32,44
$L_{12} = L_{21} = 0$	$\lambda_1 G_{11}^{-1}$	0	$\lambda_2 G_{22}^{-1}$	corresponds to the method of characteristic set.	40
$F_{12} = F_{22}$	$\lambda_1 G_{11}^{-1}$	$-\lambda_2 G_{12} 2^{-1} \lvert G \rvert^{-1}$	$\lambda_2 G_{11} \lvert G \rvert^{-1}$	condition on the potential energy distribution	56

TABLE 2

Expressions for F matrix elements under the approximation[34] $L_{12} = L_{13} = L_{23} = 0$ for third order vibrational species.

F_{ij}	The expression
F_{11}	$(\lambda_1 A + \lambda_2 G_{12}^2 + \lambda_3 G_{11} C^2 \lvert G\rvert^{-1}) / G_{11} A$
F_{12}	$-(\lambda_2 G_{12} \lvert G\rvert + \lambda_3 B C) / A \lvert G\rvert$
F_{13}	$\lambda_3 C \lvert G\rvert^{-1}$
F_{22}	$(\lambda_2 G_{11} \lvert G\rvert + \lambda_3 B^2) / A \lvert G\rvert$
F_{23}	$-\lambda_3 B \lvert G\rvert^{-1}$
F_{33}	$\lambda_3 A \lvert G\rvert^{-1}$

Where $A = (G_{11} G_{22} - G_{12}^2)$,

$B = (G_{11} G_{23} - G_{12} G_{13})$,

$C = (G_{12} G_{23} - G_{13} G_{22})$

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CHAPTER II

THEORY OF CENTRIFUGAL DISTORTION CONSTANTS AND THE T_s MATRIX FORMALISM

Abstract

The general quantum mechanical theory of centrifugal distortion constants in polyatomic molecules as developed by Kivelson and Wilson is briefly outlined. A summary of the simplified computational procedure based on Cyvin's T_S matrix formalism is given. The calculation of $t_{\alpha\beta\gamma\delta}$ elements is illustrated in the case of XY_2 bent symmetric molecular system.

2-1 Introduction:

Considering molecule as a rigid rotor, the rotational energy levels of the symmetric top molecules have been obtained by Dennison[1]. Wang[2] has given the corresponding expression for the asymmetric top molecules. Later workers[3,4] found that rotational fine structure is influenced by the non rigidity of the molecule, especialy through the coupling of the angular momenta of vibration and rotation. Another known fact is that different emperical moments of inertia are needed in applying the Wang secular equation for the asymmetric top to each vibration rotation band, presumably due to the variation of effective moments of enertia by the vibrational motion. Again the rigid top never accounts for the centrifugal stretching effects where these are observed experimentally. These points stress the fact that molecules must be treated as non-rigid rotators. The rotational energy levels of non-rigid rotor can be obtained using classical approach[5] or quantum mechanical approach[6]. Here we outline briefly the theory for the non-rigid rotator using the quantum mechanical approach based on the first order perturbation theory.

2-2 Hamiltonian for non-rigid rotor:

Let P_μ be the μ components $(\mu = x,y,z)$ of the angular coordinate system and let α', β', γ' and $\tau_{\mu\nu\zeta\xi}$ be constants independent of the rotational quantum number. Then the Hamiltonian for the non-rigid rotator is given by Benedict[7] as

$$H = H_0' + H_1' \tag{2.1}$$

where $$H_0' = \alpha' P_z^2 + \beta' P_x^2 + \gamma' P_y^2 \tag{2.2}$$

and $$H_1' = (1/4)\hbar^4 \sum \tau_{\mu\nu\zeta\xi} \; P_\mu P_\nu P_\zeta P_\xi \tag{2.3}$$

H_0' represents the Hamiltonian for the effective rigid rotor.

$$\alpha' = \hbar^2 / 2 I_z, \ \beta' = \hbar^2 / 2 I_x, \ \gamma' = \hbar^2 / 2 I_y$$

I_x, I_y and I_z are the effective principal moments of inertia for the given vibrational state. H_1' is the centrifugal distortion term, the parameters of which depends on the geometry and force constants of the molecule[8]. It is assumed that the effect of H_1' is small so that it may be treated by the first order perturbation theory. The solution of the eigen value of H_0', the zero approximation to H has been discussed by King, Hainer and Cross[8,9].

2-3 Simplification for distortion term :

The commutation rules for angular momentum[10] viz.

$$P_\nu P_\mu - P_\mu P_\nu = -i P_\rho \tag{2.4}$$

where μ, ν, ρ are in cyclic order can be used to eliminate $\mu\nu\zeta\xi$ terms in H_1'. The result of this procedure is a change in the coefficient of the remaining terms in P_μ^2 which can be absorbed into H_0'. The new form of H is then

$$H = H_0 + H_1 \tag{2.5}$$

where $$H_0 = \alpha P_z^2 + \beta P_x^2 + \gamma P_y^2 \tag{2.6}$$

and $$H_1 = (1/4) \sum_{\mu\nu} \tau'_{\mu\mu\nu\nu} \; P_\mu^2 \; P_\nu^2 \tag{2.7}$$

The relation between the new coefficients α, β, γ and $\tau'_{\mu\mu\nu\nu}$ and the previous ones are

$$\tau'_{zzzz} = \tau_{zzzz}\hbar^4 \,, \quad \tau'_{xxyy} = (\tau_{xxyy} + 2\,\tau_{xyxy})\hbar^4$$

$$\tau'_{xxxx} = \tau_{xxxx}\hbar^4 \,, \quad \tau'_{yyzz} = (\tau_{yyzz} + 2\tau_{yzyz})\hbar^4$$

$$\tau'_{yyyy} = \tau_{yyyy}\hbar^4 \,, \quad \tau'_{zzxx} = (\tau_{zzxx} + 2\,\tau_{zxzx})\hbar^4$$

$$\alpha = \alpha' + (3\tau_{xyxy} - 2\tau_{zxzx} - 2\,\tau_{yzyz})\hbar^4/4$$

$$\beta = \beta' + (3\,\tau_{yzyz} - 2\tau_{xyxy} - 2\tau_{zxzx})\hbar^4/4$$

$$\gamma = \gamma' + (3\tau_{zxzx} - 2\tau_{xyxy} - 2\tau_{zyzy})\hbar^4/4$$

The total angular momentum given by

$$P^2 = P_x^2 + P_y^2 + P_z^2 \tag{2.8}$$

commutes with H and H_o and hence it is a constant matrix with diagonal values J (J+1) as far as the present problem is concerned. Since P^2 commutes with P_x^2 and P_y^2, we can form the following useful operator products.

$$P_x^2\,P^2 + P^2\,P_x^2 = 2\,J(J+1)\,P_x^2 + 2\,P_x^4 + (P_x^2\,P_y^2 + P_y^2\,P_x^2) + (P_z^2\,P_x^2 + P_x^2\,P_z^2) \tag{2.9}$$

$$P_y^2\,P^2 + P^2\,P_y^2 = 2\,J(J+1)\,P_y^2 + 2\,P_y^4 + (P_y^2\,P_x^2 + P_x^2\,P_y^2) + (P_z^2\,P_y^2 + P_y^2\,P_z^2) \tag{2.10}$$

Another relation that is used in the expression for H_e^2 is obtained by squaring eq.(2.6),

$$H_e^2 = \alpha^2 P_z^4 + \beta^2 P_x^4 + \gamma^2 P_y^4 + \alpha\beta(P_z^2 P_x^2 + P_x^2 P_z^2) + \beta\gamma(P_x^2 P_y^2 + P_y^2 P_x^2) + \gamma\alpha(P_y^2 P_z^2 + P_z^2 P_y^2) \quad (2.11)$$

Eq.(2.8) can be used to eliminate P_y^2 in the expression for H_e from eq.(2.6). Further squaring H_o and differenciating it with respect to α, we get

$$\partial H_e^2/\partial\alpha = 2\ (\alpha-\beta)\ P_z^4 + (\beta-\gamma)\ (P_x^2 P_z^2 + P_z^2 P_x^2) + 2\ \gamma\ J\ (J+1)\ P_z^2 \quad (2.12)$$

We can derive similar expression in which P_x^2 is eliminated in a like manner. Thus,

$$\partial H_e^2/\partial\alpha = 2\ (\alpha-\beta)\ P_z^4 + (\gamma-\beta)\ (P_y^2 P_z^2 + P_z^2 P_y^2) + 2\ J\ (J+1)\ P_z^2\,\beta \quad (2.13)$$

If W_o is the energy of the rigid rotor represented by H_e, Bragg[11] has shown that

$$\langle P_z^2 \rangle = \langle \partial H_e/\partial\alpha \rangle = \partial W_o/\partial\alpha \quad (.2.14)$$

Where the bracket $\langle\ \rangle$ represents the diagonal elements (average values) of the enclosed operators in a basis which diagonalises H_o. Similarly it can be shown that

$$\langle \partial H_o^2/\partial\alpha \rangle = \partial W_o/\partial\alpha = 2\ W_o\ \langle P_z^2 \rangle \quad (2.15)$$

Since we are considering only the first order, the required energy will involve only the diagonal values of the perturbing operators. The equation containing H_1 will ultimately be used only for the diagonal values with the help of eq.(2.15). We know the fact that

$\langle H_o^2 \rangle = W_o^2$. Considering eq.(2.9) through eq.(2.13) as average value equations, they can be solved so that $\langle P_x^4 \rangle$, $\langle P_y^4 \rangle$, $\langle P_x^2 P_y^2 + P_y^2 P_x^2 \rangle$, $\langle P_y^2 P_z^2 + P_z^2 P_y^2 \rangle$ and $\langle P_z^2 P_x^2 + P_x^2 P_z^2 \rangle$ can be expressed in terms of $J(J+1)\langle P_x^2 \rangle$, $J(J+1)\langle P_y^2 \rangle$ $J(J+1)\langle P_z^2 \rangle$, $\langle P_z^4 \rangle$, W_e^2 and $W_o^2 \langle P_z^2 \rangle$. Also we can use eqs.(2.6) and (2.8) to solve for $\langle P_x^2 \rangle$ in terms of $\langle P_z^2 \rangle$.

Hence

$$\langle P_x^2 \rangle = \left\{ W_o - \gamma J(J+1) - (\alpha - \gamma) \langle P_z^2 \rangle / (\beta - \gamma) \right\} \tag{2.16}$$

Similarly we can get expression for $\langle P_y^2 \rangle$. Using these results in H_1, we get the following expression for the energy of a non-rigid asymmetric roter in the first order.

$$\begin{aligned} W = {} & W_o + A_1 W_o^2 + A_2 W_o J(J+1) + A_3 J^2 (J+1)^2 + \\ & A_4 J(J+1)\langle P_z^2 \rangle + A_5 \langle P_z^4 \rangle + A_6 W_o \langle P_z^2 \rangle \end{aligned} \tag{2.17}$$

A's are independent of the rotational quantum numbers. W_o is the rigid roter energy as solved by King, Hainer and Cross[8,9]. Evaluation of $\langle P_z^2 \rangle$ and $\langle P_z^4 \rangle$ have been done by Golden[11] and Kivelson[17,18] respectively and these are given by

$$\langle P_z^4 \rangle \simeq \langle P_z^2 \rangle^2 \approx K^4 \tag{2.17a}$$

$$A_1 = 16 R_6 / (\beta - \gamma)^2 \tag{2.17b}$$

$$A_2 = -\left[16 R_6 (\beta + \gamma) / (\beta - \gamma)^2 + 4 \delta_J / (\beta - \gamma) \right] \tag{2.17c}$$

$$A_3 = - D_J + 2\ R_6 + 16\ R_6\ (\alpha^2 - \beta\gamma)\ /\ (\beta - \gamma)^2 +$$

$$2\ \delta J\ (\beta + \gamma)\ /\ (\beta - \gamma) \qquad (2.17d)$$

$$A_4 = - D_{JK} - 2\delta J\sigma - 16\ R_6\ (\alpha^2 - \beta\gamma)\ /\ (\beta - \gamma)^2 +$$

$$4\ R_6\sigma^2 + 4\ R_5\ (\gamma + \beta)\ /\ (\beta - \gamma) \qquad (2.17e)$$

$$A_5 = - (D_K + 4\ R_5 + 2\ R_6 - 4\ R_6\sigma^2) \qquad (2.17f)$$

$$A_6 = (8\ R_5 - 16\ R_6\sigma)\ /\ (\beta - \gamma) \qquad (2.17g)$$

$$\sigma = (2\alpha - \beta - \gamma)\ /\ (\beta \cdot \gamma) \qquad (2.17h)$$

where

$$D_J = - (1/32)\ (3\tau_{xxxx} + 3\tau_{yyyy} + 2\tau_{xxyy} + 4\tau_{xyxy})\hbar^4 \qquad (2.17i)$$

$$D_K = D_J - (1/4)(\tau_{zzzz} - \tau_{zzxx} - \tau_{yyzz} - 2\tau_{xzxz} - 2\tau_{yzyz})\hbar^4 \qquad (2.17j)$$

$$D_{JK} = - D_J - D_K - (1/4)\tau_{zzzz}\hbar^4 \qquad (2.17k)$$

$$R_5 = - (1/32)\left[\tau_{xxxx} - \tau_{yyyy} - 2\ (\tau_{xxzz} + 2\tau_{xzxz}) +\right.$$

$$\left.2\ (\tau_{yyzz} + 2\tau_{yzyz})\right]\hbar^4 \qquad (2.17l)$$

$$R_6 = (1/64)\left[\tau_{xxxx} + \tau_{yyyy} - 2\ (\tau_{xxyy} + 2\tau_{xyxy})\right]\hbar^4 \qquad (2.17m)$$

and

$$\delta J = - (1/16)\ (\tau_{xxxx} - \tau_{yyyy})\hbar^4 \qquad (2.17n)$$

For symmetric rotor R_5, R_6 δJ vanish and $\beta = \gamma$. Applying this condition to eqs. (2.17) and using the result of eq.(2.17a), eq.(2.17) can be expressed as

$$W = W_0 - D_J J^2 (J+1)^2 - D_{JK} J (J+1) K^2 - D_K K^4 \qquad (2.18)$$

This equation represents the rotational energy levels of a non rigid symmetric rotor in the first order theory.

2-4 Centrifugal distortion :

Basic picture of the centrifugal distortion can be obtained by considering a diatomic molecule. Atoms are considered to be hard spheres joined by a rather rigid spring which obeys Hook's law. If the molecule is rotated about an axis perpendicular to internuclear one, then at equilibrium, centrifugal force is equal to centripetal force. Let $\mu = m_1 m_2 / (m_1 + m_2)$ be the reduced mass of the molecule at equilibrium. We then have

$$K (r - r_0) = \mu r \omega^2 = P^2 / \mu r^3 \qquad (2.19)$$

Where K is the force constant, r_0, the bond length of the stationary molecule, ω, the angular velocity and P is the angular momentum. Energy of the system is given by the Hamiltonian

$$H = P^2 / 2 \mu r^2 + (1/2) K (r - r_0)^2 \qquad (2.20)$$

Expanding the internuclear distance about r_0

$$r^2 = r_0 \left[1 + 2 (r - r_0) / r_0 + \ldots. \right] \qquad (2.21)$$

From which we get

$$H = (P^2 / 2 \mu r_0^2) - (P^4 / 2 \mu^2 K r_0^6) + 0 P^6 \qquad (2.22)$$

First term is the K.E. of the rotor and the second term arises due to centrifugal force. Cross[12], Lawrence[13] and Wilson[14] have discussed the centrifugal distortion for polyatomic molecules. Here we are giving below the formula for centrifugal distortion in polyatomic molecules using quantum mechanical approach. Wilson[15] has given the method for evaluating the centrifugal distortion constants $\tau_{gg'jj'}$ which appear as the coefficients of the matrix terms in the expression for the Hamiltonian of a non-rigid rotator given by

$$H = E_V + (1/2) \sum_{gg'} \alpha_{gg'} P_g P_{g'} + (1/4) \sum_{gg'jj'} P_g P_{g'} P_j P_{j'} \tau_{gg'jj'} \qquad (2.23)$$

E_V is a constant diagonal matrix representing the vibrational energy. P_g is the matrix of component of the total angular momentum along the g axis (represented by x, y, z). $\alpha_{gg'}$ is a numerical coefficients related to the moment of inertia of the molecule and is a fixed number for a definite vibrational state. $\tau_{gg'jj'}$ depends only on the vibrational state. Now

$$\tau_{gg'jj'} = \sum{}' \frac{(V/\mu_{gg'}/V'')(V''/\mu_{jj'}/V)}{h\nu_{V,V''}} \qquad (2.24)$$

The prime indicates that V is excluded from the sum. $h\nu_{V,V''}$ is the difference in the energy $W_V o - W_V c''$. $\mu_{gg'}$ are the functions of the normal coordinate such that

$$\mu_{xx} = (I_{yy'} I_{xx'} - I^2_{y'z})/\Delta$$

$$\mu_{yy} = (I_{xx'} I_{zz'} - I^2_{x'z})/\Delta$$

$$\mu_{zz} = (I_{xx'}\, I_{yy'} - I^2_{xy'}) \,/\Delta$$

$$\mu_{xy} = (I_{zz'}\, I_{xy'} + I_{yz'}\, I_{xz'}) \,/\Delta$$

$$\mu_{xz} = (I_{xy'}\, I_{yz'} + I_{yy'}\, I_{xz'}) \,/\Delta$$

$$\mu_{yz} = (I_{xx'}\, I_{yz'} + I_{xy'}\, I_{xz'}) \,/\Delta$$

and

$$\Delta = \begin{vmatrix} I_{xx'} & -I_{xy'} & -I_{xz'} \\ -I_{xy'} & I_{yy'} & -I_{yz'} \\ -I_{xz'} & -I_{yz'} & I_{zz'} \end{vmatrix}$$

In order to calculate these τ's we must know the molecular geometry fundamental mode of vibration (or force constants) and the normal vibrational frequencies. The τ's can be obtained as follows.

For a non linear molecule of N atoms there are (3N-6) independent internal displacement parameters. Let δq_i be the corresponding set of internal displacement coordinates. These displacement coordinates may be changes in bond length or bond angle. If $\mu^o_{gg'}$ is the equilibrium value of $\mu_{gg'}$ (all $\delta q_i = 0$) then,

$$\mu_{gg'} = \mu^o_{gg'} + \sum_i \mu^i_{gg'}\, \delta q_i + O(\delta q_i^2) \qquad (2.24)$$

where

$$\mu^i_{gg'} = \left(\partial \mu_{gg'} / \partial q_i \right)_{\partial q_i = o} \qquad (2.25)$$

All quadratic and higher order terms are neglected in eq.(2.24). Using harmonic oscilator wave functions in eq.(2.24), $\mu_{gg'}$, $\mu^o_{gg'}$ are constants since $V \neq V''$. The orthogonal property of the Hermite polynomial gives

$$(v\,/\,\mu_{gg'}\,/\,v'') = \sum_i \mu^i_{gg'}\,(v\,/\,\delta q_i\,/\,v'') \qquad (2.26)$$

Use of eq.(2.26)and (2.24) gives

$$\tau_{gg'jj'} = \sum_{v''}{}' \sum_{ik} \mu^i_{gg'}\,\mu^k_{jj'}\,\frac{(v/\delta q_i\,/\,v'')(v''/\delta q_i/\,v)}{h\,\nu_{v\,v''}} \qquad (2.27)$$

The normal coordinates Q_k may be written in terms of internal displacement coordinates δq_i as

$$\delta q_i = \sum_k b_{ik}\,Q_k \qquad (2.28)$$

Therefore

$$\begin{aligned}(v\,/\delta q_i\,/\,v'') &= (v\,/\textstyle\sum_k b_{ik}\,Q_k\,/\,v'')\\ &= \textstyle\sum_k b_{ik}\,(v\,/\,Q_k\,/\,v'')\end{aligned} \qquad (2.29)$$

For the basic functions in Harmonic Oscilator, the quantity $(v\,/\,Q_k\,/\,v'')$ is non vanishing only if all $\vartheta = \vartheta''$ except the single quantum number V_k associated with the normal coordinate Q_k. Here $\vartheta'_k = \vartheta_k \pm 1$. By considering this property τ's can be expressed as

$$\tau_{gg'jj'} = \sum \mu^i_{gg'}\,\mu^k_{jj'} \sum_l b_{il} b_{kl} \Big\{ \big[(\vartheta_l\,/Q_l/\,\vartheta_l + 1)(\vartheta_l\,/Q_l/\,\vartheta_l\,)\big]/h\,\nu_{l,l+1} + \big[(\vartheta_l/Q_l\,/\vartheta_l{-}1)(\vartheta_l{-}1/Q_l\,/\,\vartheta_l\,)/h\,\nu_{l,l-1}\big]\Big\} \qquad (2.30)$$

The matrix element for the harmonic Oscilator are easily calculated to give

$$(\vartheta_l/Q_l/\vartheta_{l+1}) = \sqrt{(\vartheta_l+1)/8\pi^2\ \nu_l^0} \tag{2.31}$$

$$(\vartheta_l/Q_l/\vartheta_{l-1}) = \sqrt{\vartheta_l\ /8\pi^2\ \nu_l^0}$$

If f_{ik} is the potential constant in the expression for the potential energy[16], when it is expressed in terms of the displacement coordinates δq_i, then

$$(f^{-1})_{ik} = \sum_l b_{il}\, b_{kl} / 4\pi^2\ (\nu)^2 \tag{2.32}$$

Using eq.(2.32) and (2.31) in eq.(2.30) we get expression for τ's as

$$\tau_{gg'jj'} = -(1/2)\sum_{ik} \mu_{gg'}\mu_{jj'}\ (f^{-1})_{ik} \tag{2.33}$$

Wilson[16] has derived the same formula using classical approach. τ's are again be simplified in terms of the inertia tensor I in place of the inverse inertia tensor μ. Expanding the inertia tensor in terms of the displacement coordinates δq_i, we get

$$I = I_0 + {}_i\ (J)_0^i\ \delta q_i + \ldots. \tag{2.34}$$

In which I_0 is the equilibrium tensor and

$$(J)^i = (\partial I/\ \partial q_i) \tag{2.35}$$

The zero subscript indicates that J^i is evaluated at $\delta q_i = 0$ since $\mu = I^{-1}$,

$$I\mu = 1 = I^0\mu^0 + I^0 \sum_i \mu^i\ \delta q_i + \sum_i (J^i)_0 \delta q_i\ {}_0 + \ldots \tag{2.36}$$

Because μ is the inverse of I for all the values of δq_i which are independent, eq.(2.36) can be expressed as

$$\mu^i = -\mu^0\ (J^i)_0\ \mu^0 \tag{2.37}$$

Now it is easy to use the principal axis system I_o and μ^o so that both of the tensors are diagonal. Therefore the diagonal element I_o are the reciprocals of the μ^o. Now eq.(2.37) is simplified and becomes

$$\mu^i_{gg'} = - (J^i_{gg'})_o / I^o_{gg'} I^o_{jj'} \tag{2.38}$$

If the average moments of inertia are not known, it is difficult to determine equilibrium moments of inertia. Therefore $I^o_{gg'}$ and $I^o_{jj'}$ must be replaced by the moments averaged over the ground vibrational state. Once averaged moments of inertia are known, we can calculate the centrifugal distortion constant. Thus

$$t_{gg'jj'} = -2 I^e_{gg} I^e_{g'g'} I^e_{jj} I^e_{j'j'} \tau_{gg'jj'} \tag{2.39}$$

$$t_{gg'jj'} = \sum_{ik} (J^i_{gg'})_o (J^i_{jj'})_o (f^{-1})_{ik} \tag{2.40}$$

The $t_{gg'jj'}$ notation is given by Kivelson and Wilson[19].

2-5 Cyvins T'$_s$ matrix formalism :

Cyvin[19] has suggested a modified method by which the quantities of $t_{\alpha\beta\gamma\delta}$ are related by the aid of certain elements $T^i{}_{\alpha\beta}$,s rather than the partial derivation of inertia tensor components used in the method of Kivelson and Wilson[18]. The $T^i_{\alpha\beta}$,s elements may easily be evaluated for a given molecular model from the equilibrium position vectors.

The centrifugal distortion constants $\tau_{\alpha\beta\gamma\delta}$ are now related to quantities $t_{\alpha\beta\gamma\delta}$ through the eq.(2.39) as

$$t_{\alpha\beta\gamma\delta} = -2 I^e_{\alpha\alpha} I^e_{\beta\beta} I^e_{\gamma\gamma} I^e_{\delta\delta} \tau_{\alpha\beta\gamma\delta} \tag{2.41}$$

Here $\alpha, \beta, \gamma, \delta$ = x, y or z and I^e_{xx}, I^e_{yy}, I^e_{zz} are the principal moments of inertia at equilibrium. Let J_Q be a matrix with 6 columns $J_{xx,Q}$, $J_{yy,Q}$, $J_{zz,Q}$, $J_{xy,Q}$, $J_{yz,Q}$ and $J_{zx,Q}$. Similarly the matrix J_S can also be expressed. Here Q and S refer to the normal and symmetry coordinates respectively. Then

$$t = \tilde{J}_Q \, \sigma \, J_Q = \tilde{J}_S \, F^{-1} \, J_S \tag{2.42}$$

Here $\sigma = 1/4\pi^2\nu^2c^2$, ν being the wave number of the fundamentals and F^{-1} is the inverse force constant matrix. The J quantities are the partial derivatives of the instantaneous inertia tensor taken at equilibrium. That is

$$J^k_{\alpha\beta,Q} = (\partial I_{\alpha\beta}/\partial Q_k)_e, \quad J^i_{\alpha\beta,S} = (\partial I_{\alpha\beta}/\partial S_i)_o \tag{2.43}$$

The new matrix Ts introduced by Cyvin again consisting of 6 columns $T_{xx,S}$, $T_{yy,S}$, $T_{zz,S}$, $T_{xy,S}$, $T_{yz,S}$ and $T_{zx,S}$ in the place of J_S. The quantities $T_{\alpha\beta,S}$ are given by the relation[19]

$$T_{\alpha\alpha,S} = 2\,B\,\overset{\alpha\alpha}{i}\,R^e \tag{2.44}$$

$$T_{\alpha\beta,S} = -\,B\,\overset{\alpha\beta}{i}\,R^e \tag{2.45}$$

Where B is the symmetric coordinate transformation matrix, R^e is a column vector composed of the equilibrium position vector components of the atom (3N elements) and $i^{\alpha\beta}$ consists of N 3x3 matrix, one for each atom along the main diagonal. One such block has the form

$$(i^{xx})_a = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad (i^{xy})_a = \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$$(i^{yy})_a = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad (i^{yz})_a = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix} \qquad (2.46)$$

$$(i^{zz})_a = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (i^{zx})_a = \begin{bmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{bmatrix}$$

In terms of Ts matrix, the t matrix is given by the relation

$$t = \widetilde{Ts} \quad \theta \quad Ts \qquad (2.47)$$

where

$$\theta = G^{-1} \quad F^{-1} \quad G \qquad (2.48)$$

t is a complete symmetric tensor or matrix defined by the twentyone distinct quantities of $t_{\alpha\beta\gamma\delta}$ arranged as

$$t = \begin{bmatrix} t_{xxxx} & t_{xxyy} & t_{xxzz} & t_{xxyz} & t_{xxzx} & t_{xxxy} \\ & t_{yyyy} & t_{yyzz} & t_{yyyz} & t_{yyzx} & t_{yyxy} \\ & & t_{zzzz} & t_{zzyz} & t_{zzzx} & t_{zzxy} \\ \text{Symmetric} & & & t_{yzyz} & t_{yzzx} & t_{yzxy} \\ & & & & t_{zxzx} & t_{zxxy} \\ & & & & & t_{xyxy} \end{bmatrix} \qquad (2.49)$$

Some explicit form of $J^{i}_{\alpha\beta,S}$ are given below

$$J^{i}_{xx,S} = 2 \sum_{a} m_a (Y^{e}_{a} A^{y}_{ai} + Z^{e}_{a} A^{z}_{ai}) \tag{2.50a}$$

$$J^{i}_{yy,S} = 2 \sum_{a} m_a (Z^{e}_{a} A^{z}_{ai} + X^{e}_{a} A^{x}_{ai}) \tag{2.50b}$$

$$J^{i}_{zz,S} = 2 \sum_{a} m_a (X^{e}_{a} A^{x}_{ai} + Y^{e}_{a} A^{y}_{ai}) \tag{2.50c}$$

$$J^{i}_{yz,S} = - \sum_{a} m_a (Y^{e}_{a} A^{z}_{ai} + Z^{e}_{a} A^{y}_{ai}) \tag{2.50d}$$

$$J^{i}_{zx,S} = - \sum_{a} m_a (Z^{e}_{a} A^{x}_{ai} + X^{e}_{a} A^{z}_{ai}) \tag{2.50e}$$

$$J^{i}_{xy,S} = - \sum_{a} m_a (X^{e}_{a} A^{y}_{ai} + Y^{e}_{a} A^{x}_{ai}) \tag{2.50f}$$

Here m_a denotes the mass of atom a and X^{e}_{a}, Y^{e}_{a}, Z^{e}_{a} contain the equilibrium position vectors. Components of the same atom are referred to the principal system of coordinate axis.The coefficients noted, A^{e}_{i} ($\alpha = x, y, z$) are the elements of A matrix[16,20].

$$\alpha_a = \sum_{i} A^{\alpha}_{ai} \; S_i \tag{2.51}$$

where α_a (x_a, y_a, z_a) represents the cartesian displacement coordinates. $J^{i}_{\alpha\beta}$ are related to $T_{\alpha\beta}$ through the relation[19]

$$J_{\alpha\beta,S} = G^{-1} \; T_{\alpha\beta,S} \tag{2.52}$$

$$J_{\alpha\alpha,S} = G^{-1} \; T_{\alpha\alpha,S} \tag{2.53}$$

Hence the expression for $T_{\alpha\beta,S}$ are given below.

$$T^{e}_{xx,S} = 2 \sum_{a} (Y^{e}_{a} B^{y}_{ia} + Z^{e}_{a} B^{z}_{ia}) \tag{2.54a}$$

$$T^{e}_{yy,S} = 2 \sum_{a} (Z^{e}_{a} B^{z}_{ia} + X^{e}_{a} B^{x}_{ia}) \tag{2.54b}$$

$$T^{e}_{zz,S} = 2 \sum_{a} (X^{e}_{a} B^{x}_{ia} + Y^{e}_{a} B^{y}_{ia}) \tag{2.54c}$$

$$T^{i}_{yz,S} = - \sum_{a} (Y^{e}_{a} B^{z}_{ia} + Z^{e}_{a} B^{y}_{ia}) \qquad (2.54d)$$

$$T^{i}_{zx,S} = - \sum_{a} (Z^{e}_{a} B^{x}_{ia} + X^{e}_{a} B^{z}_{ia}) \qquad (2.54e)$$

$$T^{i}_{xy,S} = - \sum_{a} (X^{e}_{a} B^{y}_{ia} + Y^{e}_{a} B^{x}_{ia}) \qquad (2.54f)$$

Here B^{x}_{ia} are the $B^{20,16}$ matrix elements defined by

$$S_{i} = \sum_{a} (B^{x}_{ia} X_{a} + B^{y}_{ia} Y_{a} + B^{z}_{ia} Z_{a}) \qquad (2.55)$$

It is clear that the expressions eq.(2.54) are simpler to evaluate that eq.(2.50). The A matrix elements are equivalent to ρ^{o} vector components in the notation of Polo[22], while the B matrix elements constitute the usually simpler S vectors of Wilson[16]. Another simplification arises from the important fact that the equilibrium position vectors (X^{e}_{a}, Y^{e}_{a}, Z^{e}_{a}) used in eq.(2.54) need not necessarily refer to the centre of gravity of the molecule as their origin as it is required in eq.(2.50). The procedure to find out $T_{\alpha\beta,S}$ elements of XY_2 (C_{2v}) bent symmetric molecule is given below.

2-6 XY_2 bent symmetric molecule as example :

Vibration of XY_2 (C_{2v}) type molecule is classified into 2 A_1 + B_2 species. The symmetry coordinates are

$$\begin{aligned} S_1(A) &= 2^{-1/2} (\Delta r_1 + \Delta r_2) \\ S_2(A) &= r \Delta \alpha \qquad (2.56) \\ S_3(B) &= 2^{-1/2} (\Delta r_1 - \Delta r_2) \end{aligned}$$

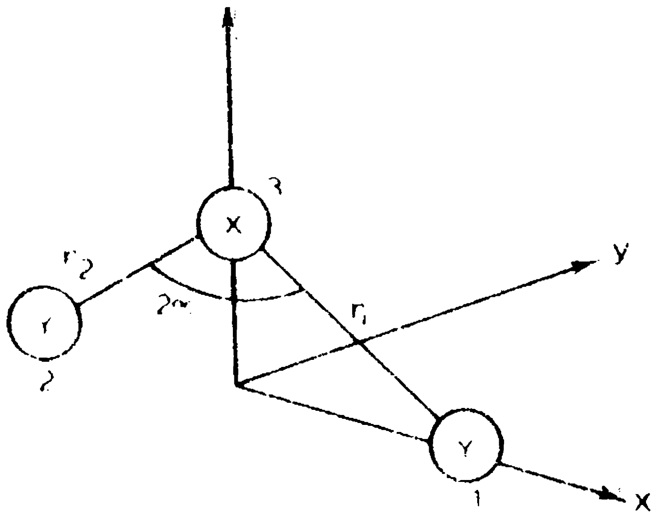

FIG.(2.1)

XY_2 bent symmetric molecule

(symmetry C_{2V})

Where Δr_1 and Δr_2 are the changes in bond length and $\Delta\alpha$ is change in interbond angle. 2α is the equilibrium Y X Y angle. Let m_X and m_Y be the masses of atoms X and Y. The components of S vectors, t° vectors, G matrix elements, components of R° vectors and the B matrix of XY_2 bent symmetric molecules are given below.

S - Vectors

Atom		S_1 (A)		
1	0	$2^{1/2}\sin\alpha$	$-2^{-1/2}\cos\alpha$	
2	0	$-2^{-1/2}\sin\alpha$	$-2^{-1/2}\cos\alpha$	(2.57)
3	0	0	$2^{1/2}\cos\alpha$	

Atom		S_2 (A)		
1	0	$\cos\alpha$	$\sin\alpha$	
2	0	$-\cos\alpha$	$\sin\alpha$	(2.58)
3	0	0	$-2\sin\alpha$	

Atom		S_2 (B)		
1	0	$2^{-1/2}\sin\alpha$	$-2^{1/2}\cos\alpha$	
2	0	$2^{-1/2}\sin\alpha$	$2^{-1/2}\cos\alpha$	(2.59)
3	0	$-2^{1/2}\sin\alpha$	0	

t° - vectors

Atom		S_1 (A)		
1	0	$2^{-1/2}\sin\alpha$	$-2^{-1/2}\, M^{-1}\, m_X \cos\alpha$	
2	0	$-2^{-1/2}\sin\alpha$	$-2^{-1/2}\, M^{-1}\, m_X \cos\alpha$	(2.60)
3	0	0	$2^{1/2}\, M^{-1}\, m_Y \cos\alpha$	

Atom		S_2 (A)		
1	0	$2^{-1}\cos\alpha$	$2^{-1}\, M^{-1}\, m_X \sin\alpha$	
2	0	$-2^{-1}\cos\alpha$	$2^{-1}\, M^{-1}\, m_X \sin\alpha$	(2.61)
3	0	0	$-M^{-1}\, m_Y \sin\alpha$	

Atom		S_2 (B)		
1	0	$2^{1/2}(M\, I^e_{xx})^{-1}\, m_X\, m_Y\, r^2\sin\alpha$	$-2^{1/2}(MI^e_{xx})^{-1} m_X m_Y r^2\cos\alpha$	
2	0	$2^{1/2}(MI^e_{xx})^{-1}\, m_X m_Y r^2\sin\alpha$	$2^{1/2}(MI^e_{xx})^{-1} m_X m_Y r^2\cos\alpha$	
3	0	$-8^{1/2}(MI^e_{xx})^{-1}\, m_Y^2\, r^2\sin\alpha$	0	(2.62)

Elements of G matrix

$$G_{11} = (2\cos^2\alpha / m_X) + (1/m_Y)$$

$$G_{12} = (-2^{1/2}\sin 2\alpha / m_X)$$

$$G_{22} = (4\sin^2\alpha / m_X) + (2/m_Y) \qquad (2.63)$$

$$G_{33} = (2\sin^2\alpha / m_X) + (1/m_Y)$$

Where $M = m_X + 2\,m_Y$. m_X and m_Y are the mass of X and Y atom.

$$I^e_{xx} = I^e_{yy} + I^e_{zz}$$

$$= 2\,M^{-1}\,r^2\,m_Y\,(m_X + m_Y \sin^2\alpha + m_Y \sin^2\alpha\ ) \qquad (2.64)$$

r is represent the bond length X-Y

R^e - matrix

$$R^e = \begin{bmatrix} 0 \\ -r \sin\alpha \\ 0 \\ 0 \\ 0 \\ r \cos\alpha \\ 0 \\ r \sin\alpha \\ 0 \end{bmatrix} \qquad (2.65)$$

B matrix

	X_1	Y_1	Z_1	X_2	Y_2	Z_2	X_3	Y_3	Z_3
S_1	0	$-2^{-1/2}\sin\alpha$	$-2^{-1/2}\cos\alpha$	0	0	$2^{1/2}\cos\alpha$	0	$2^{-1/2}\sin\alpha$	$-2^{-1/2}\cos\alpha$
S_2	0	$-\cos\alpha$	$\sin\alpha$	0	0	$-2\sin\alpha$	0	$\cos\alpha$	$\sin\alpha$
S_3	0	$-2^{-1/2}\sin\alpha$	$-2^{-1/2}\cos\alpha$	0	$2^{1/2}\sin\alpha$	0	0	$2^{-1/2}\sin\alpha$	$2^{-1/2}\cos\alpha$

$T_{\alpha\beta,S}$

	xx	yy	zz	xy	yz	zx
$S_1(A)$	$8^{1/2}r$	$8^{1/2}\,r\cos^2\alpha$	$8^{1/2}\,r\sin^2\alpha$	0	0	0
$S_2(A)$	0	$-2\,r\sin 2\alpha$	$2\,r\sin 2\alpha$	0	0	0
$S_2(B)$	0	0	0	0	$2^{1/2}\,r\sin 2\alpha$	0

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CHAPTER III

PARAMETRISATION OF CENTRIFUGAL DISTORTION CONSTANTS: APPLICATION TO XY_2 BENT SYMMETRIC MOLECULES

Abstract

A method to generate all the mathematically possible values of centrifugal distortion constants of a molecule compatible with its vibrational frequencies is developed. Application of the method to the XY_2 bent symmetric molecules enables mapping of all the $\tau_{\alpha\beta\gamma\delta}$ constants as a function of a single parameter. The use of the method in defining the limits as well as in refining the experimental values of $\tau_{\alpha\beta\gamma\delta}$ constants is discussed. The method also opens up a route to fix the force constants unambigously employing the $\tau_{\alpha\beta\gamma\delta}$ constants as additional data. The numerical example of SCl_2 molecule is given to illustrate the general procedure. Approximation formulas are derived for easier evaluation of $\tau_{\alpha\beta\gamma\delta}$ constants in XY_2 bent symmetric molecules. The $\tau_{\alpha\beta\gamma\delta}$ elements calculated under this approximation agree very well with the experimental values obtained from the microwave spectrum. Also a method is presented here to predict fundamental vibrational frequencies from $\tau_{\alpha\beta\gamma\delta}$ elements available from the microwave spectrum. Using this method fundamental vibrational frequencies of few XY_2 bent symmetric molecules are obtained from $\tau_{\alpha\beta\gamma\delta}$ elements.

3-1 Introduction :

From the theoretical discussion given in the previous chapter, we find that the centrifugal distortion constants are the functions of interatomic forces of the molecule as well as of molecular geometry. In section 4 of chapter 1 we have seen that the intramolecular force can be expressed in terms of dimensionless mixing parameters. This means that the explicit dependence of the centrifugal distortion constants on the force constant matrix elements can be eliminated and the D_J, D_{JK} values also can be expressed in terms of the same dimensionless parameters. In section 2 of the present chapter, the parametrisation of centrifugal distortion constants is discussed in detail. In section 4 of this chapter the problem of fixing the intramolecular force field uniquely by taking centrifugal distortion constant as additional experimental data is discussed within the frame work of parametric formalism for XY_2 bent symmetric molecular system. SCl_2 molecule is taken as an example and accurate values of force constants are obtained. The theoretical formula derived here leads to the interesting conclusion that the prediction of fundamental vibrational frequencies in the molecule is possible solely using the microwave spectral data, viz.rotational constants and centrifugal distortion constants. The method is demonstrated in the case of few molecules by working out the numerical values of their vibrational frequencies from microwave data and comparing them with the experimental vibrational frequencies. In section 3-7 we show how parametrisation leads to the natural approximation formulas for centrifugal

distortion constants in XY_2 molecular model.

3-2 Parametrisation of centrifugal distortion constants :

As noted earlier in eq. (2.39) the centrifugal distortion constants $\tau_{\alpha\beta\gamma\delta}$ are related[1] to $t_{\alpha\beta\gamma\delta}$. Because of the obvious advantages of T_S matrix which have already been discussed in the previous chapter, we have followed the Cyvins[2,3] modified method for computing centrifugal distortion constants. The t matrix consists of elements $t_{\alpha\beta\gamma\delta}$ through the relation

$$t = \widetilde{Ts}\ G^{-1}\ F^{-1}\ G^{-1}\ Ts \qquad (3.1)$$

where G^{-1} is the kinetic energy matrix and F^{-1} is the inverse force constant matrix. Using the eqs.(1.13), (1.7) and (1.14) of chapter 1, eq. (3.1) can be expressed in the form[4]

$$t = \tilde{K}\ C\ \Lambda^{-1}\ \tilde{C}\ K \qquad (3.2)$$

where $K = (L_0)^{-1}\ Ts$ (3.3)

The Ts matrix for few molecular models have been already discussed by Cyvin[2,3]. Eq. (3.2) is important because we can map all the mathematical values of $t_{\alpha\beta\gamma\delta}$ fitting the observed vibrational frequencies by systamatically changing $\frac{1}{2}\Sigma_i\ n_i\ (n_i -1)$ parameters of C matrix in the general case.

3-3 Application to XY_2 bent symmetric molecular models:

When L_0 is taken in the lower triangular form[4,5] $(L_0)_{ij} = 0$ for $i < j$. An advantage here is that all the non-zero elements of L_0 matrix can be obtained from the relation $L_0\ \tilde{L}_0 = G$. The non-vanishing elements of K obtained from eq.(3.3), when L_0 is taken in the lower triangular form are given below.

$$K_{11} = (L_o^{-1})_{11}\sqrt{8}\ r \qquad (3.4a)$$

$$K_{12} = (L_o^{-1})_{11}\sqrt{8}\ r \cos^2 (\alpha/2) \qquad (3.4b)$$

$$K_{13} = (L_o^{-1})_{11}\sqrt{8}\ r \sin^2)(\alpha/2) \qquad (3.4c)$$

$$K_{21} = (L_o^{-1})_{21}\sqrt{8}\ r \qquad (3.4d)$$

$$K_{22} = (L_o^{-1})_{21}\sqrt{8}\ r \cos^2 (\alpha/2) - (L_o^{-1})_{22}\, 2 r \sin\alpha \qquad (3.4e)$$

$$K_{23} = (L_o^{-1})_{21}\sqrt{8}\ r \sin^2 (\alpha/2) + (L_o^{-1})_{22}\, 2 r \sin \qquad (3.4f)$$

$$K_{36} = (L_o^{-1})_{33}\ 2 r \sin\alpha \qquad (3.4g)$$

where r represents the bond length and α represent the interbond angle. A suitable form of C that can be used for the case under consideration is given below.

$$C = \frac{1}{G} \begin{bmatrix} 1 & c & 0 \\ -c & 1 & 0 \\ 0 & 0 & G \end{bmatrix} \qquad (3.5)$$

where $G = (1+c^2)^{1/2}$

Substituting eq. (3.5) and (3.4) in eq. (3.2) gives the direct expression for $t_{\alpha\beta\gamma\delta}$ as

$$t_{xxxx} = \left[(K_{11}^2 \Lambda_2^{-1} + K_{21}^2 \Lambda_1^{-1})\, c^2 + 2\, K_{11} K_{21} (\Lambda_2^{-1} - \Lambda_1^{-1})\, c + (K_{11}^2 \Lambda_1^{-1} + K_{21}^2 \Lambda_2^{-1}) \right] / (1+c^2) \qquad (3.6a)$$

$$t_{yyyy} = \left[(K_{12}^2 \Lambda_2^{-1} + K_{22}^2 \Lambda_2^{-1})\, c^2 + 2\, K_{12} K_{22} (\Lambda_2^{-1} - \Lambda_1^{-1})\, c + (K_{12}^2 \Lambda_1^{-1} + K_{22}^2 \Lambda_1^{-1}) \right] / (1+c^2) \qquad (3.6b)$$

$$t_{zzzz} = [(K_{13}^2 \Lambda_2^{-1} + K_{23}^2 \Lambda_1^{-1}) c^2 + 2 K_{13} K_{23} (\Lambda_2^{-1} - \Lambda_1^{-1}) c + (K_{13}^2 \Lambda_1^{-1} + K_{23}^2 \Lambda_2^{-1})] / (1+c^2) \qquad (3.6c)$$

$$t_{xxyy} = [(K_{11} K_{12} \Lambda_2^{-1} + K_{21} K_{22} \Lambda_1^{-1}) c^2 + (K_{11} K_{22} + K_{12} K_{21}) (\Lambda_2^{-1} - \Lambda_1^{-1}) c + (K_{11} K_{12} \Lambda_1^{-1} + K_{21} K_{22} \Lambda_2^{-1})] / (1+c^2) \qquad (3.6d)$$

$$t_{xxzz} = [(K_{11} K_{13} \Lambda_2^{-1} + K_{21} K_{23} \Lambda_1^{-1}) c^2 + (K_{11} K_{23} + K_{21} K_{13}) (\Lambda_2^{-1} - \Lambda_1^{-1}) c + (K_{11} K_{13} \Lambda_1^{-1} + K_{21} K_{23} \Lambda_2^{-1})] / (1+c^2) \qquad (3.6e)$$

$$t_{yyzz} = [(K_{12} K_{13} \Lambda_2^{-1} + K_{22} K_{23} \Lambda_1^{-1}) c^2 + (K_{12} K_{23} + K_{13} K_{22}) (\Lambda_2^{-1} - \Lambda_1^{-1}) c + (K_{12} K_{13} \Lambda_1^{-1} + K_{21} K_{23} \Lambda_2^{-1})] / (1+c^2) \qquad (3.6f)$$

$$t_{yzyz} = (K_{36})^2 \Lambda_3^{-1} \qquad (3.6g)$$

Due to the planarity of the molecule, Kivelson and Wilson have shown that some of the $t_{\alpha\beta\gamma\delta}$ elements are related through the following equations

$$t_{xxxx} = t_{yyyy} + t_{zzzz} + t_{yyzz} + t_{yyzz} \qquad (3.7a)$$

$$t_{xxxx} = t_{xxyy} + t_{xxzz} \qquad (3.7b)$$

$$t_{xxzz} = t_{zzzz} + t_{yyzz} \qquad (3.7c)$$

Thus to study the variation of different $t_{\alpha\beta\gamma\delta}$ elements in Eq.(3.6) it is enough if we study the variation of the independent quantites t_{yyyy}, t_{zzzz} and t_{xxxx}. Also we find that the expression for t_{yzyz} is independent of c. The centrifugal distortion constants $\tau_{\alpha\beta\gamma\delta}$ are related to $t_{\alpha\beta\gamma\delta}$ are given below.

$$\tau_{yyyy} = -\epsilon\, t_{yyyy} / 2\, I_{yy}^4$$ (3.8

$$\tau_{zzzz} = -\epsilon\, t_{zzzz} / 2\, I_{zz}^4$$ (3.8

$$\tau_{xxxx} = -\epsilon\, t_{xxxx} / 2\, I_{xx}^4$$ (3.8

$$\tau_{yyzz} = -\epsilon\, t_{yyzz} / 2\, I_{yy}^2\, I_{zz}^2$$ (3.8

where $I_{xx} = I_{yy} + I_{zz}$ (3.9

$$I_{yy} = 2\, M_Y\, M_X\, r^2 \cos^2 (\alpha/2) / (2\, M_Y + M_X)$$ (3.9

$$I_{zz} = 2\, M_Y\, r^2 \sin^2 (\alpha/2)$$ (3.9

here ϵ is a constant equal to 677.3 when mass of the atom is expressed in a.m.u., bondlength in Å, frequency in cm^{-1} and τ in MHz. ϵ is a unit conversion factor to transform the unit of t into that of τ. In general eq. (3.8) can be expressed in the form

$$\tau_{\alpha\beta\gamma\delta} = (p\, c^2 + q\, c + r) / (1+c^2)$$ (3.1

Here p, q, r, are constants containing molecular geometry, fundamental vibrational frequencies and atomic masses. An importan property of eq.(3.10) is that this equation helps us to plot directly the centrifugal distortion constant $\tau_{\alpha\beta\gamma\delta}$ as a function of a single parameter c. When c = 0 $\tau_{\alpha\beta\gamma\delta} = r$ and $\tau_{\alpha\beta\gamma\delta}$ tends p when c takes very high values. Differenciating eq.(3.10) with respect to c and equating it zero for extremal values, we get the maxima and minima of τ corresponding to

$$c = (p - r) \pm \left[(p - r)^2 + q^2 \right]^{1/2} \tag{3.11}$$

Any value of τ beyond its maximum and minimum values will not be consistent with the vibrational frequencies in the harmonic approximation. The importance of this equation is that it help us to find out the range of $\tau_{\alpha\beta\gamma\delta}$ without knowing the force field of the molecule. It is really a definite advantage to the microwave spectroscopist to know the range of $\tau_{\alpha\beta\gamma\delta}$ values in interpreting the microwave spectrum.

3-4 Unique fixing of intramolecular forces :

$\tau_{\alpha\beta\gamma\delta}$ values are necessary to know the rotational energy levels of the molecule. The centrifugal distortion constant can be obtained experimentally by studying the microwave spectrum or they can be computed from the force constants of the molecule. In many molecules the force field is not fixed uniquely because the frequency data alone are not sufficient for this purpose. However if $\tau_{\alpha\beta\gamma\delta}$ are known precisely from the microwave spectrum, it helps to fix uniquely the force field of the molecules. Hence $\tau_{\alpha\beta\gamma\delta}$ are an important set of molecular data like isotopic frequencies[6], Coriolis coupling constants[7], vibrational amplitudes[8] and infrared intensities[9].

3-5 Example SCl_2 molecule:

In order to illustrate the theory outlined above, SCl_2

molecule is treated here as an example. It is one of the XY_2 bent symmetric molecules recently studied by Jerry[10] et al. Molecular geometry and fundamental vibrational frequencies are taken from reference 10 and 11. respectively. Using eq.(3.10), the variation of the $\tau_{\alpha\beta\gamma\delta}$ against c are studied and the results are shown in Fig.(3.1), (3.2) and (3.3) and this shows that values should lie within a certain range given by the extreme points of the curve. The experimentally observed values of elements alongwith uncertainities are included in Fig.(3.1), (3.2) and (3.3) and are marked by solid and dotted lines. The numerical values of p, q, r terms in eq.(3.10) for different values of $\tau_{\alpha\beta\gamma\delta}$ elements are given in Table 1. It may be noted that an experimental value of $\tau_{\alpha\beta\gamma\delta}$ generally gives two values of c. This is possible because the quadratic nature of eq.(3.10). The two values of c obtained from eq.(3.10), described as c_A and c_Y, for different values of $\tau_{\alpha\beta\gamma\delta}$ are also given in Table 1. The use of two values of c in eq.(3.2) gives two sets of force constant. This leads to an interesting conclusion that use of any one of the $\tau_{\alpha\beta\gamma\delta}$ values as additional datum yields in general two possible sets of force constants fitting the $\tau_{\alpha\beta\gamma\delta}$ as well as the fundamental vibrational frequencies. More than one set of force fields fitting the additional experimental data like isotopic frequencies[6], Coriolis coupling constants[7], vibrational ampletudes[8] and infrared intensities[9] have been noted earlier. The present result shows that the centrifugal distortion constants are no exception to this general result. In such cases of multiplicity of force constants, use of yet another datum has been suggested earlier to eliminate the anomalous sets. In this

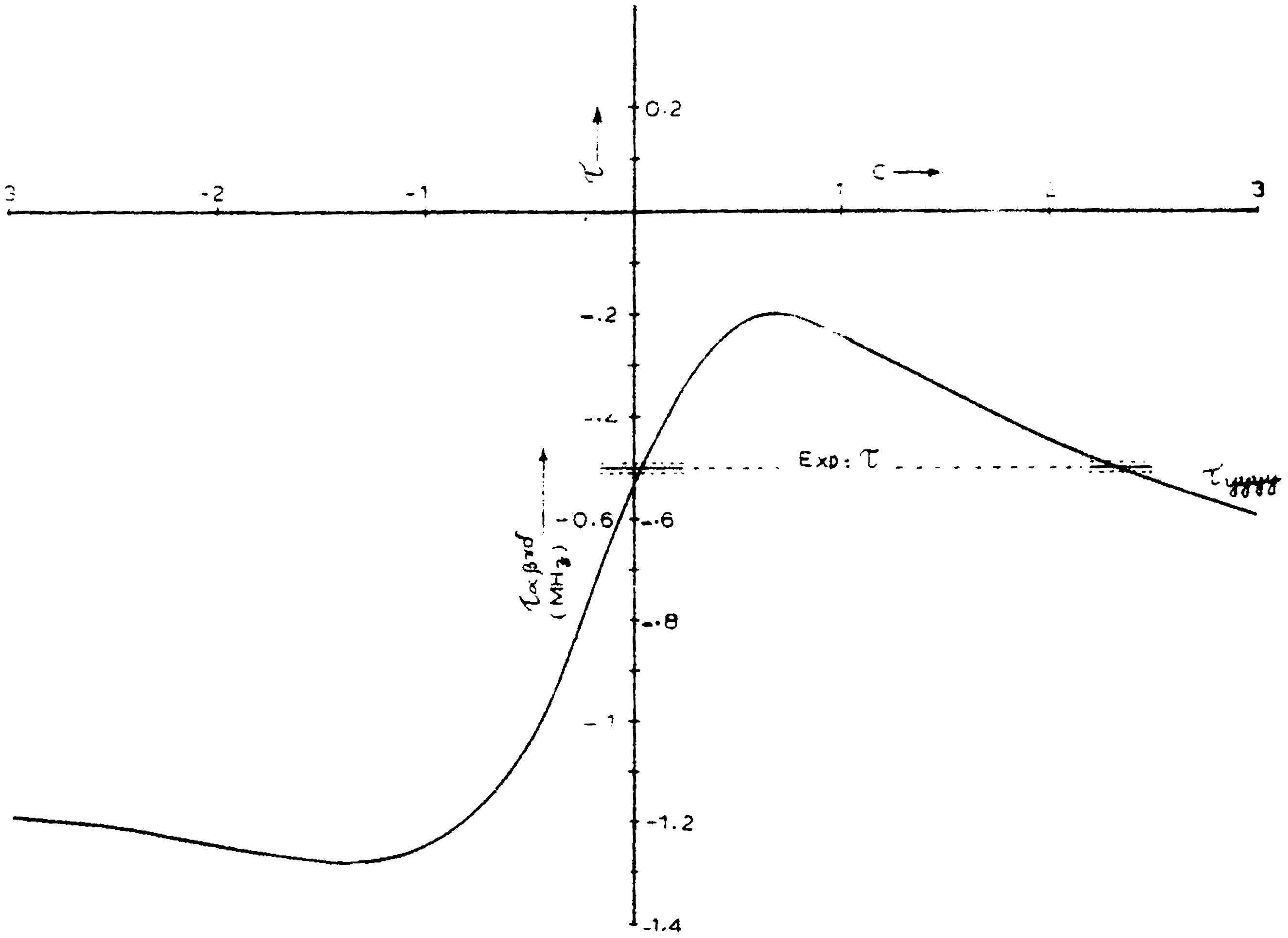

Fig. (3-1)

Variation of $\tau_{\alpha\beta\gamma\delta}$ elements with parameter c.

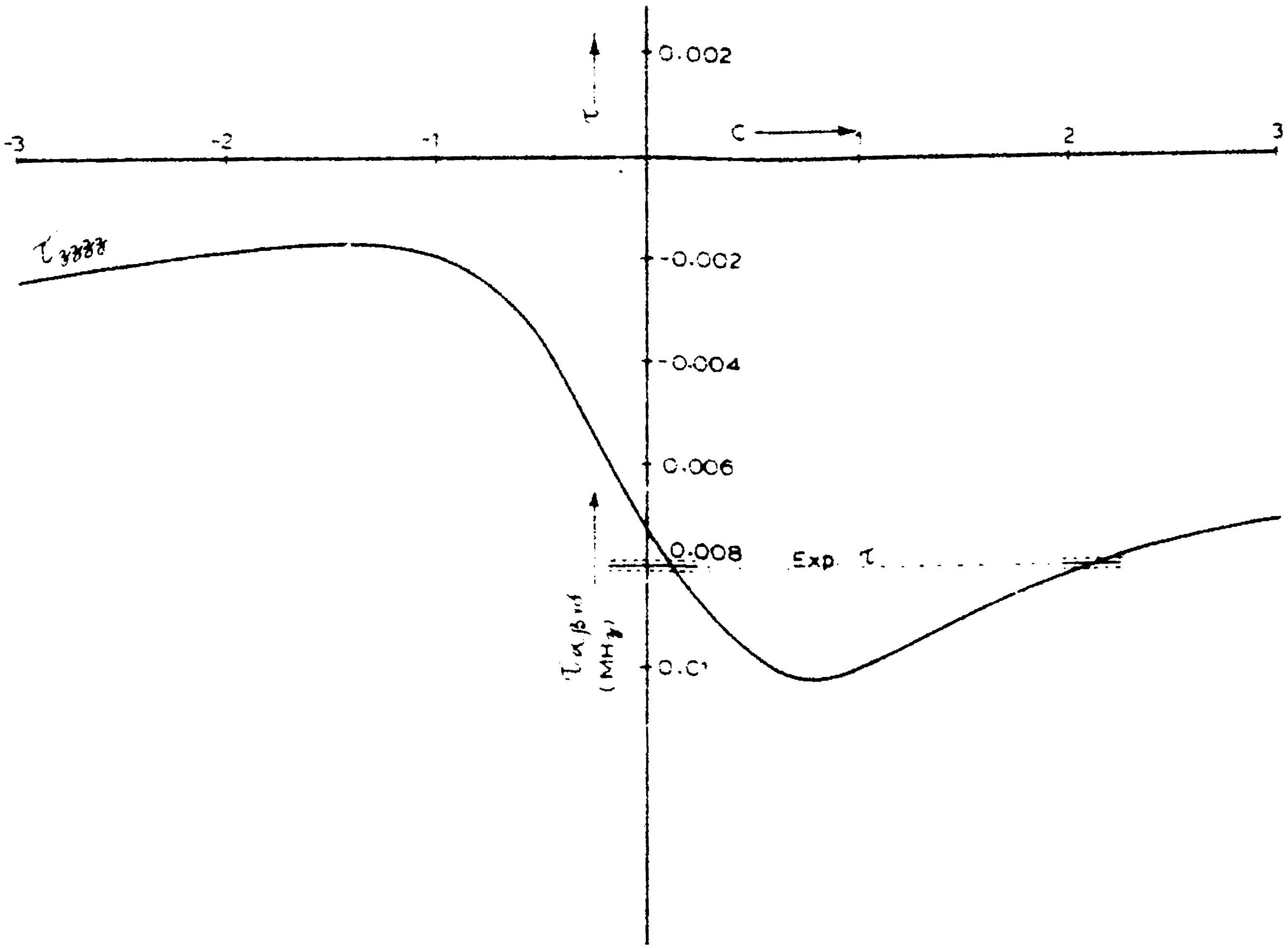

Fig. (3-2)

Variation of $\tau_{\alpha\beta\gamma\delta}$ elements with parameter c.

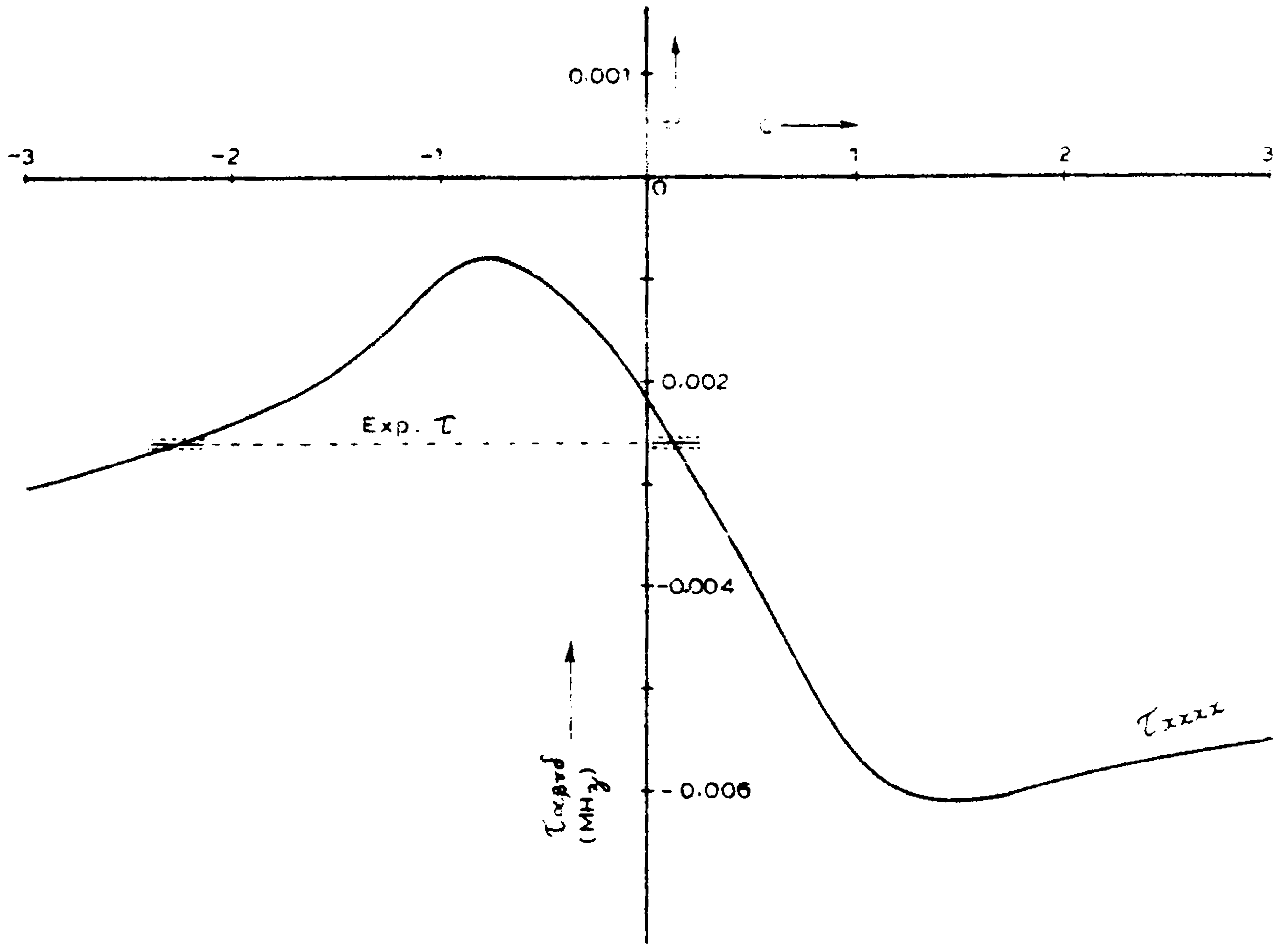

Fig. (3-3)

Variation of $\tau_{\alpha\beta\gamma\delta}$ elements with parameter c.

case there are three independent $\tau_{\alpha\beta\gamma\delta}$ elements as additional experimental data. The values of c_V given in Table 1 corresponding to each of the $\tau_{\alpha\beta\gamma\delta}$ elements show a large difference but the real value of c (c_A) corresponding to each of the $\tau_{\alpha\beta\gamma\delta}$ elements has almost a common value near origin. This shows that use of more than one $\tau_{\alpha\beta\gamma\delta}$ elements will help us to calculate the force constants in a unique way. From Table 1 the real value of c corresponding to τ_{yyyy}, τ_{zzzz} and τ_{xxxx} are 0.062 ± 0.005, 0.064 ± 0.001 and 0.065 ± 0.002 respectively. We can find that there is a slight difference in the real value of c obtained from different $\tau_{\alpha\beta\gamma\delta}$ elements. The value of c = 0.064 ± 0.001 is contained in all c values, hence we take c = 0.064 ± 0.001. The expression to calculate the force constants of XY_2 bent symmetric molecules in paramatric formalism is given below.

$$F_{11} = \Big[\big\{(L_o^{-1})_{11} \Lambda_2 + (L_o^{-1})_{21} \Lambda_1\big\}c^2 + 2\,(L_o^{-1})_{11}(L_o^{-1})_{21}(\Lambda_2 - \Lambda_1)\, c + \big\{(L_o^{-1})_{11}\Lambda_1 + (L_o^{-1})_{21} \Lambda_2\big\}\Big] / (1+c^2) \qquad (3.12a)$$

$$F_{12} = \Big[(L_o^{-1})_{22}\, (L_o^{-1})_{21}\, \Lambda_1\, c^2 + (L_o^{-1})_{11}\, (L_o^{-1})_{22}\, (\Lambda_2 - \Lambda_1)\, c + (L_o^{-1})_{21}\, (L_o^{-1})_{22} \Lambda_2 \Big] / (1+c^2) \qquad (3.12b)$$

$$F_{22} = \Big[(L_o^{-1})^2_{22} \Lambda_1\, c^2 + (L_o^{-1})^2_{22} \Lambda_2 \Big] / (1+c^2) \qquad (3.12c)$$

The force constants which have been obtained in the present work are compared with those from earlier works and are given in Table 2. The force field obtained in the present calculation is in better agreement with the results of Davis and Gerry[10]. The better accuracy of the present result is a particularly notable feature.

3-6 Prediction of fundamental vibrational frequencies from microwave data:

Use of eqs. (3.6) and (3.8) enable us to predict the infrared frequencies and the dimensionless mixing parameter c which controls the force field. The centrifugal distortion constant $\tau_{\alpha\beta\gamma\delta}$ can be rewritten as given below:

$$-\frac{(1+c^2)}{\epsilon}\, 2\, I_{yy}^4\, \tau_{yyyy} = t_{yyyy} = A\,\Lambda_1^{-1} + B\,\Lambda_2^{-1} \qquad (3.13)$$

$$-\frac{(1+c^2)}{\epsilon}\, 2\, I_{zz}^4\, \tau_{zzzz} = t_{zzzz} = D\,\Lambda_1^{-1} + E\,\Lambda_2^{-1} \qquad (3.14)$$

$$-\frac{(1+c^2)}{\epsilon}\, 2\, I_{yy}^2\, I_{zz}^2\, \tau_{yyzz} = t_{yyzz} = F\,\Lambda_1^{-1} + G\,\Lambda_2^{-1} \qquad (3.15)$$

where

$$A = K_{22}^2\, c^2 - 2\, K_{12}\, K_{22}\, c + K_{12}^2 \qquad (3.16a)$$

$$B = K_{12}^2\, c^2 + 2\, K_{12}\, K_{22}\, c + K_{22}^2 \qquad (3.16b)$$

$$D = K_{23}^2\, c^2 - 2\, K_{13}\, K_{23}\, c + K_{13}^2 \qquad (3.16c)$$

$$E = K_{13}^2\, c^2 + 2\, K_{13}\, K_{23}\, c + K_{23}^2 \qquad (3.16d)$$

$$F = K_{22}\, K_{23}\, c^2 - (K_{12}\, K_{23} + K_{13}\, K_{22})\, c + K_{12}\, K_{13} \qquad (3.16e)$$

$$G = K_{12}\, K_{13}\, c^2 + (K_{12}\, K_{23} + K_{13}\, K_{22})\, c + K_{22}\, K_{23} \qquad (3.16f)$$

From eq. (3.13) Λ_1^{-1} is expressed in terms of Λ_2^{-1} and c and applied in eq. (3.14) and (3.15). It helps us to plot a graph between Λ_2^{-1} and c as shown in Fig. (3.4), using eq. (3.14) and (3.15).

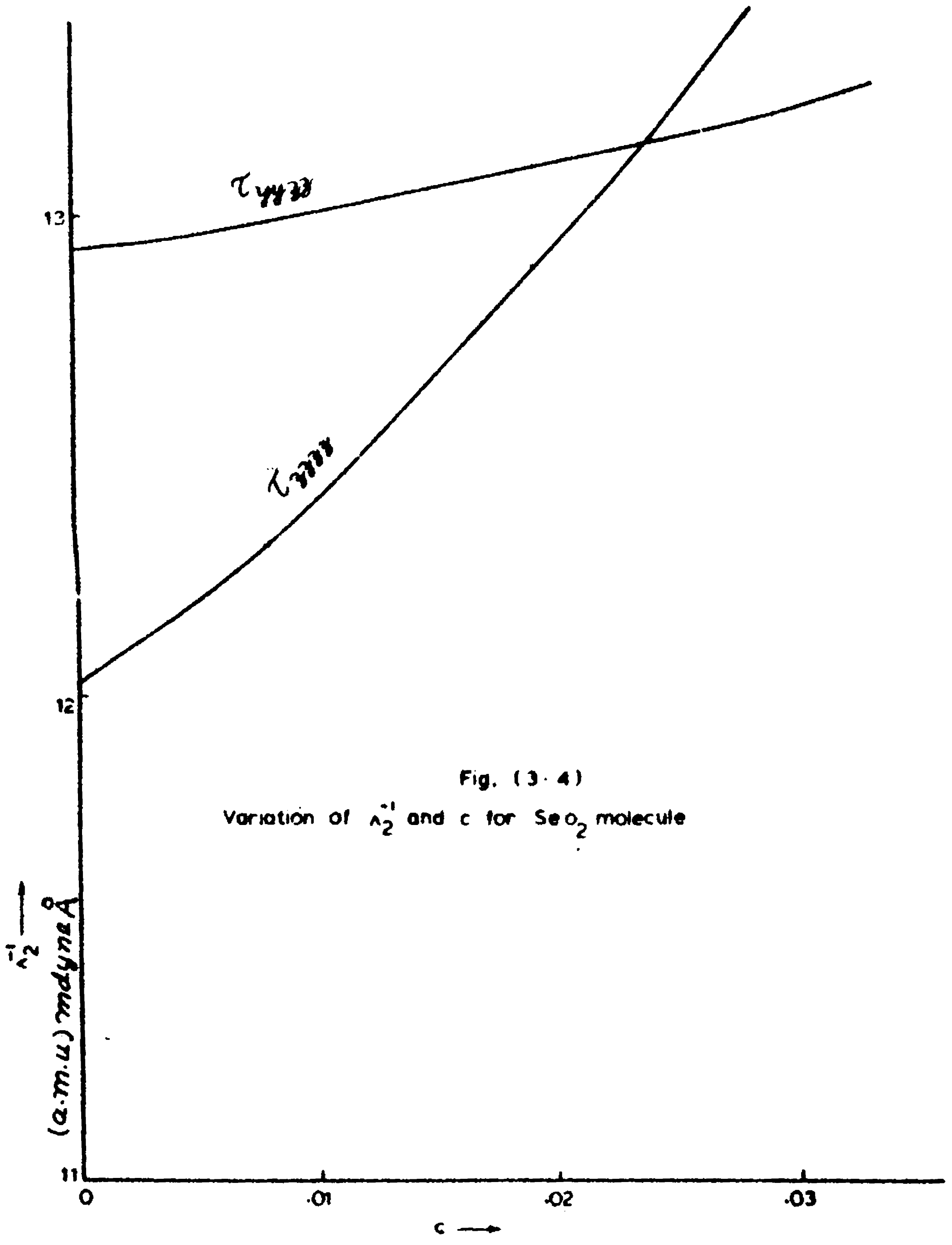

Fig. (3·4)

Variation of λ_2^{-1} and c for SeO_2 molecule

Λ_2^{-1} and e obtained from the intersection when used in any one of the eq.(3.13), (3.14) or (3.15) will give Λ_1^{-1}. This procedure is applied to evaluate the infrared frequencies from microwave data for molecules like NO_2, ClO_2, SO_2, SCl_2 and SeO_2. The result obtained is given in Table 3 which is in very good agreement with the experimental data. Such an approach is of great use to the experimental infrared spectroscopists. In the case of infrared spectra which are complicated by overtones and combination bands and their overlaps, the present calculation will be of value in locating the fundamentals in a species. Thus microwave data could be great use in the analysis of infrared spectrum.

3-7 Approximation formula for calculating $\tau_{\alpha\beta\gamma\delta}$ elements:

In section 2 of this chapter we have discussed the theory to parametrise the $\tau_{\alpha\beta\gamma\delta}$ constants in XY_2 bent symmetric molecular models. This approach leads to the natural approximation formula for $\tau_{\alpha\beta\gamma\delta}$ elements. The $t_{\alpha\beta\gamma\delta}$ elements can be expressed in the matrix form and it is given in eq.(3.2). It has been noted that the matrix C is very close to unit matrix in the case of molecules with vibrational frequencies of order two, when L_0 is taken in the lower triangular form[6,7,12] for non-hydrides and in upper triangular form[12,13] for hydrides. Hence is XY_2 bent symmetric molecules eq.(3.2) can be approximated to

$$t = \tilde{K} \; \Lambda^{-1} \; K \tag{3.17}$$

The simplefied formulas for $t_{\alpha\beta\gamma\delta}$ elements are given below.

XY_2 (C_{2v}) Non hydrides

$$t_{xxxx} = P \tag{3.18a}$$

$$t_{zzzz} = P \sin^4(\alpha/2) + \left[Q - 2\,R \sin^2 (\alpha/2)\right] \Lambda_2^{-1} \tag{3.18b}$$

$$t_{yyyy} = P \cos^4(\alpha/2) + \left[Q + 2\,R \cos^2 (\alpha/2)\right] \Lambda_2^{-1} \tag{3.18c}$$

$$t_{xxyy} = P \cos^2(\alpha/2) + R\,\Lambda_2^{-1} \tag{3.18d}$$

$$t_{xxzz} = P \sin^2(\alpha/2) - R\,\Lambda_2^{-1} \tag{3.18e}$$

$$t_{yyzz} = P \sin^2(\alpha/2) \cos^2(\alpha/2) - \left[Q + R \cos\alpha\right] \Lambda_2^{-1} \tag{3.18f}$$

where $P = 8r^2 \left(\Lambda_1^{-1} - G_{12}^2\, \Lambda_2^{-1} / |G| \right) G_{11}$

$Q = 4r^2\, G_{11} \sin^2\alpha \;/\; |G|$

$R = (4r^2 \sqrt{2}\; G_{12} \sin\alpha\,) \;/\; |G|$

$$t_{yzyz} = (2r^2/G_{33}) \sin^2\alpha\; \Lambda_3^{-1} \tag{3.18g}$$

r is the bond length and α is interbond angle.

XY_2 (C_{2v}) Hydrides

$$t_{xxxx} = A\,\Lambda_1^{-1} \tag{3.19a}$$

$$t_{yyyy} = A\,\Lambda_1^{-1} \cos^4(\alpha/2) + B\left[C + 2^{3/2} G_{12} \cos^2(\alpha/2)\right]\Lambda_1^{-1} + D\,\Lambda_2^{-1} \tag{3.19b}$$

$$t_{zzzz} = A\,\Lambda_1^{-1} \sin^4(\alpha/2) + B\left[C - 2^{3/2} G_{12} \sin^2(\alpha/2)\right]\Lambda_1^{-1} + D\,\Lambda_2^{-1} \tag{3.19c}$$

$$t_{xxyy} = A\,\Lambda_1^{-1} \cos^2 (\alpha/2) + \sqrt{2}\,B\,G_{12}\,\Lambda_1^{-1} \tag{3.19d}$$

$$t_{xxzz} = A\,\Lambda_1^{-1} \sin^2 (\alpha/2) - \sqrt{2}\,B\,G_{12}\,\Lambda_1^{-1} \tag{3.19e}$$

$$t_{yyzz} = (A/4)\ \Lambda_1^{-1} \sin^2 - B(C + 2\ G_{12} \cos\alpha)\ \Lambda_1^{-1} - D\ \Lambda_2^{-1} \qquad (3.19f)$$

$$t_{yzyz} = (2\ r^2 / G_{33}) \sin^2 (\alpha/2)\ \Lambda_3^{-1} \qquad (3.19g)$$

Here $A = 8\ r^2\ G_{22} / |G|$

$B = 4\ r^2 \sin\alpha / |G|$

$C = G_{12}^2 \sin\alpha / G_{22}$

$D = 4\ r^2 \sin^2\alpha / G_{22}$

In Table 4 the $\tau_{\alpha\beta\gamma\delta}$ values obtained using the present method is compared with the experimental values obtained from microwave spectrum. It is found that the agreement is very good. Advantages of the approximation formulas developed for calculating constants are the following.

i) The expressions contain only atomic masses, molecular geometry and fundamental vibrational frequencies.

ii) The formulas derived will be a definite advantage to the microwave spectroscopist because the method yields values of $\tau_{\alpha\beta\gamma\delta}$ elements near the real ones without recourse to a detailed force field analysis.

Hence for a quick computation of the approximate magnitude of the centrifugal distortion constants, these formulas are of great help.

TABLE 1

Values of $\tau_{\alpha\beta\gamma\delta}$ elements - p, q, r terms and parameter e

The elements of SCl_2 molecule	Unit MHz	Values of p,q,r in MHz			The two values of e	
		p	q	r	e_A	e_V
τ_{yyyy}	-0.49899 ± 0.00032	-0.91855	0.99666	-0.55715	0.062± 0.005	2.4
τ_{zzzz}	-0.008017± 0.00001	-0.004485	-0.008034	-0.007405	0.064± 0.001	2.2
τ_{xxxx}	-0.0025823± 0.0000108	-0.004609	-0.004353	-0.0023086	0.065± 0.002	-2.15

Experimental values of $\tau_{\alpha\beta\gamma\delta}$ elements are taken from reference 10

TABLE 2

F_{ij} elements (mdyn/Å) for SCl_2 molecule

F_{ij}	Present work	Previous work		
		Reference 10	Reference 22	Reference 11
F_{11}	2.9274 ± 0.0142	2.913±0.03	2.641	2.52
F_{12}	0.0983 ± 0.00052	0.0926±0.0055	-0.029	-0.055
F_{22}	0.2637 ± 0.00007	0.2624±0.0021	0.303	0.305

TABLE 3

Fundamental vibrational frequencies (cm^{-1}) obtained from centrifugal distortion constants

Molecule	ν_1		ν_2	
	Calculated	Observed	Calculated	Observed
SCl_2	510	514	203	208
ClO_2	937	943	441	445
SeO_2	903	900	401	400
SO_2	1142	1151	509	518
NO_2	1349	1357.8	750	756.8

* Observed frequencies are taken from reference 23

TABLE 4

Centrifugal distortion constants (in MHz) for few XY_2 bent symmetric molecules calculated under the present approximation method

Molecule	τ_{xxxx}	τ_{yyyy}	τ_{zzzz}	τ_{xxyy}	τ_{xxzz}	τ_{yyzz}	Reference
SeO_2	-0.00705	-2.235 (-2.195± 0.03)	-0.0416 (-0.0437± 0.006)	0.00916	-0.01283	0.218 (0.222± 0.017)	18
NO_2	-0.02549	-311.6 (-299.4± 4)	-0.03959 (-0.04144± 0.00015)	0.7821	-0.0307	1.822 (1.843± 0.02)	19
SO_2	-0.01114	-10.000 (-9.2792)	-0.03438 (-0.03553)	0.06013	-0.01703	0.3756 (0.3786)	20
ClO_2	0.01423	-8.244 (-8.529)	-0.04590 (-0.04557)	0.0588	-0.0223	0.3865 (0.3924)	21
H_2O	-0.00104 (-0.00107± 0.00027)	-0.09281 (-0.1084± 0.0012)	0.009212 (-0.0083± 0.0012)	-0.002975 (-0.00491)	-0.00158 (-0.00108)	0.001936 (0.001985)	15
H_2S	-7.94 (8.03)	-241.9 (-247.56)	-145.6 (-151.25)	-17.6	-14.84	123.7 (123.66)	16
H_2Se	5.057	-140.49 (-141.8± 0.9)	119 (121.977)	-9.988	9.317	87.38 (90.036)	17

Values within brackets correspond to those reported from microwave analysis given in the reference.

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CHAPTER IV

CENTRIFUGAL DISTORTION CONSTANTS IN XY_3 PYRAMIDAL MOLECULES AND THEIR APPLICATION FOR UNIQUE FIXING OF INTRAMOLECULAR FORCES

Abstract

A formalism is developed to evaluate all the possible sets of intramolecular force fields fitting fundamental vibrational frequencies and centrifugal distortion constants in the case of XY_3 pyramidal molecules. The method is applied to PF_3 molecule as an example. It is found that there exist as many as four sets of force field fitting all the above experimental data. A few general criteria are suggested to eliminate suprious sets, thus making further experimental data unnecessary to fix the true physical force field.

4-1 Introduction:

In the previous chapter we have seen how the parametrisation of centrifugal distortion constants enables us to find out the accurate force field of XY_2 bent symmetric molecules. In this chapter parameter method which incorporates the centrifugal distortion constants D_J and D_{JK} into vibrational problem associated with XY_3 pyramidal type molecules is presented. In this case centrifugal distortion constants D_J and D_{JK} involve simultaneous contributions from various symmetry species, unlike in the case of Coriollis coupling constants. Hence a solution using these centrifugal distortion constants becomes a separate problem by itself for each molecular model. Also the centrifugal distortion constants are expected to suffer least from anharmonicity of vibration and are obtainable with extremely high accuracy, they should form a much preferrable set of additional data in the solution of vibrational problems. The theory developed here to evaluate all the possible sets of intramolecular force field fitting the fundamental vibrational frequencies and the D_J, D_{JK} constants in XY_3 pyramidal molecules is applied to PF_3 molecule as an example. It is found that there exists as many as four sets of force fields fitting all the experimental data mentioned above. A few general criteria are suggested to eliminate the suprious sets, thus making further experimental data unnecessary to fix the true physical force field.

4-2 Theory:

Pyramidal XY_3 molecules posses two vibrational species ($\Gamma = 2A + 2E$) each of order two and hence matrix C would involve two arbitrary parameters as against one in the earlier case. Consequently, a plotting of all the mathematically possible values of $\tau_{\alpha\beta\gamma\delta}$ elements in terms of arbitrary parameters, fitting the vibrational frequency data would yield various surfaces. A method to cast the problem in two dimentions is presented here by imposing the additional constraint that the parameters should fit the experimental values of the centrifugal distortion constant also, in addition to the vibrational frequencies.

The matrix L_0 can be taken in the lower triangular form as in the earlier[1] case, $(L_0)_{ij} = 0$ for $i < j$ for each of the vibrational species. The nonvanishing K matrix elements obtained from eq. (3-3) employing this form of L_0 and the T_s matrix[2,3] is given in Appendix 1. A convenient form of C matrix which can be used here is

$$C = \begin{bmatrix} S & c_A S & 0 & 0 & 0 & 0 \\ -c_A S & S & 0 & 0 & 0 & 0 \\ 0 & 0 & Q & c_E Q & 0 & 0 \\ 0 & 0 & -c_E Q & Q & 0 & 0 \\ 0 & 0 & 0 & 0 & Q & c_E Q \\ 0 & 0 & 0 & 0 & -c_E Q & Q \end{bmatrix}. \qquad (4.1)$$

where $S = (1+c_A^2)^{-1/2}$ and $Q = (1+c_E^2)^{-1/2}$

c_A and c_E represents the parameters associated with A and E species vibrations respectively, substitution of eq.(4.1) into eq.(3.2) yields expression for $t_{\alpha\beta\gamma\delta}$. The centrifugal distortion constants D_J, D_{JK} and D_K are linear combinations of $\tau_{\alpha\beta\gamma\delta}$ elements[4,5] and they are given by

$$D_J = -(\epsilon/4)\tau_{xxxx} \tag{4.2}$$

$$D_{JK} = -2D_J - (\epsilon/2)\,(\tau_{xxzz} + 2\,\tau_{xzxz}) \tag{4.3}$$

$$D_K = -D_J - D_{JK} - (\epsilon/4)\tau_{zzzz} \tag{4.4}$$

Use of eqs. (3.2) and (2.41) in eqs.(4.2), (4.3) and (4.4) thus yields direct expressions for D_J, D_{JK} and D_K as functions of parameters c_A and c_E as

$$D_J = \frac{(p_J\, c_A^2 + q_J\, c_A + r_J)}{(1+c_A^2)} + \frac{(l_J\, c_E^2 + m_J\, c_E + n_J)}{(1+c_E^2)} \tag{4.5}$$

$$D_{JK} = \frac{(p_{JK}\, c_A^2 + q_{JK}\, c_A + r_{JK})}{(1+c_A^2)} + \frac{(l_{JK}\, c_E^2 + m_{Jk}\, c_E + n_{JK})}{(1+c_E^2)} \tag{4.6}$$

$$D_K = \frac{(p_K\, c_A^2 + q_K\, c_A + r_K)}{(1+c_A^2)} + \frac{(l_K\, c_E^2 + m_K\, c_E + n_K)}{(1+c_E^2)} \tag{4.7}$$

The various p, q, r, l, m, n terms are as mentioned earlier, functions of molecular geometry and vibrational frequencies. Explicit expressions for these quantities are given in Appendix 2. The three relations (4.5), (4.6) and (4.7) are best suited for simultaneous mapping of all the mathematically possible values of D_J, D_{JK} and D_K compatible with vibrational frequencies. This immediately indicates that any theoretical calculation of D_J, D_{JK} and D_K constants employing the vibrational frequencies and molecular geometry as input data is bound to lack uniqueness due to the two degrees of freedom still left open in the determination of molecular force field, as these parameters are directly controlled by the matrix F and vice versa, as is evident from eq. (1.23)

$$F = (\tilde{L}_o)^{-1} \quad C \; \Lambda^{-1} \; \tilde{C} \quad (L_o)^{-1}$$

On the other hand any of the two centrifugal distortion constants D_J, D_{JK} and D_K are known from the analysis of microwave spectrum, the exact values of c_A and c_E can be solved from their respective relations in eqs.(4.5), (4.6) and (4.7) and can be used to determine F matrix through eq. (1.23). However the difficulties due to the multiplicities of solutions arising from the quadratic nature of these equations are bound to complicate the problem. Further, the experimental uncertainties in the values of D_J, D_{JK} and D_K (though very small) make the three equations slightly inconsistent thus making a direct mathematical solution undesirable. Considering the probable extent of uncertainties in the experimental data, the best possible values of c_A and c_E can be obtained by graphical methods. For different values of c_A, the values of c_E can be calculated and c_A versus c_E curve can be plotted corresponding to eqs.(4.5), (4.6) and (4.7) In the ideal case, a unique point must exist in the parameter space, the coordinates of which would correspond to the actual force field of the molecule and satisfy eqs. (4.5), (4.6) and (4.7). If the experimental uncertainties in the values of centrifugal distortion constants are also taken into account, then each of the curve gets the uncertainity spread and the region where they intersect should contain the point corresponding to the exact force field. The force field fitting the experimental values of the vibrational frequencies and centrifugal distortion constant can be calculated from eq. (1.23) using the values of c_A and c_E corresponding to the boundaries of the intersection of these curves.

4-3 Example: PF_3 molecule

PF_3 provides an excellent test case, since for this molecule:

(i) the centrifugal distortion constants are known to very high degree of accuracy[6]

(ii) the geometry is accurately known from microwave and electron diffraction studies[7,8]

(iii) the vibrational frequencies are known accurately, the spectrum being almost non-overlapped[9]

(iv) the vibrational frequencies are supposed to suffer least from anharmonicity corrections[10]

(v) the force field has been well established by the use of additional data[6,7,9,10,11]

The value of D_K is not available experimentally, but this is the case for most of symmetric top molecules as the frequencies in pure rotational spectrum are independent of D_K. However, this does not present any problem since the correct values of c_A and c_E will be contained in the solution of eqs.(4.5) and (4.6).

The numerical values of p, q, r, l, m, n for D_J, D_{JK} and D_K terms in eqs. (4.5), (4.6) and (4.7) for PF_3 are given in Table 1 alongwith the required experimental data. The c_A versus c_E curves corresponding to the experimental values of D_J and D_{JK} are drawn in the range $-2 < c_A < +2$ as shown in Fig.4-1.

The curves show four intersections and are indicated as I, II, III and IV by arrows in the figure. The coordinate values, c_A and c_E, corresponding to each of these intersections are given in Table 2. The F_{ij} elements, characterising the intramolecular force field, corresponding to each of these intersections calculated are also included in the Table 2. The results thus obtained, indicate that there exists four sets of force field that would fit the experimental data on all the four vibrational frequencies and the two centrifugal distortion constants.

4-4 Elimination of the anomalous force fields:

Existence of four sets of force field fitting as many as six experimental data, in this case, leads to a puzzling situation, since only one of these would correspond to the actual force field in the molecule. In situations where such multiplicities occur elimination of the anomalous sets can be done

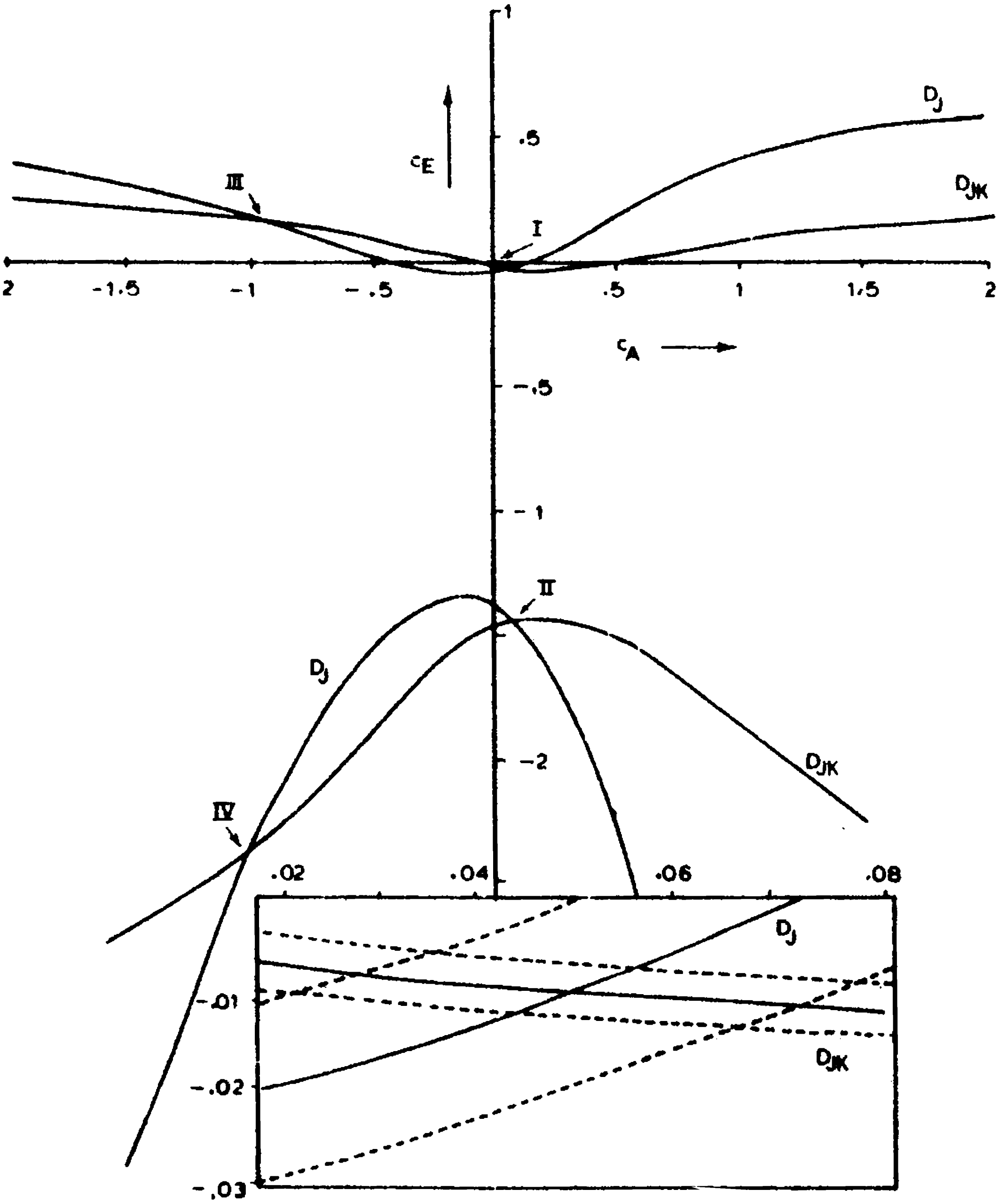

Fig. (4-1)

c_A versus c_E curves in conformity with the experimental values of D_J and D_{JK}

with the use of yet another experimental datum like mean amplitudes of vibration[11,12,13,14], absolute infrared intensities[9] etc. But there exist chances that even this procedure may not resolve the ambiquity completely thus making a unique solution still impossible. For example, it has been noted that the vibrational amplitudes corresponding to the non bonded atom pairs fit both the real and anomalous solutions arising from the use of Coriolis coupling constants or isotopic frequencies as additional data into the vibrational problem[11,12,13]. In the present case we note that both the solutions corresponding to intersections I and II given in Table 2 fit the coriolis data extremely well. Considering also the situation in which the required additional data are not readily available, it would be preferrable to use some general criteria for the elimination of the anomalous force fields and the following are suggested for this purpose.

(i) For the true force field in XY_3 pyramidal type molecules, there exists a relation $F_{12} \gtrsim - 2 F_{34}$. Ponomarev and Khovrin[15] have shown that this criterion is even superior to the coriolis data.

(ii) For most cases of vibrational species possessing one stretching and one bending motion, it is well known[16,1] that the later is highly characteristic and the L matrix is best approximated in a lower triangular form. Since we have taken L_0 in the lower triangular form, C in eq.(4.1) should be very nearly a unit matrix and this therefore suggests extremely small values for values of $\tau_{\alpha\beta\gamma\delta}$ elements, thus yielding different surfaces for D_J, D_{JK} and D_K values. This projects the physics of the problem in a much better fashion than in a blind computer calculation which merely seeks a best fit solution. Eqs.(4.5), (4.6) and (4.7) alongwith eq.(1.23) leads to a streamlined mathematical procedure incorporating the centrifugal distortion constants in the vibrational problem, thus leading to the various solutions of intramolecular force field. The multiplicity of solutions must be anticipated because of the inherent nonlinearity of such problems and in the present case the criteria discussed in the previous section conveniently serve towards the elimination of the unphysical solutions.

Table 1

Values of p,q,r,l,m,n terms (in MHz), D_J and D_{JK} constants for PF_3 molecule

Centrifugal distortion constant Reference 6	p	q	r	l	m	n
D_J = 0.007845±0.000045	0.005302	0.001276	0.001725	0.002545	−0.005127	0.005995
D_{JK} = −0.01177±0.00004	−0.005567	0.001341	−0.001203	−0.001553	0.013294	−0.010486
D_K = ———	0.001672	−0.001105	0.000862	−0.000992	−0.008163	0.004481

Table 2

The four sets of force constants (mdyn/Å) fitting the experimental data on vibrational frequencies and centrifugal distortion constants

Intersection point in Fig.(4.1)	F_{ij} elements					
	F_{11}	F_{12}	F_{22}	F_{33}	F_{34}	F_{44}
I ($c_A = 0.05$, $c_E = -0.0095$)	6.266	0.432	0.795	4.987	-0.199	0.500
II ($c_A = 0.05$, $c_E = -1.45$)	6.266	0.432	0.795	1.183	0.491	2.279
III ($c_A = -1.02$, $c_E = 0.19$)	6.814	2.660	1.086	5.446	-0.875	0.532
IV ($c_A = -1.02$, $c_E = -2.33$)	6.814	2.660	1.086	0.905	-0.056	2.717

Table 3

F_{ij} Elements (mdyn/Å) corresponding to the actual force field for PF_3

F_{ij}	Present work	Earlier work		
	Corresponding to $c_A = 0.02$ to 0.08 and $c_B = -0.0055$ to -0.0135	Reference 7	Reference 9	Reference 10
F_{11}	6.2638 ± 0.13	6.23 ± 0.13	6.2	6.18 ± 0.01
F_{12}	0.4331 ± 0.08	0.41 ± 0.09	0.41	0.314 ± 0.06
F_{22}	0.7978 ± 0.0004	0.80 ± 0.016	0.80	0.823 ± 0.008
F_{33}	4.9865 ± 0.0124	4.98 ± 0.05	4.98	4.96
F_{34}	−0.1987 ± 0.0131	−0.192 ± 0.05	−0.19	−0.2047
F_{44}	0.5004 ± 0.0002	0.499 ± 0.013	0.50	0.4914

Appendix 1

Nonvanishing elements of K matrix

$$K_{11} = (L_o^{-1})_{11}\ (2/\sqrt{3})\ R\ (1+2\cos^2 A)$$

$$K_{21} = (L_o^{-1})_{21}\ (2/\sqrt{3})\ R\ (1+2\cos^2 A) - (L_o^{-1})_{22}\ (2/\sqrt{3})\ R\ (4\cos^2 A - 1)\ \tan A$$

$$K_{31} = -(L_o^{-1})_{33}\ (2\sqrt{2}/\sqrt{3})\ R\ \sin^2 A$$

$$K_{41} = -(L_o^{-1})_{43}\ (2\sqrt{2}/\sqrt{3})\ R\ \sin^2 A + (L_o^{-1})_{44}\ (2/\sqrt{3})\ R\ (1+2\cos^2 A)\ \tan A$$

$$K_{12} = (L_o^{-1})_{11}\ (2/\sqrt{3})\ R\ (1+2\cos^2 A)$$

$$K_{22} = (L_o^{-1})_{21}\ (2/\sqrt{3})\ R\ (1+2\cos^2 A) - (L_o^{-1})_{22}\ (2/\ 3)\ R\ (4\cos^2 A - 1)$$

$$K_{32} = (L_o^{-1})_{33}\ (\sqrt{8}/\sqrt{3})\ R\ \sin^2 A$$

$$K_{42} = (L_o^{-1})_{43}\ (\sqrt{8}/\sqrt{3})\ R\ \sin^2 A - (L_o^{-1})_{44}\ (\sqrt{2}/\sqrt{3})\ R\ (1+2\cos^2 A)\ \tan A$$

$$K_{13} = (L_o^{-1})_{11}\ (8/\sqrt{3})\ R \sin^2 A$$

$$K_{23} = (L_o^{-1})_{21}\ (8/\sqrt{3})\ R \sin^2 A + (L_o^{-1})_{22}\ (4/\sqrt{3})\ R\ (4 \cos^2 A - 1) \tan A$$

$$K_{54} = (L_o^{-1})_{33}\ 2\sqrt{2}\ R \sin A \cos B$$

$$K_{64} = (L_o^{-1})_{43}\ 2\sqrt{2}\ R \sin A \cos B + (L_o^{-1})_{44}\ 2\sqrt{2}\ R \sin A \tan A \cos B$$

$$K_{35} = (L_o^{-1})_{33}\ 2\sqrt{2}\ R \sin A \cos B$$

$$K_{45} = (L_o^{-1})_{43}\ 2\sqrt{2}\ R \sin A \cos B + (L_o^{-1})_{44}\ 2\sqrt{2}\ R \sin A \tan A \cos B$$

$$K_{56} = (L_o^{-1})_{33}\ (2\sqrt{2}/\sqrt{3})\ R \sin^2 A$$

$$K_{66} = (L_o^{-1})_{43}\ (2\sqrt{2}/\sqrt{3})\ R \sin^2 A - (L_o^{-1})_{44}\ (\sqrt{2}/\sqrt{3})\ R\ (1+2 \cos^2 A) \tan A$$

Here R refers to the bondlength X — Y, A refers to half the interbond angle Y – X – Y and B is given by the relation $\cos B = \sqrt{(4 \cos^2 A - 1)/3}$

Appendix 2

Expressions for p, q, r and l, m, n terms

$$p_J = (K_{11}^2 \Lambda_2^{-1} + K_{21}^2 \Lambda_1^{-1}) / 8(I_{xx}^e)^4$$

$$q_J = (\Lambda_2^{-1} - \Lambda_1^{-1}) K_{11} K_{21} / 4(I_{xx}^e)^4$$

$$r_J = (K_{11}^2 \Lambda_1^{-1} + K_{21}^2 \Lambda_2^{-1}) / 8(I_{xx}^e)^4$$

$$l_J = (K_{31}^2 \Lambda_4^{-1} + K_{41}^2 \Lambda_3^{-1}) / 8(I_{xx}^e)^4$$

$$m_J = (\Lambda_4^{-1} - \Lambda_3^{-1}) K_{31} K_{41} / 4(I_{xx}^e)^4$$

$$n_J = (K_{31}^2 \Lambda_3^{-1} + K_{41}^2 \Lambda_4^{-1}) / 8(I_{xx}^e)^4$$

$$p_{JK} = \left[(K_{11} K_{13} \Lambda_2^{-1} + K_{23} K_{21} \Lambda_1^{-1}) (I_{xx}^e)^2 - (K_{11}^2 \Lambda_2^{-1} + K_{21}^2 \Lambda_1^{-1})(I_{zz}^e)^2\right] / 4(I_{xx}^e)^4 (I_{zz}^e)^2$$

$$q_{JK} = \left[(K_{13} K_{21} + K_{23} K_{11})(\Lambda_2^{-1} - \Lambda_1^{-1})(I_{xx}^e)^2 - 2K_{11} K_{21}(\Lambda_2^{-1} - \Lambda_1^{-1})(I_{zz}^e)^2\right] / 4(I_{xx}^e)^4 (I_{zz}^e)^2$$

$$r_{JK} = \left[(K_{13}\, K_{11}\, \Lambda_1^{-1} + K_{21}\, K_{23}\, \Lambda_2^{-1})(I_{xx}^e)^2 - (K_{11}^2\, \Lambda_1^{-1} + K_{21}^2\, \Lambda_2^{-1})(I_{zz}^e)^2 \right] / \; 4(I_{xx}^e)^4\, (I_{zz}^e)^2$$

$$l_{JK} = \left[2(K_{35}^2\, \Lambda_4^{-1} + K_{45}^2\, \Lambda_3^{-1})(I_{xx}^e)^2 - (K_{31}^2\, \Lambda_4^{-1} + K_{41}^2\, \Lambda_3^{-1})(I_{zz}^e)^2 \right] / \; 4(I_{xx}^e)^4\, (I_{zz}^e)^2$$

$$m_{JK} = \left[2\, K_{35}\, K_{45}\, (\Lambda_4^{-1} - \Lambda_3^{-1})\, (I_{xx}^e)^2 - K_{31}\, K_{41}\, (\Lambda_4^{-1} - \Lambda_3^{-1})\, (I_{zz}^e)^2 \right] / \; 2(I_{xx}^e)^4\, (I_{zz}^e)^2$$

$$n_{JK} = \left[2(K_{35}^2\, \Lambda_3^{-1} + K_{45}^2\, \Lambda_4^{-1})(I_{xx}^e)^2 - (K_{31}^2\, \Lambda_3^{-1} + K_{41}^2\, \Lambda_4^{-1})(I_{zz}^e)^2 \right] / \; 4(I_{xx}^e)^4\, (I_{zz}^e)^2$$

$$p_K = \Big[(K_{11}^2\, \Lambda_2^{-1} + K_{21}^2\, \Lambda_1^{-1})(I_{zz}^e)^4 - 2(K_{13}\, K_{11}\, \Lambda_2^{-1} + K_{23}\, K_{21}\, \Lambda_1^{-1})\, (I_{xx}^e)^2\, (I_{zz}^e)^2 +$$

$$(K_{13}^2\, \Lambda_2^{-1} + K_{23}^2\, \Lambda_1^{-1})(I_{xx}^e)^4 \Big] / \; 8(I_{xx}^e)^4\, (I_{zz}^e)^4$$

$$q_K = \Big[K_{11}\, K_{21}\, (\Lambda_2^{-1} - \Lambda_1^{-1})(I_{zz}^e)^4 - (K_{13}\, K_{21} + K_{23}\, K_{11})(\Lambda_2^{-1} - \Lambda_1^{-1})(I_{xx}^e)^2\, (I_{zz}^e)^2 +$$

$$K_{13}\, K_{23}\, (\Lambda_2^{-1} - \Lambda_1^{-1})(I_{xx}^e)^4 \Big] / \; 4(I_{xx}^e)^4\, (I_{zz}^e)^4$$

$$r_K = \Big[(K_{11}^2 \Lambda_1^{-1} + K_{21}^2 \Lambda_2^{-1})(I_{zz}^e)^4 - 2(K_{13} K_{11} \Lambda_1^{-1} + K_{23} K_{21} \Lambda_2^{-1})(I_{xx}^e)^2 (I_{zz}^e)^2 +$$

$$(K_{13}^2 \Lambda_1^{-1} + K_{23}^2 \Lambda_2^{-1})(I_{xx}^e)^4 \Big] / \; 8(I_{xx}^e)^4 (I_{zz}^e)^4$$

$$l_K = \Big[(K_{31}^2 \Lambda_4^{-1} + K_{41}^2 \Lambda_3^{-1})(I_{zz}^e)^4 - 4(K_{35}^2 \Lambda_4^{-1} + K_{45}^2 \Lambda_3^{-1})(I_{xx}^e)^2 (I_{zz}^e)^2 \Big] / \; 8(I_{xx}^e)^4 (I_{zz}^e)^4$$

$$m_K = \Big[K_{31} K_{41} (\Lambda_4^{-1} - \Lambda_3^{-1})(I_{zz}^e)^4 - 4 K_{35} K_{45} (\Lambda_4^{-1} - \Lambda_3^{-1})(I_{xx}^e)^2 (I_{zz}^e)^2 \Big] / \; 4(I_{xx}^e)^4 (I_{zz}^e)^4$$

$$n_K = \Big[(K_{31}^2 \Lambda_3^{-1} + K_{41}^2 \Lambda_4^{-1})(I_{zz}^e)^4 - 4(K_{35}^2 \Lambda_3^{-1} + K_{45}^2 \Lambda_4^{-1})(I_{xx}^e)^2 (I_{zz}^e)^2 \Big] / \; 8(I_{xx}^e)^4 (I_{zz}^e)^4$$

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CHAPTER V

EVALUATION OF MOLECULAR GEOMETRY OF SYMMETRIC TOP MOLECULES USING CENTRIFUGAL DISTORTION CONSTANTS:

Abstract

Expressions are derived to obtain the centrifugal distortion constants in symmetric top molecules. It is found that the centrifugal distortion constants obtained using the above expressions is in very good agreement with the experimental values. Considering the mixing parameter to be very small, the formulas derived to calculate the centrifugal distortion constants contains only molecular geometry, atomic masses and fundamental vibrational frequencies. This leads to an interesting conclusion that centrifugal distortion constants can be used as an additional data, along with the rotational constants to fix the molecular geometry of symmetric top molecules with insufficient data on the isotopic substituents. Using the above approach molecular geometry of PF_3, AsF_3 and OPF_3 are evaluated. The structural parameters obtained using the above expression is in close agreement with the available experimental values.

5-1 Introduction :

We have already discussed the theory of parametrisation of centrifugal distortion constants D_J, D_{JK} and D_K in XY_3 symmetric top molecules. In this chapter, it is shown that a paramatric approach leads naturaly to a set of approximation formulas for centrifugal distortion constants. These approximation formulas derived here have the advantage that they contain only molecular geometry, atomic masses and fundamental vibrational frequencies of the molecule. It is found that the centrifugal distortion constants calculated using these expressions agree very well with the standard experimental results available from the litrature. This observation leads to a very interesting conclusion that with the help of these expressions the centrifugal distortion constants together with rotational constant can be used to fix the geometry of symmetric top molecules like PF_3, AsF_3 for which rotational data on the isotopic substituents are not available.

In symmetric top molecules ~~the~~ pure rotational spectrum in the microwave gives only one rotational constants B_0. When the structural parameters exceed the number of available rotational constants, molecular geometry is usually obtained from the microwave spectrum of its isotopic substituents. There are molecules like PF_3 and AsF_3 for which there exists no stable isotopic substituents. The bond length and interbond angle of these molecules cannot be obtained from one rotational constant B_0. Similarly in the case of certain XY_3Z type symmetric top molecules like OPF_3, which have only one stable isotopic substituent, though two values of rotational constants can be obtained, the two bondlength and one interbond angle needed to fix the geometry of such molecules cannot be evaluated from these. Under such circumstances, it is suggested in this chapter that experimental values of centrifugal distortion constants can serve as additional data to evaluated the molecular geometry.

5-2 Approximation formulas to evaluate D_J, D_{JK} and D_K in XY_3 symmetric top molecules :

In section 2 of chapter IV we have seen that D_J, D_{JK} and D_K can be parametrised and represented by the eqs.(4.3), (4.4) and (4.5) as

$$D_J = \frac{(p_J c_A^2 + q_J c_A + r_J)}{(1+c_A^2)} + \frac{(l_J c_E^2 + m_J c_E + n_J)}{(1+c_E^2)}$$

$$D_{JK} = \frac{(p_{JK} c_A^2 + q_{JK} c_A + r_{JK})}{(1+c_A^2)} + \frac{(l_{JK} c_E^2 + m_{JK} c_E + n_{JK})}{(1+c_E^2)}$$

$$D_K = \frac{(p_K c_A^2 + q_K c_A + r_K)}{(1+c_A^2)} + \frac{(l_K c_E^2 + m_K c_E + n_K)}{(1+c_E^2)}$$

It is known that the mixing parameters are very small for the vibrational species of order two and the matrix C is very close to an orthogonal matrix. In chapter III we found that by assuming the mixing parameter c equal to zero, the $\tau_{\alpha\beta\gamma\delta}$ elements of XY_2 bent symmetric molecules calculated is very close to the experimental values[7,8,9]. Though XY_3 symmetric top molecules also come under second order vibrational problem, one important difference in this case is that instead of a single mixing parameter c as in the case of XY_2, it contains two parameters c_A and c_E connected with A and E species of vibration. Also from the actual calculations of c_A and c_E on a number of XY_3 pyramidal type molecules, we find that c_A and c_E to be very small. As an approximation, considering each parameter c_A and c_E equal to zero, we get

$$D_J = r_J + n_J \tag{5.1}$$

$$D_{JK} = r_{JK} + n_{JK} \tag{5.2}$$

$$D_K = r_K + n_K \tag{5.3}$$

On expanding r and n terms in the above equations

$$D_J = (K_{11}^2 \Lambda_1^{-1} + K_{21}^2 \Lambda_2^{-1} + K_{31}^2 \Lambda_3^{-1} + K_{41}^2 \Lambda_4^{-1}) / (8 I_{xx}^4) \tag{5.4}$$

$$\begin{aligned} D_{JK} = {} & (K_{11} K_{13} \Lambda_1^{-1} + K_{21} K_{23} \Lambda_2^{-1}) / (4 I_{xx}^2 I_{zz}^2) + \\ & (2 K_{35}^2 \Lambda_3^{-1} + 2 K_{45}^2 \Lambda_4^{-1}) / (4 I_{xx}^2 I_{zz}^2) - \\ & (K_{11}^2 \Lambda_1^{-1} + K_{21}^2 \Lambda_2^{-1} + K_{31}^2 \Lambda_3^{-1} + K_{41}^2 \Lambda_4^{-1}) / (4 I_{xx}^4) \end{aligned} \tag{5.5}$$

$$\begin{aligned} D_K = {} & (K_{13}^2 \Lambda_1^{-1} + K_{23}^2 \Lambda_2^{-1}) / (8 I_{zz}^4) + D_J - \\ & (K_{11} K_{13} \Lambda_1^{-1} + K_{21} K_{23} \Lambda_2^{-1}) / (4 I_{xx}^2 I_{zz}^2) + \\ & (2 K_{35}^2 \Lambda_3^{-1} + 2 K_{45}^2 \Lambda_4^{-1}) / (4 I_{xx}^2 I_{zz}^2) \end{aligned} \tag{5.6}$$

In hydride type molecules L_0 is taken in upper triangular form[4,5,6] and in non hydride type L_0 is taken in the lower triangular form.[1,2,3]

The non-vanishing K matrix elements which are used for the calculation of D_J, D_{JK} and D_K constants in hydride and non hydride molecules are given below.

K matrix elements for XY_3 hydride molecules;

$$K_{11} = (L_o^{-1})_{11}\ (2/3^{1/2})\ R\ (1+2\cos^2 A) - (L_o^{-1})_{12}\ (2/3^{1/2})\ R\ (4\cos^2 A - 1)\tan A \qquad (5.7a)$$

$$K_{21} = -(L_o^{-1})_{22}\ (2/3^{1/2})\ R\ (4\cos^2 A - 1)\tan A \qquad (5.7b)$$

$$K_{31} = -(L_o^{-1})_{33}\ (8/3)\ R\sin^2 A - (L_o^{-1})_{34}\ (2/3)\ R\ (1+2\cos^2 A)\tan A \qquad (5.7c)$$

$$K_{41} = (L_o^{-1})_{44}\ (2/3)\ R\ (1+2\cos^2 A)\tan A \qquad (5.7d)$$

$$K_{13} = (L_o^{-1})_{11}\ (8/3)\ R\sin^2 A + (L_o^{-1})_{12}(4/3^{1/2})\ (4\cos^2 A - 1)\tan A \qquad (5.7e)$$

$$K_{23} = (L_o^{-1})_{22}\ (4/3^{1/2})\ R\ (4\cos^2 A - 1)\tan A \qquad (5.7f)$$

$$K_{35} = (L_o^{-1})_{33}\ 8^{1/2}\ R\sin A\cos B + (L_o^{-1})_{34}\ 8^{1/2}\ R\sin A\cos B\tan A \qquad (5.7g)$$

$$K_{45} = (L_o^{-1})_{44}\ 8^{1/2}\ R\sin A\tan A\cos B \qquad (5.7h)$$

Where $\cos B = \sqrt{(4\cos^2 A - 1)/3}$ R refers to the bond length and A refers to half the interbond angle.

Here $(L_o^{-1})_{11} = (G_{22})^{1/2} / G^{1/2}$, $-(L_o^{-1})_{12} = + G_{12} / \sqrt{G_{22}\,|G|}$

$(L_o^{-1})_{22} = 1/G_{22}^{1/2}$, $(L_o^{-1})_{33} = (G_{44})^{1/2} / \sqrt{|G^*|}$

$(L_o^{-1})_{34} = -G_{34} / \sqrt{G_{44}\,|G^*|}$, $(L_o^{-1})_{44} = 1/ G_{44}^{1/2}$

Where $|G| = G_{11}\,G_{22} - G_{12}^2$, $|G^*| = G_{33}\,G_{44} - G_{34}^2$

$G_{11} = (4 \cos^2 A - 1) / m_X + 1/m_Y$

$G_{12} = -2\,(4 \cos^2 A - 1) \tan A / m_X$

$G_{22} = (4 - \sec^2 A)\,(4 \sin^2 A / m_X) + 1/m_Y$

$G_{33} = 2 \sin^2 A / m_X + 1/m_Y$

$G_{34} = 2 \sin^2 A \tan A / m_X$

$G_{44} = (2 \sin^2 A \tan^2 A / m_X) + (1+2^{-1} \sec^2 A) / m_Y$

m_X and m_Y are the mass of X and Y atom respectively

K matrix elements for XY_3 non hydride molecules

$K_{11} = (L_o^{-1})_{11}\,(2/3^{1/2})\,R\,(1+2 \cos^2 A)$ (5.8a)

$K_{21} = (L_o^{-1})_{21}\,(2/3^{1/2})\,R\,(1+2 \cos^2 A) -$

$(L_o^{-1})_{22}\,(2/3^{1/2})\,R\,(4 \cos^2 A - 1) \tan A$ (5.8b)

$K_{31} = -\,(L_o^{-1})_{33}\,(8/3)^{1/2}\,R \sin^2 A$ (5.8c)

$$K_{41} = - (L_o^{-1})_{43} \, (8/3)^{1/2} \, R \sin^2 A + (L_o^{-1})_{44} \, (2^{1/2}/3) \, R \, (1+2 \cos^2 A) \tan A \qquad (5.8d)$$

$$K_{13} = (L_o^{-1})_{11} \, (8/\sqrt{3}) \, R \sin^2 A \qquad (5.8e)$$

$$K_{23} = (L_o^{-1})_{21} \, (8/\sqrt{3}) \, R \sin^2 A + (L_o^{-1})_{22} \, (4/\sqrt{3}) \, R \, (4 \cos^2 A - 1) \tan A \qquad (5.8f)$$

$$K_{35} = (L_o^{-1})_{33} \, 8^{1/2} \, R \sin A \cos B \qquad (5.8g)$$

$$K_{45} = (L_o^{-1})_{43} \, 8^{1/2} \, R \sin A \cos B + (L_o^{-1})_{44} \, 8^{1/2} \, R \sin A \tan A \cos B \qquad (5.8h)$$

Where $(L_o^{-1})_{11} = G_{11}^{-1/2}$, $(L_o^{-1})_{21} = - G_{12} \, G_{11}^{-1/2} \, |G|^{-1/2}$

$(L_o^{-1})_{22} = G_{11}^{1/2} \, |G|^{-1/2}$, $(L_o^{-1})_{33} = G_{33}^{-1/2}$

$(L_o^{-1})_{43} = -G_{43} \, G_{33}^{-1/2} \, |G^*|^{-1/2}$, $(L_o^{-1})_{44} = G_{33}^{1/2} \, |G^*|^{-1/2}$

$$I_{xx} = 3 \, m_Y \, R^2 \left[2 - (1-3 \, m_Y \, m_X^{-1}) \, (4/3) \sin^2 A\right] / \, (2+6 \, m_Y \, m_X^{-1}) \qquad (5.9)$$

$$I_{zz} = 4 \, m_Y \, R^2 \sin^2 A \qquad (5.10)$$

Using the above expressions the D_J, D_{JK} and D_K constants of NH_3, PH_3, SbH_3, $AsCl_3$, PCl_3 and NF_3 are calculated and the results are given in Table 1. It is found that the D_J, D_{JK} and D_K constants calculated using the above expressions agrees very well with the experimental results.

5-3 Molecular geometry of XY_3 symmetric top molecules using centrifugal distortion constants D_J and D_{JK}

Many attempts have been made in the past to evaluate by other means the bondlength and interbond angle of XY_3 pyramidal type molecules for which the microwave data are inadequate. One of the methods employed in this context is to make use of the Coriolis zeta sum rule of Johnson and Dennison. Hokins[10] in this way tried to fix the interbond angle of NF_3, PF_3 and AsF_3 molecules. Since the error involved in the zeta constants are fairly large, the interbond angle evaluated from them are not quite correct.

Ponomarev[11] and Khovrin tried to fix the geometry of these molecules using Coriolis zeta constants and centrifugal distortion constants along with a certain constraint on the quadratic force field of the molecule. Their work showed that the variation of molecular geometry has an extremely marked effect on the centrifugal distortion constants D_J and D_{JK}. Conversely we infer that the molecular geometry evaluated using D_J, D_{JK} constants must be very close to the actual geometry of the molecule. Indirect evaluation of molecular geometry is therefore possible when the centrifugal distortion constants D_J and D_{JK} are available from the microwave spectrum with sufficient accuracy. Determination of these constants with an accuracy of 1% or better is possible for symmetric top molecules from the measurement of high J rotational transitions[12]. In this context we suggest here a method to determine the structure of XY_3 symmetric top molecules from the centrifugal distortion constants and the fundamental vibrational frequencies.

Eq.(5.1) and (5.2) are of great importance when the structural parameters of the molecule are not known precisely. With the help of eq.(5.4) and (5.5) the bondlength and interbond angle may be calculated from the experimental values of D_J and D_{JK}. We have adopted the following procedure for obtaining the molecular geometry of XY_3 symmetric top molecules. For different values of interbond angle α , the bond length R was solved from eq.(5.4) and (5.5). R against ($\alpha/2$) is plotted in both cases. The intersection gives the currect value of the bondlength R and half the interbond angle as shown in Fig.(5.1) and (5.2). Using this procedure we have obtained the molecular geometry of PF_3 and AsF_3 for which there are no stable isotopic substituents. The structural parameters obtained for these molecules is in very good agreement with the experimental values obtained from the electron diffraction and they are given in Table 2.

5-4 Approximation formula for centrifugal distortion constants in XY_3Z symmetric top molecules

In this chapter we have already seen that approximation formulas to evaluate D_J, D_{JK} in XY_3 pyramidal type molecules help us to obtain the molecular geometry of symmetric top molecules whose isotopic substituents are not available. This encourages one to extend the method to develop approximate expressions for centrifugal distortion constants in XY_3Z symmetric top molecules. Among XY_3Z symmetric tops also there exist certain molecules

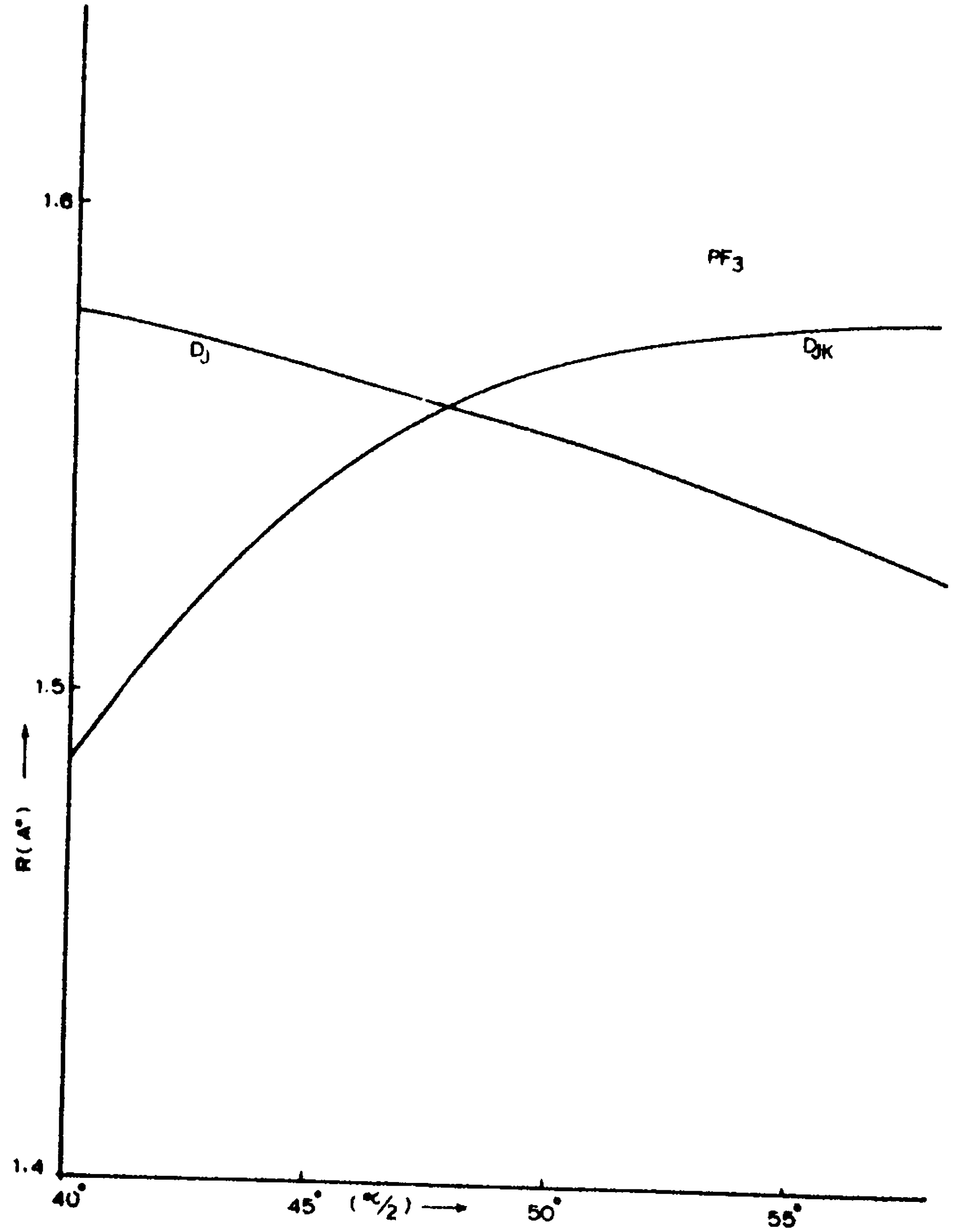


Fig. (5-1) PF3

Variation of R against ($\alpha/2$) for PF_3 molecule using centrifugal distortion constants D_J and D_{JK} as experimental data.

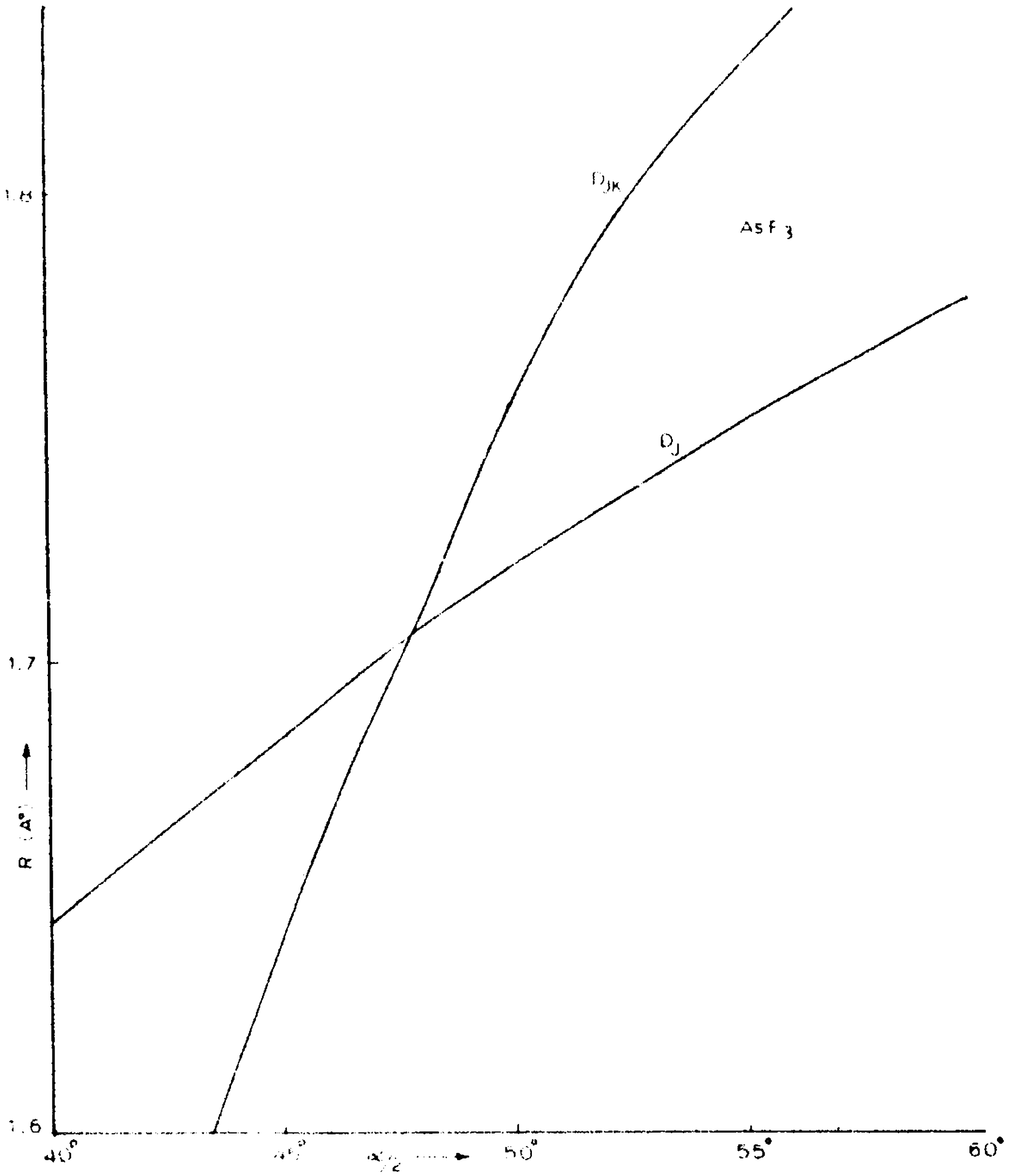


Fig. (5·2)

Variation of R against (α/2) for AsF_3 molecule using centrifugal distortion constants D_J and D_{JK} as experimental data.

like OPF_3 for which data on isotopic substituent are not sufficient enough to fix the molecular geometry. The analysis of microwave spectrum of OPF_3 molecule yields one rotational constant B_0. An isotopic substitution of the OPF_3 molecule $(O^{18} PF_3)$ yields one more rotational constant B'. From two rotational constants three structural parameters viz. two bondlength and one interbond angle cannot be evaluated. If one more datum containing the structural parameters is available, we can fix the molecular geometry.

Here we have taken D_J as this additional data. Expression to evaluate D_J is derived with the assumption that the mixing parameters in the different species of vibrations are neglegible. The approch developed by Muller[13] et al to higher order problems can be highly useful here. A detailed discussion of this aspect is given in chapter VII. The coupling between any two symmetric coordinates S_i and S_j are governed to a large extend by ϕ_{ij} which in turn may be set to zero, provided that S_i and S_j corresponds to stretching and bending vibrations. ϕ_{ij}'s are the mixing parameter expressed in the angular form. We have calculated the force constants of many XY_3Z symmetric top molecules by setting all the ϕ_{ij}'s equal to zero and have compared with the force constants calculated using additional experimental data. The observation is that even if there are small changes in the off-diagonal force constants, the diagonal force constants are reproduced well. "The centrifugal distortion constants $\tau_{\alpha\beta\gamma\delta}$ are often well defined by the diagonal force constants" as observed by Mills[14]. Therefore setting the mixing parameter matrix equal to unit matrix for the calculation of D_J is quite reasonable.

According to eq.(2.41) $t_{\alpha\beta\gamma\delta}$ are related to $\tau_{\alpha\beta\gamma\delta}$ as

$$t_{\alpha\beta\gamma\delta} = -2 \, I^e_{\alpha\alpha} \, I^e_{\beta\beta} \, I^e_{\gamma\gamma} \, I^e_{\delta\delta} \, \tau_{\alpha\beta\gamma\delta}$$

hence $t_{xxxx} = -2 \, I^4_{xx} \tau_{xxxx}$

Therefore

$$\tau_{xxxx} = - \, t_{xxxx} / (2 \, I^4_{xx}) \qquad (5.11)$$

From eq.(4.2) τ_{xxxx} is related to D_J as

$$D_J = -(\epsilon/4) \tau_{xxxx}$$

with the help of eq.(5.11) we can write the above expression as

$$D_J = (\epsilon/8 \, I^4_{xx}) \; t_{xxxx} \qquad (5.12)$$

Using eq.(3.17) t matrix can be expressed as

$$t = \tilde{K} \quad \Lambda^{-1} \quad K \qquad \text{where } K = (L_o^{-1}) \, Ts$$

The Ts matrix used for calculating centrifugal distortion constants is given in in Appendix 1. (We have noted an error in the T_S matrix formulated earlier by Joseph and Venkateswarlu[16]. The second term in T_{xx} is actually negative). Now t_{xxxx} can be expressed as

$$t_{xxxx} = K^2_{11} \; \Lambda^{-1}_1 + K^2_{21} \; \Lambda^{-1}_2 + K^2_{31} \; \Lambda^{-1}_3 +$$

$$K^2_{41} \; \Lambda^{-1}_4 + K^2_{51} \; \Lambda^{-1}_5 + K^2_{61} \; \Lambda^{-1}_6 \qquad (5.13)$$

Using eq.(5.12) and (5.13) we can write

$$D_J = (\epsilon/8\, I_{xx}^4)\, (K_{11}^2 \Lambda_1^{-1} + K_{21}^2 \Lambda_2^{-1} + K_{31}^2 \Lambda_3^{-1} + K_{41}^2 \Lambda_4^{-1} + K_{51}^2 \Lambda_5^{-1} + K_{61}^2 \Lambda_6^{-1}) \qquad (5.14)$$

Where $K_{11} = 2\, R\, (L_o^{-1})_{11}$

$$K_{21} = 2\, R\, (L_o^{-1})_{21} - (L_o^{-1})_{22}\, 3^{1/2}\, (1+\cos^2\beta)$$

$$K_{31} = 2\, R\, (L_o^{-1})_{31} - (L_o^{-1})_{32}\, 3^{1/2}\, (1+\cos^2\beta) + (L_o^{-1})_{33}\, 3\, r\, (3 + 3\, p^2)^{-1/2} \left[2 \cos^2\beta\, (\cos\alpha - 1)(\sin\alpha)^{-1} + p\, q\, \sin\beta \cos\beta\right]$$

$$K_{41} = - (L_o^{-1})_{44}\, (3/2)^{1/2} \sin^2\beta\, r$$

$$K_{51} = - (L_o^{-1})_{54}\, (3/2)^{1/2} \sin^2\beta\, r - (L_o^{-1})_{55}\, (3/2)^{1/2}\, q\, r \sin\beta \cos\beta$$

$$K_{61} = - (L_o^{-1})_{64}\, (3/2)^{1/2} \sin^2\beta\, r - (L_o^{-1})_{65}\, (3/2)^{1/2}\, q\, r \sin\beta \cos\beta + (L_o^{-1})_{66}\, (3/2)^{1/2}\, r \sin^2\beta (2+\cos\alpha)(\sin\alpha)^{-1}$$

Here $p = 3^{1/2} \cos\beta / \cos(\alpha/2)$, $q = (R/r)^{1/2}$

R is the Z - X bondlength, r is the X - Y bondlength, α is the Y - X - Y angle, β is the Z - X - Y angle given by the relation $\sin\beta = 180 - \left[2\, 3^{-1/2} \sin(\alpha/2)\right]$

The relation between (L_o^{-1}) and G matrix elements is given below.

$(L_o^{-1})_{11} = 1/T_{11}$, $T_{11} = G_{11}^{1/2}$, $(L_o^{-1})_{22} = 1/T_{22}$, $T_{22} = (G_{22} - T_{21}^2)^{1/2}$

$T_{21} = G_{21} / T_{11}$, $(L_o^{-1})_{33} = 1/T_{33}$, $T_{33} = \sqrt{G_{33} - (T_{31}^2 + T_{32}^2)}$

$T_{31} = G_{31} / T_{11}$, $T_{32} = (G_{32} - T_{21} T_{31}) / T_{22}$, $(L_o^{-1})_{21} = -T_{21}(T_{11}T_{22})^{-1}$

$(L_o^{-1})_{31} = (T_{32} T_{21} - T_{31} T_{22}) (T_{11} T_{22} T_{33})^{-1}$, $(L_o^{-1})_{32} = -T_{32}(T_{22}T_{33})^{-1}$

$(L_o^{-1})_{44} = 1/T_{44}$, $T_{44} = (G_{44})^{1/2}$, $(L_o^{-1})_{55} = 1/T_{55}$, $T_{55} = (G_{55} - T_{54})^{1/2}$

$T_{54} = G_{54} / T_{44}$, $(L_o^{-1})_{66} = 1/T_{66}$, $T_{66} = [G_{66} - (T_{64}^2 + T_{65}^2)]^{1/2}$

$T_{64} = G_{64} / T_{44}$, $T_{65} = (G_{65} - T_{54} T_{64}) / T_{55}$, $(L_o^{-1})_{54} = -T_{54}(T_{44}T_{55})^{-1}$

$(L_o^{-1})_{64} = (T_{65} T_{54} - T_{64} T_{55}) (T_{44} T_{55} T_{66})^{-1}$, $(L_o^{-1})_{65} = -T_{65}(T_{55}T_{66})^{-1}$

$G_{11} = m + 3 M \cos^2\beta$

$G_{22} = (K^2 + 1)(m + 3 M \sin^2\beta)$

$G_{33} = M + I$

$G_{21} = 3 M (K^2 + 1)^{1/2} \sin\beta \cos\beta$

$G_{31} = 3^{1/2} M \cos\beta$

$G_{32} = 3^{1/2} M (K^2 + 1)^{1/2} \sin\beta$

$G_{44} = m + M (1 - \cos\alpha)$

$G_{55} = m (3 - K^2 2^{-1}) + M (1 - \cos\alpha)^3 / \sin^2\alpha$

$G_{66} = m + 1.5 M (\cos\beta - \lambda)^2 + 1.5 I \lambda^2$

$G_{45} = M (1 - \cos\alpha)^2 / \sin\alpha$

$$G_{64} = 3\ M \sin\beta(\cos\beta - \lambda)\ 2^{-1}$$

$$G_{65} = (K/2)\left[m - M\ (\cos\beta - \lambda)\ (1 - \cos\alpha)\ (\cos\beta)^{-1}\right]$$

where $K = -3 \sin\beta \cos\beta / \sin\alpha$, $\lambda = r/R$, α is the Y-X-Y angle, m, M, and X are the reciprocal masses of X, Y and Z atoms.

Making use of eq.(5.14) we have evaluated the D_J for few heavy symmetric top molecules given in Table 3. We can find that the D_J calculated using the above expressions agrees with the experimental values available from the literature.

5-5 Molecular geometry of XY_3Z symmetric top molecules :

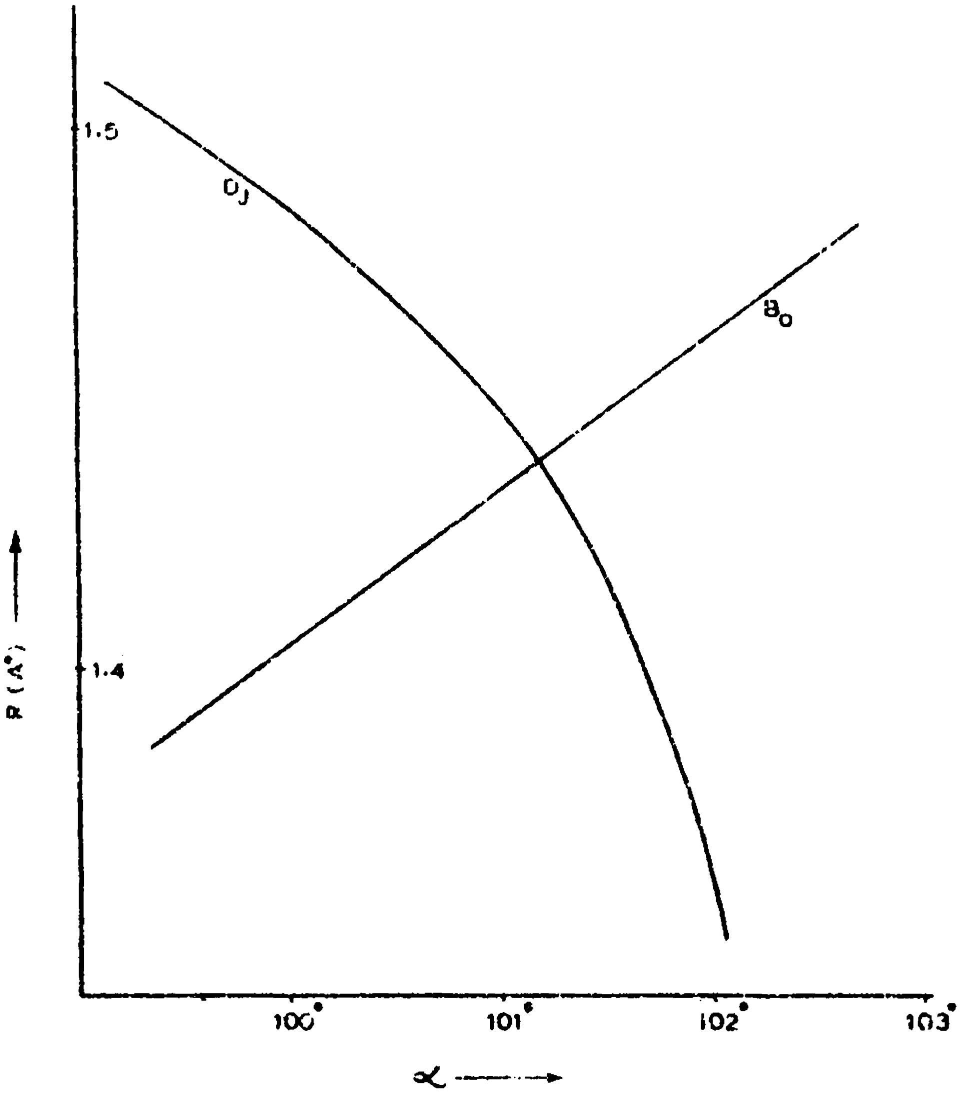
In section 3 of this chapter we have seen that one of the important application of the approximation formula used for calculating centrifugal distortion constants is in the evaluation of molecular geometry of symmetric top molecules whose isotopic substituents are not easily available. Among XY_3Z symmetric tops also this becomes applicable. Here the molecules may posses isotops but the number of rotational constants available from them may not be sufficient to fix the molecular geometry. A typical case is that of OPF_3 molecule. It posseses only one additional isotopic species namely $O^{18}PF_3$. Hence from $O^{16}PF_3$ and $O^{18}PF_3$ we get two rotational constants which are not sufficient to fix structural parameters namely two bondlengths and one interbond angle. In this situation we suggest to use D_J as an additional datum.

OPF_3 is a heavy symmetric top molecule, the microwave spectrum of which has been very recently studied[15]. The centrifugal distortion here induces a small change in the dipole moment and hence a study of the Q branch of the spectrum yields the value of $(B_0 - A_0)$. The selection rules of the distortion moment spectrum is that $\Delta J = 0, \pm 1, \Delta K = \pm 3$. Knowledge of B_0 from the R branch and $(B_0 - A_0)$ from Q branch enable us to determine A_0. Now for OPF_3 molecule A_0, B_0 and D_J are known. Hence we can evaluate the molecular geometry without the need of an isotopic substitution. The expression for A_0 and B_0 are given below.

$$A_0 = 2\, m_Y\, r^2\, (1 - \cos\alpha) \tag{5.15}$$

$$\begin{aligned} B_0 = {} & m_Y\, r^2\, (1 - \cos\alpha) + m_Y(m_X + m_Z)(3\, m_Y + m_Z + m_X)\, r^2 (1 + 2\cos\alpha) + \\ & (3\, m_Y + m_X + m_Z)^{-1} m_Z\, R \left[(3\, m_Y + m_X) R + 6\, m_Y\, r \sqrt{(1 + 2\cos\alpha)} \,/\, \sqrt{3} \right] \end{aligned} \tag{5.16}$$

Here m_Y is the mass of F atom, m_X is the mass of P atom, m_Z is the mass of O atom, R is the OP bondlength, r is the PF bondlength and α is the F-P-F angle. The molecular geometry can be obtained from eq.(5.14), (5.15) and (5.16). As a direct solution is not easy we have adopted here a graphical method. From eq.(5.15) r is expressed in terms of α and that is used in eq.(5.14) which along with eq.(5.16) gives us a relation between R and α. Hence a graph is plotted between R and α using D_J and B_0 represented by eqs. (5.14) and (5.16) as shown in Fig.(5.3). The intersection gives the values of R and α. The value of α obtained from the graph is used in eq.(5.15) to evaluate r. In Table 4 the molecular geometry obtained using the present method with D_J as additional data is compared with values obtained from the literature. The agreement is very good. The above approach thus shows a new



Plot of R against α for OPF_3 molecule

Fig. (5-3)

application for centrifugal distortion constants which can be used as additional data to fix the molecular geometry of XY_3Z symmetric top molecules for which the microwave data are inadequate.

TABLE 1

D_J, D_{JK} AND D_K CONSTANTS (in MHz) OF XY_3 SYMMETRIC TOP MOLECULES

Molecule	D_J Calculated	D_J Observed	D_{JK} Calculated	D_{JK} Observed	D_K Calculated	D_K Observed	Ref.
NH_3	23.86	24.27	-42.47	-43.65	24.7	23.5	20
PH_3	3.91	3.95	-4.98	-5.2	3.5	4.09	21
AsH_3	2.61	2.13	-3.32	..	2.53	..	22
PCl_3	0.0012	0.00117	-0.0017	-0.00188	0.00085	..	23
$AsCl_3$	0.00074	0.00077	-0.00106	-0.00114	0.0005	..	24
NF_3	0.0138	0.0145	-0.0218	-0.0227	0.0098	..	14

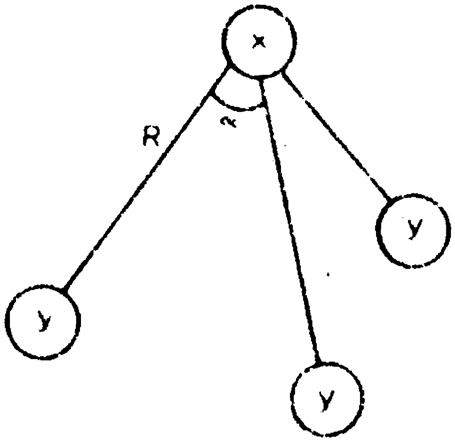


FIG.(5.4)

XY_3 Symmetric top molecule

TABLE 2

Geometry of PF_3 and AsF_3 Molecules

PF_3		AsF_3		Reference
Bondlength R (Å)	Bond angle α	Bondlength R (Å)	Bond angle α	
1.561	$97^\circ 34'$	1.706	$95^\circ 37'$	Present work*
1.55	102°	1.712 ± 0.005	$102^\circ \pm 2^\circ$	10
1.562	98°	1.708	98°	12
1.563 ± 0.002	$96^\circ 53' \pm 41'$			17
	$97^\circ 30'$		96°	11
	$97^\circ 48' \pm 12'$			18**
			$95.87^\circ \pm 0.28^\circ$	19**

*D_J and D_{JK} from Reference 12 and observed frequencies from Reference 10 are used for the calculation

**Electron diffraction studies.

TABLE 3

CENTRIFUGAL DISTORTION CONSTANT D_J (in MHz) OF XY_3Z HEAVY SYMMETRIC TOP MOLECULES

Molecule	Calculated using the present method	Calculated from force field	Ref.	Experimental values	Ref.
SPF_3	0.000298	0.000225	16	0.0003	26
CF_3Cl	0.000534	0.00055	23	0.00059	24
$SPCl_3$	0.00007	0.000089	16	--	--
CCl_3Br	0.000061	0.000074	23	--	--
CCl_3F	0.00038	0.00046	23	0.00046	25

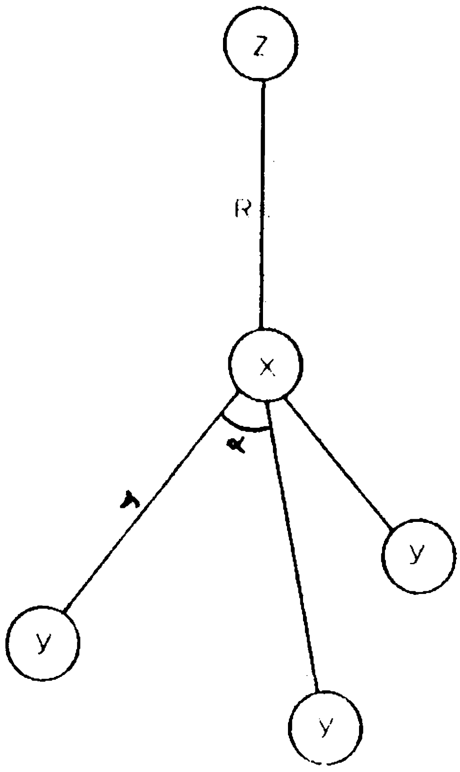


FIG.(5.5)

XY_3Z Symmetric top molecule

TABLE 4

MOLECULAR GEOMETRY OF OPF_3

Structural Parameters	Present method	Earlier work	
		Microwave Analysis*	Electron Diffraction**
Bondlength O-P R(Å)	1.4385	1.437 ± 0.004	1.4356 ± 0.006
Bondlength P-F r(Å)	1.5216	1.522 ± 0.004	1.524 ± 0.003
Interbond angle F-P-F °	101.18	101.14 ± 0.1	101.3 ± 0.2

Fundamental vibrational frequencies used in the present calculation is taken from Selling and Claassen 1966 J.Chem.Phys. 44, 1414

Experimental rotational constants and centrifugal distortion constant is taken from Kagann R.H, Ozier I and Gerry M.C.L. 1978 J.Mol.Spectrosc. 61, 281

*Microwave analysis from Kagann et al 1978 J.Mol.Spectrosc. 61, 281

**Electron diffraction from Moritani T and Kuchitsu K 1970 Inorg.Chem. 10, 344

Appendix 1A

T_s matrix for XY_3 symmetric top molecules

$T_{\alpha\beta}, S$	T_{xx}	T_{yy}	T_{zz}
$S_1(A_1)$	$3^{-1/2}\, 2\, R(1+2\cos^2 A)$	$3^{-1/2}\, 2\, R(1+2\cos^2 A)$	$8\, 3^{-1/2}\, R \sin^2 A$
$S_2(A_1)$	$-3^{-1/2}\, 2\, R(4\cos^2 A-1)\tan A$	$-3^{-1/2}\, 2\, R(4\cos^2 A-1)\tan A$	$4\, 3^{-1/2}\, R(4\cos^2 A-1)\tan A$
$S_{1a}(E)$	$-3^{-1/2}\, 2^{3/2}\, R \sin^2 A$	$3^{-1/2}\, 2^{3/2}\, R \sin^2 A$	0
$S_{2a}(E)$	$2^{1/2}\, 3^{-1/2} R(1+2\cos^2 A) \tan A$	$-2^{1/2}\, 3^{-1/2} R(1+2\cos^2 A)\tan A$	0
$S_{1b}(E)$	0	0	0
$S_{2b}(E)$	0	0	0

Continued

Appendix 1A continued

$T_{\alpha\beta,S}$	T_{yz}	T_{zx}	T_{xy}
$S_1(A_1)$	0	0	0
$S_2(A_1)$	0	0	0
$S_{1a}(E)$	0	$2^{3/2}R \sin A \cos B$	0
$S_{2a}(E)$	0	$2^{3/2}R \sin A \tan A \cos B$	0
$S_{1b}(E)$	$2^{3/2}R \sin A \cos B$	0	$2^{3/2}\ 3^{-1/2}R \sin^2 A$
$S_{2b}(E)$	$2^{3/2}R \sin A \cos B \tan A$	0	$-2^{1/2}\ 3^{-1/2}R(1+2\cos^2 A)\tan A$

Here R is the bondlength X - Y, A is half the interbond angle Y - X - Y and

$\cos B = 3^{-1/2}\ (4 \cos^2 A - 1)^{1/2}$

Appendix 1B

T_s matrix for XY_3Z symmetric top molecules

$T_{\alpha\beta},S$	T_{xx}	T_{yy}	T_{zz}
$S_1(A_1)$	$2R$	$2R$	0
$S_2(A_1)$	$-3^{1/2}r(1+\cos^2\beta)$	$-3^{1/2}r(1+\cos^2\beta)$	$2\,3^{1/2}r\sin^2\beta$
$S_3(A_1)$	$3rH(3+3p^2)^{-1/2}$	$3rH(3+3p^2)^{-1/2}$	$6rG(3+3p^2)^{-1/2}$
$S_{4a}(E)$	$-3^{1/2}\,2^{-1/2}\,r\sin^2\beta$	$3^{1/2}\,2^{-1/2}\,r\sin^2\beta$	0
$S_{5a}(E)$	$-3^{1/2}\,2^{-1/2}r\,q\sin\beta\cos\beta$	$3^{1/2}\,2^{-1/2}r\,q\sin\beta\cos\beta$	0
$S_{6a}(E)$	$3^{1/2}\,2^{-1/2}\,rI$	$-3^{1/2}\,2^{-1/2}\,rI$	0
$S_{4b}(E)$	0	0	0
$S_{5b}(E)$	0	0	0
$S_{6b}(E)$	0	0	0

Continued

Appendix 1B continued

$T_{\alpha\beta}, S$	T_{yz}	T_{zx}	T_{xy}
$S_1(A_1)$	0	0	0
$S_2(A_1)$	0	0	0
$S_3(A_1)$	0	0	0
$S_{4a}(E)$	0	$-6^{1/2} r \sin\beta \cos\beta$	0
$S_{5a}(E)$	0	$-3^{1/2}\, 2^{1/2}\, J$	0
$S_{6a}(E)$	0	$-6^{1/2} r\, K$	0
$S_{4b}(E)$	$-6^{1/2} r \sin\beta \cos\beta$	0	$3^{1/2}\, 2^{-1/2} r \sin^2\beta$
$S_{5b}(E)$	$-3^{1/2}\, 2^{1/2}\, J$	0	$3^{1/2}\, 2^{-1/2}\, r \sin\beta \cos\beta$
$S_{6b}(E)$	$-6^{1/2}\, r\, K$	0	$-3^{1/2}\, 2^{1/2}\, r\, I$

Where

$H = -2 \cos^2\beta \, (1-\cos\alpha) \, (\sin\alpha)^{-1} + p \, q \sin\beta \cos\beta$

$G = \sin^2\beta \, (1+2 \cos\alpha) \, (\sin\alpha)^{-1} - p \, q \sin\beta \cos\beta$

$I = \sin^2\beta \, (2+\cos\alpha) \, (\sin\alpha)^{-1}$

$J = q \, r \, (\sin^2\beta - \cos^2\beta) + q' R$

$K = (1-\cos\alpha) \sin\beta \cos\beta \, (\sin\alpha)^{-1}$

R is the Z - X bondlength,

r is the X - Y bondlength,

α is the Y - X - Y angle,

β is the Z - X - Y angle,

$q = (R/r)^{1/2}$

$q' = (r/R)^{1/2}$

$p = 3^{1/2} \cos\beta \, / \cos(\alpha/2)$

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CHAPTER VI

SOME ASPECTS OF VIBRATIONAL MIXING PARAMETER IN RELATION WITH MOLECULAR STRUCTURE AND PROPERTIES

Abstract

Analytical expression is given for the mixing parameter that characterises the vibrational eigen vector matrix in the second order case based on the criterion of minimisation of average bending energy of molecular vibration. The expression which is derived on the assumption that the parameter c is small contains only interbond angle and the two normal frequencies of the species. Bent XY_2 molecular system is taken as an example and it is found that the calculated values of the parameter are in good agreement with the standard values. The value of c obtained using the average bending energy criterion is directly plotted against the mass ratio m_Y/m_X of XY_2 (C_{2V}) molecules and the graph shows an interesting linear relationship. This relation helps to evaluate the interbond angle of XY_2 bent symmetric molecules from mass ratio and the two normal frequencies of the A species.

6-1 Introduction:

As observed in earlier chapters vibrational eigen vector matrix is of crucial importance in the studies connected with the internal mechanics of molecules as many molecular quantities like force constants, centrifugal distortion constants and vibrational amplitudes are directly related to this. The normal coordinates for a vibrating molecule is given by eq.(1.1) as S = LQ. The eigen vector matrix L, determined by the molecular geometry and the true harmonic force field of the molecule is obtained from eq.(1.11). Recent studies[1,2] have shown that a reasonably valid L matrix can be obtained from the G matrix alone. Such kinematically defined eigen vector matrices are of great help in determining the vibrational normal coordinates as well as approximate internal force field in the molecule.

6-2 Average vibrational potential energy:

Using eq.(1.2) the potential function may be expressed in terms of internal valance coordinates as

$$2V = \sum_{i,j} f_{ij} r_i r_j$$

Taking average in the sense defined by Cyvin[4]

$$\langle 2V \rangle = \sum_{i,j} f_{ij} \langle r_i r_j \rangle \tag{6.1}$$

$$\langle 2V \rangle = \sum_{i,j} f_{ij} \sigma_{ij} \tag{6.2}$$

Where σ_{ij} are the mean square amplitudes defined as $\sigma_{ij} = \langle r_i r_j \rangle$

The average of the square of the instantaneous change in the equilibrium distance between an arbitrary pair of atoms is called the mean square amplitude. The spectroscopic calculation of mean square amplitudes of vibration, which are themselves a set of characteristic constants of the molecule, utilizes the data on vibrational frequencies. Cyvin[4,5] has developed a detailed formalism for the spectroscopic evaluation of mean square amplitudes in terms of the symmetrised mean square amplitudes matrix Σ . The mean square amplitude of vibration refering to internal coordinates are called paralel mean square amplitudes to distinguish them from the general mean square amplitudes based on cartesion coordinates. Σ_{ij} are defined by the matrix relation

$$\Sigma = \langle S \tilde{S} \rangle \qquad (6.3)$$

By eq.(1.1) $\Sigma = L \Delta L$ (6.4)

Where $\Delta = \langle Q \tilde{Q} \rangle$. From quantum mechanical considerations it can be shown to be a diagonal matrix elements

$$\Delta_r = (h/8\pi^2 c \omega_r) \cot h \, (hc \omega_r/2KT) \qquad (6.5)$$

Here h is the Planck's constant, K is the Boltzman constant and T is the absolute temprature.

At any finite temprature, vibrational excitation occurs with a Boltzman distribution and the above mentioned averaging process implies a thermal averaging in addition to quantum mechanical averaging. In order to avoid higher vibrational states and consequent variation of $\langle V \rangle$ with temprature, ground states undergoing zero point vibrations are considered in this study.

In terms of symmetry coordinates one may express eq.(6.2) as

$$\langle 2\ V \rangle = \sum_{i,j} F_{ij}\ \Sigma_{ij} \qquad (6.6)$$

For n internal coordinates, the right hand side of this equation would contain n (n+1)/2 terms, many of which are identical. By parametrising F_{ij} and Σ_{ij}, one can study the symmetric variation of $\langle V \rangle$

6-3 Application to XY_2 (C_{2V}) type molecules;

For this type of molecules, the potential energy can be expressed as

$$2\ V = f_r\ (\Delta r_1^2 + \Delta r_2^2) + r^2\ f_\alpha\ (\Delta\alpha)^2 + 2\ f_{rr}\ \Delta r_1\ \Delta r_2 + 2\ r\ f_{r\alpha}\ (\Delta r_1 + \Delta r_2) \qquad (6.7)$$

Where Δr_1 and Δr_2 are the stretch increments and $\Delta\alpha$ is the change in bond angle. r denotes the equilibrium X - Y distance. Averaging eq.(6.7)

$$\langle 2\ V \rangle = 2\ f_r \sigma_r + f_\alpha \sigma_\alpha + 2\ f_{rr} \sigma_{rr} + 4\ f_{r\alpha} \sigma_{r\alpha} \qquad (6.8)$$

Here the first term arises from pure stretching, the second term is pure bending, third term is stretch-stretch interaction and the last term represents the stretch-bend interaction.

6-4 Average bending energy criterion:

For all the XY_2 bent symmetric nonhydrides studied, Girijavallabhan et al[6,7] find that there exists a minimum for the average bending energy $F_{22}\ \Sigma_{22}$. The value of the mixing parameter c corresponding to the minimum of bending energy term is found to yield a force field, which agrees exceedingly well with that fixed with the aid of additional experimental data. This criterion is called the average bending energy criterion. It is known that c is quite small[3] when L_o is taken in the lower triangular form. Hence we can neglect terms containing c^3 and higher powers of c and write the average bending energy with sufficient accuracy as,

$$\langle 2\ V_\alpha \rangle = F_{22}\ \Sigma_{22} \approx \left[(pn+rl)\ c^2 + rmc + rn \right] / \ (1+2c^2) \tag{6.9}$$

Where F_{22} is the symmetry force constant corresponding to bending vibration given by the expression[9]

$$F_{22} = (pc^2 + r)\ (1+c^2)^{-1} \tag{6.10}$$

and Σ_{22} is the corresponding mean amplitude[10] given by

$$\Sigma_{22} = (l\ c^2 + mc + n)\ (1+c^2)^{-1} \tag{6.11}$$

where $p = (L_o)^{-1}_{22}\ \Lambda_1, \quad r = (L_o)^{-1}_{22}\ \Lambda_2$

$l = (L_o)^2_{22}\ \Delta_1 + (L_o)^2_{21}\ \Delta_2$

$m = 2(L_o)_{21}\ (L_o)_{22}\ (\Delta_2 - \Delta_1)$

$n = (L_o)^2_{21}\ \Delta_1 + (L_o)^2_{22}\ \Delta_2$

$(L_o)^{-1}_{22} = G_{11}\ |G|^{-1}, \quad (L_o)_{21} = G_{12}\ G_{11}^{-1/2}, \quad (L_o)_{22} = |G|^{-1/2}\ G_{11}^{-1/2}$

$|G| = G_{11}\ G_{22} - G_{12}^2$

Differenciating with respect to c and setting the result equal to zero

$$\frac{d(F_{22}\Sigma_{22})}{dc} = -\left[(pn+rl)\ c^{2} + rmc + rn\right] 4\ c\ (1+2c^{2})^{-2}\ +$$

$$2\ (pn+rl)\ c + rm\ \ (1+2c^{2})^{-2} = 0 \qquad (6.12)$$

$$\frac{d(F_{22}\Sigma_{22})}{dc} = 4\ c^{3}\ (pn+rl) - 4\ c^{3}\ (pn+rl) + 2\ rm\ c^{2} - 4\ rm\ c^{2}\ +$$

$$2\ (pn+rl)\ c - 4\ rn\ c + rm = 0$$

$$\frac{d(F_{22}\Sigma_{22})}{dc} = -\ 2\ rm\ c^{2} + 2\ (pn+rl-2\ rn)\ c + rm = 0$$

When c is very small one can express c as

$$c = -\ rm/2\ (pn+rl-rn) \qquad (6.13)$$

Where $-\ rm = -\ \frac{G_{11}}{|G|}\,\omega_2^{2}\ 2\ \frac{G_{12}}{\sqrt{G_{11}}}\sqrt{\frac{|G|}{G_{11}}}\ \ (\omega_2^{-1} - \omega_1^{-1})$

$$-\ rm = 2\ G_{12}\ \ |G|^{-1/2}\ \ (\omega_1\omega_2 - \omega_2^{2})\omega_1^{-1} \qquad (6.14a)$$

$$2\ pn+2\ rl - 4\ rn = 2\ G_{12}^{2}\ |G|^{-1}\ \ (\omega_1+\omega_2 - 2\omega_2^{2}\omega_1^{-1})\ +$$

$$2\ \ (\omega_1^{2}\omega_2^{-1} + \omega_2^{2}\ \omega_1^{-1} - 2\,\omega_2) \qquad (6.14b)$$

$$\text{Hence } c = E/(J + K) \qquad (6.15)$$

Here $E = G_{12}\ \ |G|^{-1/2}\ (\omega_1\ \omega_2 - \omega_2^{2})\ \omega_1^{-1}$

$J = G_{12}^{2}\ |G|^{-1}\ (\omega_1 + \omega_2 - 2\omega_2^{2}\ \omega_1^{-1})$

$K = \omega_1^{2}\,\omega_2^{-1} + \omega_2^{2}\ \omega_1^{-1} - 2\ \omega_2$

From this expression for c, the vibrational eigen vector matrix can be constructed using the eq.(1.14) with $L_{12} = 0$ and

$$C = (1+c^2)^{-1/2} \begin{bmatrix} 1 & c \\ -c & 1 \end{bmatrix} \qquad (6.16)$$

6-5 Results:

i) The present result for the value of the parameter c helps to clarify a number of recent observations. For example the result indicates that as a first approximation the value of the mixing parameter is directly proportional to square root of $G_{12}^2/|G|$ as noted by Muller[10].

ii) The mass dependence of the eigen vector matrix element noted by Muller et al[10] and Ananthakrishnan et al[11] can be explained on this basis. It can also be shown that the ratio of L_{12} / L_{21} of the matrix element is proportional to the parameter and also proportional to G_{11} / G_{12} since $L_{12} / L_{21} \simeq G_{11}\, c/G_{12}$.

iii) Another important feature of the present expression is that the eigen vector matrix is not defined solely on a kinematic basis. The molecular force field as expressed through the frequency factors in the expression for c also has an important role in determining the true vibrational eigen vector matrix. In Table 1 the result calculated using the present formula for a number of XY_2 non-hydride molecules are compared with the c values determined from standard force field obtained with the help of additional experimental data.

6-6 Application of the average bending energy criterion:

Values of the mixing parameter c obtained from average bending energy criterion when plotted directly against the mass ratio m_Y/m_X gives an interesting linear relationship[11]. Hence for molecules of small mass coupling also certain regularities between the L matrix elements and the mass ratio can be established. One interesting feature of this graph is that all the c values are positive for non-hydrides and negative for hydrides. Since it is impossible to pinpoint the force field or the c values by virtue of the inherent spreads in the experimental values as well as of errors due to anharmonicity, the observations of such regularities in the value of L_{12}/L_{21} or of c with molecular structures are bound to help refinement of our knowledge of many of the molecular constants. A very interesting result arising from such observation is that the L_{ij} show almost complete dependence upon geometry and atomic masses at least in such simple cases. Here we find for molecules of small mass ratio

$$c = 0.03\ m_Y/m_X + 0.034 \qquad (6.17)$$

and for molecules of large mass ratio

$$c = 0.005\ m_Y/m_X + 0.088 \qquad (6.18)$$

These relation are useful in determining the interbond angle 2α of XY_2 bent symmetric molecules when the frequencies are known

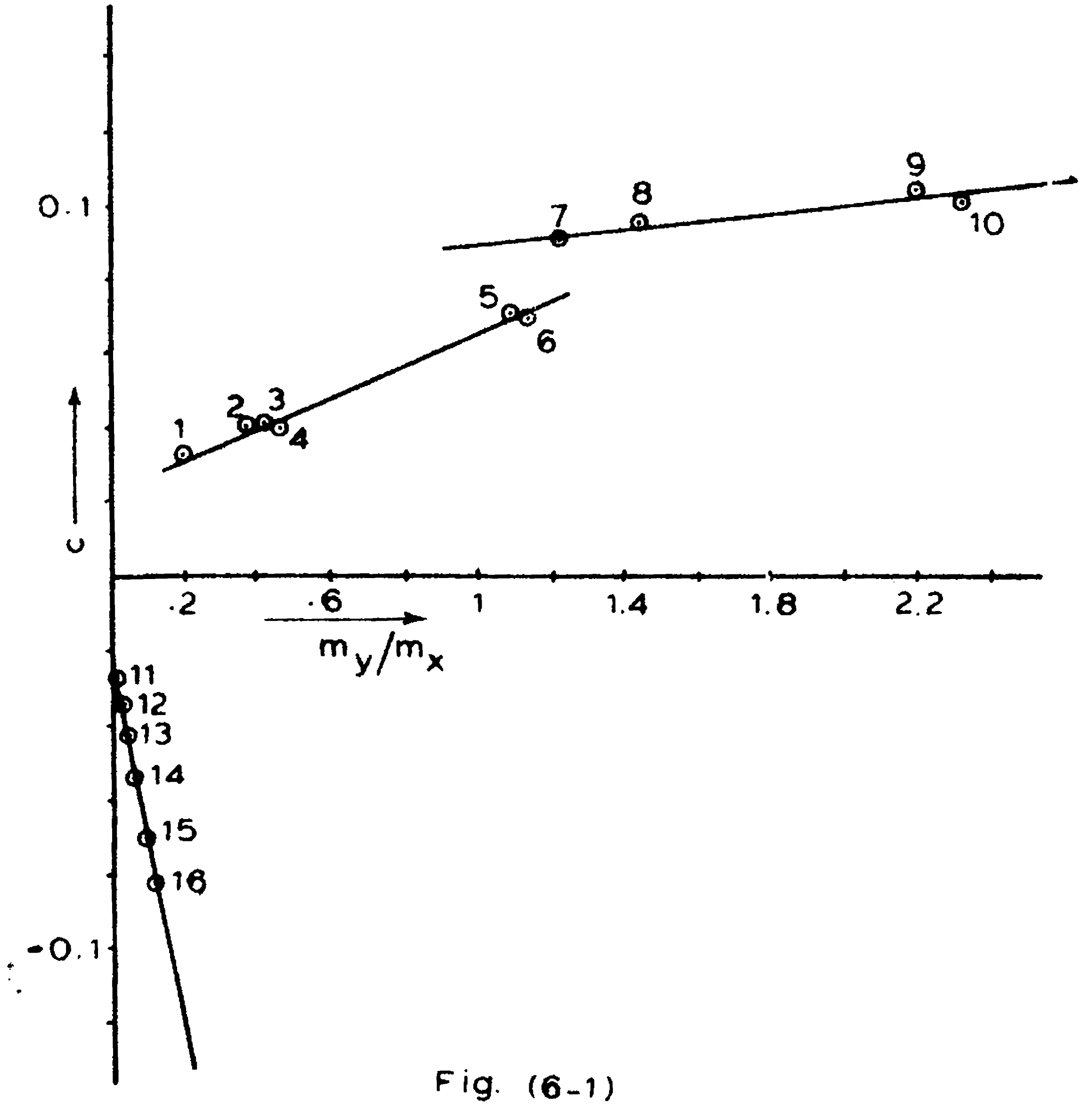

Fig. (6-1)

Variation of c with m_Y/m_X in molecular types $XY_2(C_{2V})$

1) SeO_2 2) $^{37}ClO_2$ 3) $^{35}ClO_2$ 4) SO_2 5) SCl_2

6) $S^{37}Cl_2$ 7) OF_2 8) NO_2 9) $^{35}Cl_2O$ 10) $^{37}Cl_2O$

11) H_2Se 12) H_2S and T_2Se 13) H_2O and D_2S

14) T_2S 15) D_2O and 16) T_2O.

along with the mass ratio. With the help of eqs.(6.15), (6.17) and (6.18) here we have calculated the interbond angle of some XY_2 non-hydride molecules. Herzberg[12] has already given a method to find out the interbond angle of XY_2 bent symmetric molecules using the formula

$$W^3 - (1+2m_Y m_X^{-1})(\nu_1^2 + \nu_2^2 + \nu_3^2)\,\nu_3^2\, W\,(\nu_1^2\,\nu_2^2)^{-1} + (1+2m_Y m_X^{-1})(1+m_Y m_X^{-1})\,\nu_3^4\,(\nu_1^2\;\nu_2^2)^{-1} = 0 \qquad (6.19)$$

Where $W = 1+2m_Y m_X^{-1} \sin^2 2\alpha$, 2α is the interbond angle. m_Y and m_X are the mass of X and Y atom. The interbond angles evaluated using the present method and the Herzberg's method are given in Table 2. We can find that the interbond angle evaluated using the present method is very close to the experimental value . The present method requires only two frequencies ν_1 and ν_2 and the atomic masses. Eventhough Herzberg's method make use of all the three frequencies ν_1, ν_2 and ν_3 the interbond angle obtained are widely different when compared with the experimental values except in the case of SO_2.

6-7 Interbond angle of XY_2 (C_{2v}) hydride molecules using isotopic frequencies:

In hydride XY_2 bent symmetric molecules, it is possible to calculate the interbond angle using the expression[12]

$$\sin 2\alpha = \sqrt{\frac{m_X\,(\omega_3^2\, m_Y - \omega_3^{*2}\, m_Y^{*})}{2\, m_Y\, m_X\,(\omega_3^{*2} - \omega_3^2)}} \qquad (6.20)$$

Here 2α is the interbond angle, ω_1^* represent frequencies of the isotopically substituted molecule. If this equation is used to evaluate the bondangle of H_2O, H_2S and H_2Se we can find from Table 3 that interbond angle of H_2Se is imaginary even if the bondangle of H_2O and H_2S come out correctly.

The force constant and hence the F matrix are invariant under isotopic substitution of atom in the molecule. This in turn, enable us to write eq.(1.23) as

$$\tilde{L}_0^{-1}\, C\, \Lambda\, \tilde{C}\, L_0^{-1} = \tilde{L}_0^{*-1}\, \overset{*}{C}\, \overset{*}{\Lambda}\, \tilde{\overset{*}{C}}\, L_0^{*-1} \tag{6.21}$$

Here the * denotes the case after isotopic substitution. Now by virtue of the orthoganality of $\overset{*}{C}$, we can write the condition from eq.(6.21) as

$$\text{Trace}\ (\tilde{L}_0^{*}\ \tilde{L}_0^{-1}\ C\ \Lambda\ \tilde{C}\ L_0^{-1}\ L_0^{*}) = \text{Trace}\ \overset{*}{\Lambda} \tag{6.22}$$

This in turn leads to a simple equation of the form

$$p\,c^2 + q\,c + r = 0 \tag{6.23}$$

$$\text{Where } p = G_{11}^{*}\, G_{11}^{-1}\, (\Lambda_2 + G_{12}^{2}\, \Lambda_1\, |G|^{-1}) - (\Lambda_1^* + \Lambda_2^*) + (G_{11}\, G_{22}^{*} - 2\, G_{12}\, G_{12}^{*})\, \Lambda_1\, |G|^{-1} \tag{6.24a}$$

$$q = 2\, (G_{12}^{*} - G_{12}\, G_{11}^{*}\, G_{11}^{-1})\, (\Lambda_2 - \Lambda_1)\, |G|^{-1/2} \tag{6.24b}$$

$$r = G_{11}^{*}\, G_{11}^{-1}\, (\Lambda_1 + G_{12}^{2}\, \Lambda_2\, |G|^{-1}) - (\Lambda_1^* + \Lambda_2^*) + (G_{11}\, G_{22}^{*} - 2\, G_{12}\, G_{12}^{*})\, \Lambda_2\, |G|^{-1} \tag{6.24c}$$

Since c is very small, higher powers of c can be neglected hence

$$c = - r/q \qquad (6.25)$$

We know that for hydride molecules c

$$c = - (0.4\ m_Y/m_X + 0.025) \qquad (6.26)$$

From eq.(6.25) and (6.26) we can write r

$$r/q = (0.4\ m_Y/m_X + 0.025) \qquad (6.27)$$

Since R.H.S. is known the interbond angle can be evaluated from this equation. This has been done here in the case of H_2O, H_2S and H_2Se

The results are given in Table 3, along with the conventional method given by Herzberg. We can find that the interbond angle of hydride molecules evaluated using the present method agrees extremely well with the experimental values available from litrature. Thus a knowledge of the vibrational mixing in a symmetry species of a molecule is highly useful in determining the geometry of the system when frequencies of isotopic molecules are available.

TABLE 1

Parameter value for XY_2 bent symmetric molecules

Molecule	c calculated using present method	c obtained from standard force field	Reference for standard force field
NO_2	0.095	0.093 ± 0.006	13
ClO_2	0.051	0.057	14
SCl_2	0.065	0.061	15
SO_2	0.041	0.027 ± 0.003	16
OF_2	0.102	0.13 ± 0.02	17
SeO_2	0.025	0.034	18

TABLE 2

Interbond angle of XY_2 (C_{2V}) non-hydride molecules

Molecule	Present method	Herzberg method	Experimental values
SO_2	117.5°	122°	119.5°
SCl_2	98.45°	68°	101°
ClO_2	121°	30°	118.5°
NO_2	134.5°	87°	134.25°
OF_2	104.25°	60°	104.2°
OCl_2	110.5°	113°	110.8°

Experimental values and frequencies that are used for calculating the interbond angle of XY_2 bent symmetric molecules is taken from reference 15

TABLE 3

Interbond angle of XY_2 bent symmetric hydride molecules

Molecule	Present method	Herzberg method	Experimental values	Reference for harmonic frequencies and experimental values
H_2O	104.8°	103.9°	104.45°	19
H_2S	91.7°	92.67°	92.2°	20
H_2Se	90.8°	Imaginary	90.95°	21

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CHAPTER VII

PSEUDOEXACT PARAMETER METHOD FOR THE ANALYSIS OF HIGHER ORDER MOLECULAR VIBRATIONS

Abstract

The normal coordinate tranformation matrix L associated with a vibrational problem of order 3 is expressed in the parameter form so that its elements become functions of 3 independent angular parameters ϕ_{12}, ϕ_{13} and ϕ_{23}. In order to solve higher order vibrational problems, possessing insufficient experimental data, the possibility of imposing constraints on these parameters is analysed in the light of coupling they provide between the various symmetry coordinates in a normal mode. It is shown that the constraints like $\phi_{12} = \phi_{13} = 0$ are best valid in the case of XY_3Z (C_{3V}) type molecules when (ω_1^* / ω_1) is approximately equal to $(G_{11}^* / G_{11})^{1/2}$, a term which is calculable purely from molecular geometry and atomic masses. The applicabilit of the constraint is illustrated in the case of CH_3F molecule, the force field which is already well established.

7-1 Introduction :

A complete analysis of molecular vibration requires unambiguous knowledge of the potential energy matrix F characterizing the intramolecular forces. In the general valance force field representation, the matrix F associated with a vibrational species of order n involves $(1/2)n(n-1)$ elements and their evaluation with n vibrational frequencies is mathematically impossible. Recent works[1-5] indicates that one may require as many as four independent experimental data to fix unambiguously the force field associated with the simplest case of order $n = 2$. For higher order problems this number would increase disproportionately, thus making the available experimental data insufficient for unambiguous calculation of force constants for most of the molecules. The scarcity of enough number of additional experimental data accurate enough to provide unique solutions of the force field F leaves open scopes for techniques based on approximations.

Attempts in this direction indicate that such approximations can best be initiated upon matrix L which actually tranforms the symmetry coordinates S to the normal coordinate Q as given by eq.(1.1). The possibility of obtaining the L matrix near enough to the true one and hence the force field F in cases where the available experimental data are comfined only to frequencies of vibration for a pair of isotopic substituents is presented here by applying certain constraints upon the mixing parameter which bring about mixing between symmetry coordinates in each of the normal modes. The C matrix can be expressed in terms of angular parameters ϕ_{ij} as given in eq.(1.16b) as

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

ϕ_{ij}'s are called the mixing parameter in the sense that they determine the contribution from each normal mode to a given symmetry coordinate or vice versa.

7-2 Mixing parameter and vibrational problem :

According to eq.(1.11)the matrix relation GFL=LΛ states the vibrational problem in a nutshell.The eq.(1.13)projects the significance of L matrix in the determination of F from vibrational frequencies. Differentiation of eq.(1.11) yields

$$\Delta\Lambda = L^{-1}(\Delta G)\tilde{L}^{-1} + \tilde{L}(\Delta F)L + \Lambda L^{-1}(\Delta L) - L^{-1}(\Delta L)\Lambda \qquad (7.1)$$

Noting that ΔF_{ij} becomes zero and the last two terms together do not contribute to the diagonal elements, the above expression for the shift in frequencies due to isotopic shift can be written as

$$(\Delta\Lambda)_{ii} = \left[L^{-1} (\Delta G) \tilde{L}^{-1} \right]_{ii} \qquad (7.2)$$

Substitution of L from eq.(1.14) gives

$$\left(\frac{\Delta\Lambda}{\Lambda}\right)_{ii} = \tilde{C} \; J \; C \qquad (7.3)$$

Where

$$J = L_0^{-1} (\Delta G) \tilde{L}_0^{-1} \qquad (7.4)$$

If L_0 is taken in the lower triangular form[1,2,3,8,10-13] J can be directly calculated from the molecular geometry and atomic masses. The unique evaluation of all ϕ_{ij}'s from eq.(7.3) would be impossible since:

i) the sum rule $\sum_i \frac{\Delta\Lambda}{\Lambda} = \sum J_{ii}$ implied in eq.(7.3) constrains the n independent relations emerging from the equation to only (n-1) which is always less than (1/2) n (n-1) for n grater than 2.

ii) Each of the relation will be of the second order in terms of the ϕ_{ij}'s to be solved. Much discussions have been made on the ambigeous solutions emerging due to the quadratic nature of these equations and the methods have been suggested to spot correct ones in simple cases of n = 2[1-5] as we have already seen in chapters III and IV. However this problem poses greater difficulty in the case of higher order vibrational species and it is in this context that a physicaly meaningful approximation becomes worthy of consideration.

7-3 Constraints on mixing parameter:

The form of L_0 obtained when it is taken in the lower triangular form[8], presents a certain progressive rigidity model for L where the mixing between the symmetry coordinates in a normal mode is developed purely on a kinematic basis. The validity of this model as a very good approximation to the actual L matrix has been well established. The model is found to hold extremely well when the different symmetry coordinates are least coupled with one another - a consequence which follows due to the difference in the charactericity of two normal modes corresponding to one stretching and the other bending. Substitution of eq.(1.14) in eq.(1.1) indicates that any additional mixing between S_i and S_j can be brought about through parameter ϕ_{ij}. The approximation that emerges from such considerations allows certain ϕ_{ij} to be set equal to zero provided the related coordinates S_i and S_j corresponding to stretching and bending respectively have negligible interaction, L_0 here being taken in the lower triangular form. The consequence of this approximation in the present context follows from eq.(7.3). For example the symmetry coordinates S_1 involves least coupling with others, one would expect $(\Delta \wedge_1/\wedge_1) \approx J_{11}$ in the approximation $\phi_{12} = 0$ and $\phi_{13} = 0$ in the third order case. This inturn brings a considerable reduction in the number of ϕ_{ij}'s to be solved from eq.(7.3).

7-4 Application of the present technique: -

As an illustration of the technique, the third order vibrational problem associated with XY_3Z symmetric top molecules is analysed. There exist two vibration species (A and E) each of order 3 associated with this type of molecules and the frequency data required are readily available from the litrature[14] with high accuracy. The first mode vibration in each species corresponds to stretching vibration. This leads to the approximation $\phi_{12} = \phi_{13} = 0$ in line with the discussion in the previous section, thus leading to a relation

$$\frac{\Delta\Lambda_1}{\Lambda_1} = J_{11} = (\Delta G_{11}/G_{11}) \qquad (7.5)$$

From eq.(7.3) this can be further be simplified to the form of the frequency ratio as

$$\omega_1^* / \omega_1 = (G_{11}^* / G_{11})^{1/2} \qquad (7.6)$$

Conversely, whenever this relation holds good one can reasonably expect the stretching vibrations to be highly characterstic with least perturbation, thus giving the mixing parameters ϕ_{12} and ϕ_{13} to be negligibly small.

In this case, the coupling between the two bending modes, ϕ_{23} alone need to be determined for which the relation

$$J_{22}\cos^2\phi_{23} + J_{33}\sin^2\phi_{23} + 2J_{23}\cos\phi_{23}\sin\phi_{23} = \left(\frac{\Delta\Lambda}{\Lambda}\right)_{22} \qquad (7.7)$$

$$J_{22}\sin^2\phi_{23} + J_{33}\cos^2\phi_{23} - 2J_{23}\cos\phi_{23}\sin\phi_{23} = \left(\frac{\Delta\Lambda}{\Lambda}\right)_{33} \qquad (7.8)$$

emerging from eq.(7.3) can be used and a solution of this equation yields

$$\tan\phi_{23} = (-J_{23} \pm H) / \left[J_{33} - \left(\frac{\Delta\Lambda}{\Lambda}\right)_{22}\right] \qquad (7.9)$$

$$\text{where } H = \sqrt{J_{23}^2 - \left[J_{22} - \left(\frac{\Delta\Lambda}{\Lambda}\right)_{22}\right]\left[J_{33} - \left(\frac{\Delta\Lambda}{\Lambda}\right)_{22}\right]}$$

$$\tan\phi_{23} = (J_{23} \pm P) / \left[J_{22} - \left(\frac{\Delta\Lambda}{\Lambda}\right)_{33}\right] \qquad (7.10)$$

$$\text{where } P = \sqrt{J_{23}^2 - \left[J_{22} - \left(\frac{\Delta\Lambda}{\Lambda}\right)_{33}\right]\left[J_{33} - \left(\frac{\Delta\Lambda}{\Lambda}\right)_{33}\right]}$$

The quadratic nature of the eq.(7.7) and (7.8) leads theoretically to two different roots for ϕ_{23}, say ϕ_{23} actual and ϕ_{23} virtual represented by $\phi_{23}A$ and $\phi_{23}V$. This inturn leads to two sets of theoretically possible force fields. The ϕ_{23} values and the two roots of force fields calculated for CH_3F are given in Table 1, using molecular geometry and frequency data. The force field of CH_3F is well studied by Aldous and Mills[15] by employing as many as 22 experimental data. The force field obtained using the present approach is compared with Aldous and Mills in Table 1. The force field obtained using $\phi_{23}A$ (smaller of the two values) agrees well with the standard force field obtained from the literature. Elimination of anomalous force field can be done by use of additional experimental data like Coriolis coupling constants or mean amplitude of vibration. The criteria that mixing parameter value must be less than 45° in order to hold the assignment proper may also be useful[16] in many cases to eliminate the anomalous sets.

7-5 Conclusions:

1) The method presented is only pseudoexact in the sense that it brings in a certain amount of decoupling of one of the normal modes from the remaining ones and is expected to work well in cases where such decoupling almost truely exists by virtue of the characteristic nature of vibrations, which is easily checked by $(\Delta\Lambda_1/\Lambda_1)$ observed $\approx J_{11}$ calculated.

2) The method gives almost the correct values of force constants, though we do not apply a sufficient number of additional experimental data.

3) The method gives two solutions as a consequence of the quadratic nature of equations (7.9) and (7.10). However there are infinite sets of force fields fitting the frequency data (including those of isotopic substituents), but the present state of affairs which yields definite solutions certainly improves the situation. In fact multiplicities of solutions are inherent in many such approaches to the problem as has been noted earlier.

4) The present approach of setting selective constraints on the mixing parameters appears more logical and physically meaningful.

TABLE 1

The E species force field of CH_3F fitting the experimental data on vibrational frequencies and isotopic substitution

F_{ij}	Present method		Previous results	
	Set for $\phi_{23}A=5^{\circ}11'$	Set for $\phi_{23}V=36^{\circ}31'$	Aldous and Mills[15]	Muller et a
F_{11}	4.843 (5.371)	4.844 (5.368)	4.948±0.065 (5.422±0.054)	
F_{22}	0.467 (0.497)	0.393 (0.417)	0.470±0.006 (0.4[illegible]±0.005)	(0.5)
F_{33}	0.724 (0.762)	0.857 (0.904)	0.722±0.009 (0.756±0.007)	(0.76)
F_{12}	-0.086 (-0.090)	-0.054 (-0.062)	-0.108±0.013 (-0.113±0.012)	
F_{13}	0.108 (0.142)	0.087 (0.102)	0.217±0.093 (0.244±0.084)	
F_{23}	-0.061 (-0.064)	0.023 (0.024)	-0.060±0.006 (-0.063±0.005)	(-0.09)

*The values in parenthesis correspond to those obtained after unharmonicity corrections of the observed vibrational frequencies. All F_{ij} are in mydn/A

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APPENDIX

Computer programme for calculating p,q,r,l,m and n terms in equation (4.5) and (4.6)

```
0005 REM.PGM FOR FORCEFIELD (XY3) BY CM PAUL
0008 DIM J (14)
0010 FOR I = 1 TO 14
0020 READ J (I)
0030 NEXT I
0040 LET X1 = SIN (J (3))
0050 LET X2 = COS (J (3))
0060 LET X3 = X1/X2
0070 LET X4 = 1/J (1)
0080 LET X5 = 1/J (2)
0090 LET X6 = 1/X2
0100 LET X7 = 2*J(4)*(1+2*X2*X2)
0110 LET X8 = 1/SQR(3)
0120 LET X9 = 2*J(4)*(4*X2*X2-1)
0130 LET X0 = SQR(4*X2*X2-1)
0140 LET A1 = (4*X2*X2-1)*X4+X5
0150 LET A2 = - (4*X2*X2-1)*X4*X3*2
0160 LET A3 = (4-X6*X6)*(4*X4*X1*X1+X5)
0170 LET A4 = (2*X4*X1*X1+X5)
0180 LET A5 = 2*X4*X1*X1*X3
0190 LET A6 = 2*X4*X1*X1*X3*X3+(1+.5*X6*X6)*X5
0200 LET A7 = A1*A3-A2*A2
0210 LET A8 = A4*A6-A5*A5
0220 LET B1 = 1/(SQR(A1))
0230 LET B2 = -A2/(SQR(A1*A7))
```

```
0240 LET B3 = (SQR(A1/A7))
0250 LET B4 = 1/(SQR(A4))
0260 LET B5 = -A5/(SQR(A4*A8))
0270 LET B6 = SQR(A4/A8)
0280 PRINT B1, B2, B3
0290 PRINT B4, B5, B6
0300 LET R1 = B1*X8*X7
0310 LET R2 = B2*X7*X8-B3*X9*X8*X3
0320 LET R3 = -B4*2*(SQR(2))*X8*J(4)*X1*X1
0330 LET R4 = (R3*B5/B4)+B6*(SQR(2))*X8*.5*X7*X3
0340 LET R5 = B1*8*J(4)*X1*X1*X3
0350 LET R6 = (R5*B2/B1)+B3*2*X8*X9*X3
0360 LET R7 = B4*2*(SQR(2))*J(4)*X1*X0
0370 LET R8 = (R7*B5/B4)+B6*2*(SQR(2))*J(4)*X1*X3*X0
0380 PRINT R1, R2, R3, R4
0390 PRINT R5, R6, R7, R8
0400 LET P1 = 677.3*(R1*R1*J(6)+R2*R2*J(5))/(2*J(13))
0410 LET Q1 = 677.3*(R1*R2*J(7))/J(13)
0420 LET C1 = 677.3*(R1*R1*J(5)+R2*R2*J(R))/(2*J(13))
0430 LET L1 = 677.3*(R3*R3*J(12)+R4*R4*J(11))/(2*J(13))
0440 LET M1 = 677.3*(R3*R4*J(8))/J(13)
0450 LET N1 = 677.3*(R3*R3*J(11)+R4*R4*J(12))/(2*J(13))
0460 LET Y1 = (R1*R5*J(6)+R6*R2*J(5))*J(9)*J(9)/J(14)
0470 LET Y2 = (R1*R1*J(6)+R2*R2*J(5))*J(10)*J(10)/J(14)
0480 LET P2 = (Y1-Y2)*677.3
0490 LET Y3 = (R5*R2+R6*R1)*J(7)*J(9)*J(9)/J(14)
```

```
0500 LET Y4 = 2*R1*R2*J(7)*J(10)*J(10)/J(14)
0510 LET Q2 = (Y3-Y4)*677.3
0520 LET Y5 = (R5*R1*J(5)+R2*R6*J(6))*J(9)*J(9)/J(14)
0530 LET Y6 = (R1*R1*J(5)+R2*R2*J(6))*J(10)*J(10)/J(14)
0540 LET C2 = (Y5-Y6)*677.3
0550 LET Y7 = 2*(R7*R7*J(12)+R8*R8*J(11))*J(9)*J(9)/J(14)
0560 LET Y8 = (R3*R3*J(12)+R4*R4*J(11))*J(10)*J(10)/J(14)
0570 LET L2 = (Y7-Y8)*677.3
0580 LET Z1 = (2*R7*R8*J(8))*J(9)*J(9)/(.5* J(14))
0590 LET Z2 = (R3*R4*J(8))*J(10)*J(10)/(.5* J(14))
0600 LET M2 = (Z1-Z2)*677.3
0610 LET Z3 = 2*(R7*R7*J(11)+R8*R8*J(12))*J(9)*J(9)/J(14)
0620 LET Z4 = (R3*R3*J(11)+R4*R4*J(12))*J(10)*J(10)/J(14)
0630 LET N2 = (Z3-Z4)*677.3
0640 PRINT P1, Q1, C1
0650 PRINT L1, M1, N1
0660 PRINT P2, Q2, C2
0670 PRINT L2, M2, N2
```

0680 DATA m_X, m_Y, $\alpha/2$, R, Λ_1^{-1}, Λ_2^{-1}, $\Lambda_2^{-1} - \Lambda_1^{-1}$, $\Lambda_4^{-1} - \Lambda_3^{-1}$

0690 DATA I_x, I_z, Λ_3^{-1}, Λ_4^{-1}, $4I_{xx}^4$, $4I_{xx}^4\ I_{zz}^2$

Where P1 = p_J of eq.(4.5), Q1 = q_J of eq.(4.5)

C1 = r_J of eq.(4.5), L1 = l_J of eq.(4.5)

M1 = m_J of eq.(4.5), N1 = n_J of eq.(4.5)

P2 = p_{JK} of eq.(4.6), Q2 = q_{JK} of eq.(4.6)

C2 = r_{JK} of eq.(4.6), L2 = l_{JK} of eq.(4.6)

M2 = m_{JK} of eq.(4.6), N2 = n_{JK} of eq.(4.6)