STUDIES IN MOLECULAR MECHANICS USING SPECTROSCOPIC DATA: EXACT FORCE FIELD AND BOND INHOMOGENEITY

by

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CERTIFICATE

This is to certify that this thesis is a bonafide record of work carried out by Smt. B. SanthaKumari under my supervision for the degree of Doctor of Philosophy and that no part of this has hitherto been submitted for a degree in any University.

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PREFACE AND ACKNOWLEDGEMENTS

The investigations presented in this thesis were carried out by the author, as a part-time research scholar in the Physics Department of the Cochin University, during 1971-'76, while working as Lecturer in Physics at the Maharaja's College, Ernakulam, Cochin.

This thesis deals with some studies in molecular mechanics using spectroscopic data. It includes an improvement in the parameter technique for the evaluation of exact force fields, the introduction of a new and simple algebraic method for the force field calculation and a study of asymmetric variation of bonding forces along a bond.

Chapter I is a general introduction in which the various types of assumed molecular force fields in use and different methods of calculation of force constants are reviewed briefly.

Chapter II deals with the problem of determination of force constants using isotopic frequencies. Of the many attempts made, one of the latest and probably the most elegant one seems to be the parameter

method. In this attempt a graphical method, making use of isotopic frequencies, is followed. It has been observed that many times it is not possible to have a unique solution, especially if the number of isotopic species exceeds two. In the first part of the chapter criteria for the selection of correct solution, out of the many probable ones, are laid and applied to a few molecules. In the second part of the chapter, within the framework of parameter formalism, a new method and the relevant theory for the determination of exact force field from isotopic frequencies are put forward. The merits of the new method and its superiority above the other existing methods are discussed.

The remaining chapters, except the last one, deal with the study of the spatial distribution of bonding forces between atoms in a molecule. Such a study has not been made till now. To characterise the non-aymmetric variation of binding forces at the centre of a bond (b), a bond asymmetry parameter η_b is defined in terms of cartesian force constants. Theoretical expressions for the asymmetry parameters are derived with particular reference to the bent XY_2, planar XY_3, pyramidal XY_3 and tetrahedral XY_4 type molecular models. Results obtained in the case of typical molecules for which established valence force fields exist indicate

that the asymmetry parameter is related to molecular properties and the parameter has definite characteristics, such as approximate invariance in the case of XY_3 (D_{3h}) and XY_4 (T_d) molecules, for each molecular model. On the basis of the relationship between the bond asymmetry parameter and molecular properties, the force fields of a number of molecules have been evaluated, thereby bringing out the significante role this newly formulated parameter can play in the determination of force field.

The last chapter of the thesis deals with the IR spectrum of Coumarin and an explanation for the doublet nature of the carbonyl bond is given.

The original contributions contained in the thesis are the following:

1. Additional criteria for the selection of exact solution out of the many probable ones obtained in the graphical method in parameter formalism are put forward. The validity of these criteria is tested.

2. A new algebraic method is formulated to employ isotopic frequency data in the determination of molecular force field. The advantages and superiority of this method are brought out.

3. An asymmetry parameter to characterize the non-symmetric variation of binding forces at the

centre of a bond is defined.

4. General theoretical expression for the bond asymmetry parameter is derived.

5. The theory thus developed is applied to different molecular species and general conclusions regarding its properties and the usefulness of asymmetry parameter in molecular force field determination are drawn.

6. IR spectrum of Coumarin is recorded and an explanation for the doublet nature of the carbonyl bond is given.

A part of the investigations carried out by the author has been published in the following papers:

1. Infrared Spectrum of Coumarin - Proceedings of All India Symposia on Physics Education and Research-1974, Cochin University. Part II Research Section. p.203-211.

2. Asymmetries in Bonding Forces - ibid p.213-222.

3. Bond Inhomogeneity and Asymmetry Parameters - Indian J. Pure Appl. Phys. 13, 294-298 (1975)

4. Parameter Study of Force Fields of some Tetrahedral Molecules and Ions - Acta Physica Polonica. (in press).

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A concise review of the various types of assumed molecular force fields in use and different methods of calculation of force constants is made.

CHAPTER I

INTRODUCTION

1. Introduction

In the course of the last fifty years very considerable progress has been made in the investigation and theoretical interpretation of molecular spectra, and molecular spectroscopy has emerged as one of the most important, if not the most important, tool for investigating molecular structure. With the discovery of Raman effect in 1928 and with the introduction of very sophisticated instruments, significant amount of work has been done in the application of infrared and Raman spectra of molecules for the elucidation of molecular structure. Many approximation techniques that have been developed made it possible to use the experimental data for getting a clearer understanding of the nature of the chemical bond.

A molecule may be regarded as a group of atoms bound together by certain forces. These forces acting between the atoms tend to keep the molecule in equilibrium. Small oscillations of atoms about their

equilibrium positions in the molecule cause the appearance of infrared and Raman spectra. The fundamental vibrational frequencies are determined by the geometry of the molecule, atomic masses and the restoring forces. An analysis of the vibrational spectra of polyatomic molecules provides much valuable information about the electronic binding and the nature of the interatomic forces. Considerable work has been done in the determination of the molecular force field from the observed vibrational frequencies, obtained from the infrared and Raman spectra. However, to the present, no attempt has been reported in the literature, envisaging a study of the spatial distribution of binding forces between atoms in a molecule. Such an attempt is made and the results obtained are reported in the present work. In the following pages a brief review of the theory of molecular vibrations and different methods developed for the determination of molecular force fields is made.

2. Analysis of molecular vibrations

The mathematical analysis of molecular vibrations [1-3] requires, as the first step, the formulation of expressions for kinetic and potential energies of the molecule in any convenient set of co-ordinates. In the course of a vibration, the change on the equilibrium

configuration of a molecule may be represented by a set of cartesian displacement co-ordinates q_i ($i = 1, 2, \ldots, n$) where $n = 3N$ for an N-atomic molecule. For small displacements, the potential energy V of the molecule, which depends only on the internal configuration, is a homogeneous quadratic function of the displacements of the atoms about their equilibrium positions. This constitutes the well known harmonic approximation in the theory of small vibrations. The potential energy is accordingly written in the form

$$V = \frac{1}{2}\sum k_{ij} \; q_i \; q_j \qquad \ldots (1.1)$$

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

$$T = \frac{1}{2}\sum \; C_{ij} \; q_i \; q_j \qquad \ldots (1.2)$$

the coefficients C_{ij} are constants related to atomic masses. These two sets of coefficients k_{ij} and C_{ij} control the frequencies and modes of the normal vibrations. The numerical values depend on the choice of co-ordinates. The cross terms in the kinetic and potential energy expressions can be eliminated by a linear transformation of the displacement co-ordinates q to a set of normal co-ordinates Q. The expressions for V and T then take the form

$$V = \frac{1}{2} \sum_k \lambda_k Q_k^2 \qquad \ldots (1.3)$$

$$T = \frac{1}{2} \sum_k \dot{Q}_k^2 \qquad \ldots (1.4)$$

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

$$\ddot{Q}_k = -\lambda_k Q_k \qquad \ldots (1.5)$$

It can hence be shown that the λ's are given by the roots of the determinantal equation

$$\begin{vmatrix} k_{11} - C_{11}\lambda & k_{12} - C_{12}\lambda & k_{13} - C_{13}\lambda & \ldots\ldots & k_{1n} - C_{1n}\lambda \\ k_{21} - C_{21}\lambda & k_{22} - C_{22}\lambda & k_{23} - C_{23}\lambda & \ldots\ldots & k_{2n} - C_{2n}\lambda \\ \ldots\ldots & \ldots\ldots & \ldots\ldots & \ldots & \ldots\ldots \\ \ldots\ldots & \ldots\ldots & \ldots\ldots & \ldots & \ldots\ldots \\ k_{n1} - C_{n1}\lambda & k_{n2} - C_{n2}\lambda & k_{n3} - C_{n3}\lambda & \ldots & k_{nn} - C_{nn}\lambda \end{vmatrix} = 0$$

$$\ldots (1.6)$$

This secular equation is a polynomial of degree n (i.e., $3N$) in λ, with n real roots, λ_k. Each normal co-ordinate Q_k corresponds to an independent mode of vibration of the molecule and has a characteristic parameter λ_k. The frequency parameter λ_k is related to the vibrational frequency ν_k as

$$\lambda_k = 4\pi^2\nu_k^2 \qquad \ldots (1.7)$$

A normal co-ordinate Q_k can represent a genuine vibration of the molecule, only if its characteristic frequency parameter $\lambda_k > 0$.

On solving the secular equation, we get, in general, 3N-6 non-zero real roots, (3N-5 for linear molecules), equal in number to the vibrational degrees of freedom. The zero roots of the secular equation represent the translational and rotational modes of the molecule.

The internal configuration of the atoms in the molecule can be completely specified by 3N-6 (3N-5 for a linear molecule) internal displacement co-ordinates, which are changes in bond lengths, interbond angles and other geometrical parameters from their equilibrium values. Expressing the potential and kinetic energies of the molecule in terms of these internal co-ordinates, we get a secular equation of degree 3N-6 (3N-5 for a linear molecule) which does not possess any zero-root. The characteristic roots and vectors of the secular determinant determine the fundamental vibrational frequencies and the forms of the normal modes of vibration.

In practice, using experimentally observed fundamental vibrational frequencies, the secular equation is solved for the force constants and normal modes. As the number of unknown force constants far exceeds the number of normal frequencies, a unique solution is not possible using the vibrational frequencies alone.

Usually the interpretation of the molecular potential function is based on some simplified model, employing an approximate force field so as to reduce the number of unknown force constants. The ideas underlying some of these force fields are given below.

3. Approximate force fields

In the central force field (CFF) approximation, the forces in the molecule are acting along the lines joining the atoms, irrespective of whether they are connected by a valence bond or not [4, 5]. The number of force constants in this model is smaller than that of the vibrational frequencies, and the evaluation of force constants is made trivially easy. But this assumption holds only if the atoms are held by ionic interactions. Moreover the force field does not account for the bending vibrations of a linear molecule and the out-of-plane vibrations of a planar one. Now-

a-days the practical application of this force field is very little.

The valence force field (VFF) postulated by Bjerrum [4] is superior to the central force field and is chemically more meaningful. According to this model, the restoring forces oppose the changes in valence co-ordinates, like bond lengths and interbond angles. Here also the number of force constants is less than that of the vibrational frequencies. However, interactions between stretching and bending of different bonds in the molecule are not considered. The valuence force assumption is of fundamental importance and is close to the correct one, eventhough the correct reproduction of vibrational frequencies is not always possible.

To give more accurate vibrational frequencies, several model force fields have been proposed and widely used as modifications of VFF and CFF, the two major earlier attempts. A combination of central and valence type force fields has been postulated by Mecke [6] for XY_2 molecules. Taking into account Pauling's idea that the stability of a molecule is due to the overlap of the orbitals of the bonded atoms, Wilson and Howard formulated a modified valence force field (MVFF) for XY_3 type molecules [7].

Based on the idea of directed valence, Linnet and Heath introduced a new force field [8-10] called the orbital valence force field (OVFF). In this model, the electron density in each bond is represented by localized molecular orbitals. This assumption takes into consideration the effect of change in hybridization during a vibration and is assumed to be due to the angular deformation of the molecule. The bond stretching force constant is taken as independent of the change in hybridization. Hence in this theory no interactions between bond-stretching and bond-bending co-ordinates are included. But the properties of bonds in a molecule are well related to the inter-bond angles [11, 12]. The hybrid bond force field (HBFF), a modification of OVFF based on the correlation of bond strength with bond angle, is successfully applied to ammonia molecule [13].

Another widely used model is the Urey-Bradley force field (UBFF) [14] which takes into account the valence forces between bonded atoms and also the central forces between non-bonded atoms. This model satisfactorily reproduces the vibrational frequencies. Forces acting between the non-bonded atoms are of the Vander Waal's type and the values calculated using the UBFF agree well with the forces computed from the Lennard - Jones potential. Shimanouchi [15-16] has demonstrated

the general validity of the UBFF. The number of force constants is not too many. The transferability of Urey-Bradley force constants has been pointed out by several workers. But the UBFF does not account properly for the interaction between different internal valence co-ordinates. In several cases, it is found that UBFF fails to reproduce some of the observed data.

Several modifications have been suggested for the UBFF introducing different concepts like bond flexibility, trans interaction and trans and gauche interaction [17, 18, 19] . One such modification, accounting for the presence of lone pair electrons in the molecule has been shown to yield a useful force field model [20] .

A more complete picture of the intramolecular force field is presented by the general valence force field (GVFF), which includes, in addition to the valence force constants, all possible interactions between stretching and stretching, bending and bending and stretching and bending. The GVFF furnishes the most general and physically meaningful model and many a normal co-ordinate analysis has been carried out using this picture. In the present investigation the general valence force field is employed. The force constants are evaluated using Wilson's FG matrix method [21, 22]. The principal

merit of this method is that by exploiting molecular symmetry, the vibrational secular equation can be factored into lower orders.

4. The FG matrix method

In terms of the internal valence co-ordinates [23] the potential energy of a molecule is written as

$$2V = \sum f_{ij} r_i r_j \qquad \ldots (1.8)$$

where the summation extends over all the internal co-ordinates. In matrix form the above equation becomes

$$2V = \tilde{r} f r \qquad \ldots (1.9)$$

where f is the force constant matrix, and r represents the set of internal co-ordinates.

Applying group theoretical methods, the number of genuine normal vibrations belonging to each symmetry species is found. The internal co-ordinates r are transformed into an orthonormal set of symmetry co-ordinates, which are linear combinations of the internal co-ordinates and are constructed in such a way that they transform according to the characters of the vibration type of the point group to which they belong. The symmetry co-ordinates are defined by the transformation

$$S = U r \qquad \ldots (1.10)$$

where U is an orthogonal matrix. In symmetry coordinates the expression for the potential energy is

$$2V = \tilde{S} \; F \; S \qquad \ldots (1.11)$$

where F is the matrix of symmetry force constants. F is related to f by the equation

$$F = U \; f \; \tilde{U} \qquad \ldots (1.12)$$

The corresponding expression for the kinetic energy of the molecule is

$$2T = \tilde{\dot{r}} \; g^{-1} \; \dot{r}$$

$$= \tilde{\dot{S}} \; G^{-1} \; \dot{S} \qquad \ldots (1.13)$$

where $$G = U \; g \; \tilde{U} \qquad \ldots (1.14)$$

The kinetic energy matrix G^{-1} is determined by the geometry of the molecule. The method for the formulation of the inverse kinetic energy metrix G is reported in literature [23 - 27]. The G_{ij} elements for a non-degenerate species are of the form

$$G_{ij} = \sum_p \mu_p \; g_p \; S_i^t \; S_j^t \qquad \ldots (1.15)$$

and for a degenerate species

$$G_{ij} = \frac{1}{d} \sum_p \mu_p \; g_p \; (S_{ia}^t \; S_{ja}^t + S_{ib}^t \; S_{jb}^t + \ldots .) \qquad \ldots (1.16)$$

where p refers to a set of equivalent atoms, t a typical atom, μ_p the reciprocal mass of the atom, g_p the number of equivalent atoms in the p^{th} set. and d is the degree of degeneracy. The S vectors in the above expressions are given by

$$S_i^t = \sum_k U_{ik} \, s_{kt} \qquad \ldots (1.17)$$

Here i represents the i^{th} symmetry co-ordinate and U_{ik} the coefficient of the k^{th} internal co-ordinate in it. Expressions for the s_{kt} vectors are given by Wilson, Decius and Gross [3] and by Meister and Cleveland [24].

In terms of the symmetry force constant matrix F and inverse kinetic energy matrix G, the secular equation may be written as

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

or

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

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

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

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

For an F matrix of order n the difficulty is that there are $n(n+1)/2$ force constants, whereas there are only n values of λ. Hence a unique calculation of F matrix using only the G matrix and a set of observed λ values is not possible.

The normal co-ordinate transformation matrix L plays a significant role, in the analysis of the molecular force field. The normal co-ordinates Q are related to the symmetry co-ordinates S through the transformation matrix L

$$S = LQ \qquad \ldots (1.21)$$

In normal co-ordinates, the potential and kinetic energies are expressed as

$$2V = \tilde{Q} \Lambda Q \qquad \ldots (1.22)$$

$$2T = \dot{\tilde{Q}} \dot{Q} \qquad \ldots (1.23)$$

Introducing the matrix L, it can be shown that [3]

$$\tilde{L} F L = \Lambda \qquad \ldots (1.24)$$

$$L\tilde{L} = G \qquad \ldots (1.25)$$

The resulting characteristic equation is of the form

$$G F L = L \Lambda \qquad \ldots (1.26)$$

The roots Λ_i of the equation represent the normal frequencies and the eigenvectors L_i, the normal modes

of vibration. The force constant matrix F is given by

$$F = \tilde{L}^{-1} \Lambda L^{-1} \qquad \ldots (1.27)$$

5. Parameter representation

Taylor [28] has shown that the eigenvector matrix L can be written in parametric form as

$$L = L_0 X \qquad \ldots (1.28)$$

where L_0 is an approximate normal co-ordinate transformation matrix and X an arbitrary orthogonal matrix containing $\frac{1}{2}$ n (n-1) free parameters. The matrix L_0 is selected so as to satisfy the condition

$$L_0 \tilde{L}_0 = G. \qquad \ldots (1.29)$$

The L_0 matrix may be identified, for example, with a triangular matrix T, in the model based on the shear method [29] . If the frequencies are ordered in the sequence $\Lambda_1 > \Lambda_2 > \ldots\ldots \Lambda_n$, the lower triangular matrix corresponds to the mode of vibration of highest frequency being uncoupled, while the upper triangular matrix represents the uncoupling of the symmetry mode of lowest frequency [30].

The orthogonal matrix X in terms of $\frac{1}{2}$ n(n-1) free parameters can be formulated in different ways. The nature and characteristics of the matrix X does not impose any restriction upon the force constant matrix F

[28, 31, 32]. A widely used representation of X is in terms of angle parameters α_{ij}:

$$X(\alpha) = \prod_{i=1}^{n-1} \prod_{j=i+1}^{n} A_{ij}(\alpha_{ij}) \quad \ldots(1.30)$$

A_{ij} are elementary rotational matrices in the ij-plane. The ii^{th} and jj^{th} elements are $\cos \alpha_{ij}$ and the ij^{th} element is $-\sin \alpha_{ij}$ and ji^{th} element is $\sin \alpha_{ij}$. All other diagonal elements are unity and off-diagonal elements zero.

With the parametric form of L matrix, the corresponding parametrized F matrix can be written as

$$F = \tilde{L_o^{-1}} X \Lambda \tilde{X} L_o^{-1} \quad \ldots (1.31)$$

$\frac{1}{2}$ n (n+1) elements of this symmetric matrix F of order n are controlled by the n eigenvalues λ_i and the $\frac{1}{2}$n (n-1) free parameters of the orthogonal matrix X. All possible solutions of the force constant matrix F which reproduce the frequencies lie on a $\frac{1}{2}$ n (n-1) dimentsional hyper surface defined by the systematic variation of $\frac{1}{2}$n (n-1) paremeters. With the help of some additional data or employing some constraint, the point in the parameter space corresponding to the proper force field can be fixed. With the given parameters, numerical

computation of the force constant matrix is made. In recent years the parameter technique has become very popular in the study of molecular force fields.

6. Use of additional data

Additional experimental data such as isotopic frequencies, Coriolis coupling constants, mean amplitudes of vibration, and centrifugal distortion constants are often made use of, in addition to vibrational frequencies, to fix the exact force field.

Under the Born-Oppenheimer approximation, the molecular force field is unaltered by isotopic substitution, as the force field is a function of the electronic structure of the molecule. But, due to the change in atomic masses, the inverse kinetic energy matrix G and hence the secular equation are altered. An extra set of equations connecting the same force constants to the observed isotopic frequencies is obtained.

The Coriolis coupling coefficients ζ, represent the mutual interaction of pairs of normal vibrations due to Coriolis forces which arise when a system of particles are both vibrating and rotating simultaneously. Two vibrational states can couple through Coriolis interaction only if the product of the corresponding species contains a rotational species [33].

Because of the Coriolis interaction, the band positions are shifted or the degeneracies are removed. According to the theory outlined by Meal and Polo [34], the Coriolis constants ζ^{α} are given by the relation

$$\zeta^{\alpha} = \tilde{L}^{-1} C^{\alpha} L^{-1} \qquad \ldots (1.32)$$

The elements of the matrix C^{α} can be calculated from the geometry of the molecule and atomic masses [35-37] using the relation

$$C_{ij} = \sum_{a} \mu_{a} (S_{ia} \times S_{ja}) e_{\alpha} \qquad \ldots (1.33)$$

Mean amplitudes of vibration, obtained from electron diffraction data, are also of help in determining the force constants. The atoms constituting the molecule are vibrating at all temperatures and each interatomic distance for bonded or nonbonded atom pairs is associated with a mean square amplitude quantity $\langle (R - R_e)^2 \rangle$ where R_e represents the equilibrium interatomic distance and $(R - R_e)$ the instantaneous deviation from the equilibrium value. Cyvin et. al. [35, 36] have made a detailed theoretical analysis and the mean square amplitudes are evaluated in terms of the mean square amplitude matrix Σ. Σ is related to the vibrational frequencies ω_i through the equation

$$\Sigma = L \Delta \tilde{L} \qquad \ldots (1.34)$$

where Δ is a diagonal matrix with elements

$$\Delta_{ii} = \frac{h}{8\pi^2 c\,\omega_i} \coth \frac{hc\,\omega_i}{k\,T} \quad \ldots (1.35)$$

Here h is Planck's constant, T the absolute temperature and k Boltzmann's constant.

Using the bond polarizability theory [38, 39] which relates the overall molecular properties such as polarizability, dipole moment etc. to bond properties, a physically meaningful set of force constants can be evaluated. The method is known as the relative Raman intensities approach [40, 41].

Centrifugal distortion constants obtained from microwave spectra of molecules are yet another additional input that is utilised. Kivelson and Wilson [42, 43], and later, Cyvin et.al. [44, 45] have formulated theoretical expressions for these constants as functions of force constants. Attempts have been made in the case of XY_2 type molecules to obtain a set of force constants simultaneously making use of the vibrational frequencies and centrifugal distortion constants [46, 47].

7. Approximation methods

Many attempts have been made, in recent years, to develop a method, based on some mathematical constraint,

to determine an approximate force field from the vibrational frequencies alone. An excellent survey of approximation methods for the calculation of force constants is made by Alix et. al. [48].

Iterative methods. A number of such methods are iterative. In this approach one starts with an approximate inverse kinetic energy matrix G_0 and force constant matrix F_0. The transformation from F_0 to the true F matrix which reproduces the experimental frequencies, is achieved by an iterative procedure. In the method proposed by Fadini and Sawodny [49-51] the choice of the initial set of force constants corresponds to a complete neglect of the kinematic coupling of the vibrational modes. The true G matrix without the off-diagonal elements is taken as the initial G_0 matrix and the corresponding F_0 matrix is given by

$$F_0 = \Lambda \exp G_0^{-1} \qquad \ldots (1.36)$$

The final true force constant matrix F is determined by a stepwise introduction of the off-diagonal elements of the G matrix. At each step a correction ΔF to the force constant matrix is calculated by solving a system of equations based on the Cayley - Hamilton theorem. According to this theorem, which states that a square matrix satisfies its own characteristic equation, the secular equation for the n x n matrix [G F] is written as

$$\sum_{i=1}^{n} c_i \, [GF]^i = 0 \qquad \ldots (1.37)$$

The experimental vibrational frequencies determine the coefficients c_i. For the k^{th} step of iteration the equation is of the form

$$\sum_{i=1}^{n} c_i \left\{ G_k \, (F_{k-1} + \Delta F_k) \right\}^i = 0 \qquad \ldots (1.38)$$

Neglecting the higher powers of the correction term ΔF_k, a linear equation is obtained for the solution of ΔF_k.

Starting with the same initial set of matrices, Becher and Mattes [52] also suggested a stepwise coupling method, in which the final F matrix is calculated by simple matrix multiplication. The iteration is made possible by the successive application of the relation (1.27).

$$F = \tilde{L}^{-1} \Lambda L^{-1}$$

The approximate F matrix at each step is used to formulate the eigenvector matrix L of the next step. For the k^{th} step L_k is calculated from the secular equation

$$G_k \, F_{k-1} \, L_k = L_k \, \Lambda_k \qquad \ldots (1.39)$$

The same eigenvector method has been formulated independently by Johansen [53] .

Taking into account the different symmetry representations and the possible interdependence of force constants Chacon and Matzke [54] formulated a modified approach for the transformation to the final set.

In these stepwise coupling methods, the final result depends on the choice of the initial set of F_0 and G_0 matrices and on the method of introducing the off-diagonal elements of G [55-58]. These methods impose no restrictions or conditions on the choice of the co-ordinate system. As such one can use a co-ordinate system in which the complete G matrix is diagonal. In this case the stepwise transition from G_0 to G is of little meaning [59] . It is also pointed out against the Becher and Mattes method that the G_k and F_k matrices at each step, automatically reproduce the vibrational frequencies. Fadini's method yields reasonable diagonal force constants, but it shows a tendency to minimize the values of the off-diagonal elements [60] .

Based on the same principle of stepwise coupling and transferability of the eigenvectors from an approximate solution to the exact solution of the secular equation,

Alix et.al. presented the matrix polynomial expansion method [56-58]. In this approach a commutation relation of the form

$$[\, G_k \;\; F_{k-1} \;\; , \;\; G_k \;\; \Delta \; F_k \,] = 0 \qquad \ldots (1.40)$$

exists between the solutions of the k^{th} and $k-1^{th}$ steps. With the use of the Cayley - Hamilton theorem, this commutation relation yields a unique solution of the correction terms ΔF_k. The formulation of the eigenvector matrix L at each step, in accordance with the assignment of frequencies, is not necessary [61]. From the practical point of view the method is identical to the Logarithmic steps Method [62]. In problems of large kinematic coupling, application of this polynomial method fails [63].

Non-iterative methods. In some of the important non-iterative methods, constraints are imposed on the values of the elements of the force constant matrix F. In the F-trace approach [64-66] the eigenvector matrix L is considered in the parametric form

$$L = V \Gamma^{1/2} X \qquad \ldots (1.41)$$

where Γ denotes the matrix of eigenvalues of G. The approximation is based on the assumption that the same orthogonal matrix diagonalises the matrices F and G. The proper orthogonal matrix corresponds to the extremal

values of the sum of the diagonal force constants. Using the Lagrangian multipliers, the stationary value of tr F is reduced to the form

$$\text{tr } F^s = \sum_i \Gamma_i^{-1} \Lambda_i^s \qquad \ldots (1.42)$$

The value of tr F is a minimum on choosing the eigenvalues in the increasing sequence and Γ_i in the decreasing sequence. For the reverse ordering tr F is found to be a maximum.

By a graphical method Strey [67] has investigated the extremal properties of force constants in n = 2 cases, varying the angle parameter Φ systematically over the range $0 \leq \Phi \leq 2\pi$. According to Strey, the constraint that the force constant f_r is a maximum with respect to the parameter, gives good force fields for hydrides. For many other types of molecules the condition f_α minimum represents a satisfactory force field.

External values of off-diagonal force constants have also been exploited for approximating the molecular force field [68-72]. The necessary condition assumed is that the Jacobian J, whose elements are given by $J_{ij} = L_{ji}^2$, is singular. Successful formulation of a complete set of F matrix elements is obtained only for the second and third order cases. However, the method does

not always yield a physically meaningful set of force constants.

In another approach [73-77] based on the extremal values of tr L, the constraint employed is that the mixing of different symmetry co-ordinates in any normal co-ordinate is small. According to this approximation, the proper L matrix is the one with maximum trace and smaller off-diagonal elements. The corresponding orthogonal matrix X is shown to be $\tilde{V}$. For problems of small mass-coupling the method is found to be successful. According to Pulay and Torok [74-75], the characteristic matrix L must be such that the sum of the distances between the co-ordinates Qi and Si is minimum. On imposing this condition,

$$\sum_{i=1}^{n} |Qi - Si|_{min} = n + tr\ G - 2\,[tr\ L\ max.] \quad \ldots (1.43).$$

the proper L matrix is then shown to be $G^{1/2}$. The result in n = 2 cases is equivalent to the assumption that $L_{12} = L_{21}$, but this is not true in all cases [78]. The F-trace and L-trace approaches do not possess the property of invariance under scaling [66, 74, 79, 80].

Müller et.al. [81-85] developed the 'L matrix approximation method', imposing the condition $L_{ij} = 0$ $i < j$. The method is equivalent to Torkington's [86, 87]

approximation

$$(G\,F)_{ij} = 0 \qquad i<j \qquad \ldots (1.44)$$

If the vibrations are characteristic, the approach yields reasonable force constants [81-85]. The method has been successfully applied to n = 3 cases [85] and widely investigated in second order problems [80-85, 88-91]. This approximation is found to be physically reasonable for molecules exhibiting small mass coupling, where a high stretching and a low bending vibration occur in the same species. For strongly coupled vibrations several empirical improvements have been reported [92, 93].

In the extended L matrix approximation method (for n = 2 cases) Müller et.al. [94] assumed the general mixing of the two normal modes. From an empirical study of the L matrix elements, determined from the exact force field data, the ratio L_{12} / L_{21} is found to have a special dependence on the kinematic coupling, bearing a constant value for the molecules of a particular point group. Empirical values have been reported for the types C_{2v} (XY_2) D_{3h} (XY_3) and T_d (XY_4). In the parametric form of L Matrix, the approximate mass dependence of the orthogonal matrix X is reported [95].

According to the approximation method formulated by Reddington and Aljibury [96], the constraints

are made directly on the restoring forces acting on a molecule in any displaced position, and not on the force constant matrix. The basic assumptions of this method rest on considerations of minimum potential energy. The parametrized restoring force M_k is assumed to be parallel to the corresponding internal co-ordinte. It is also assumed that the restoring force exerted by the molecule for each internal co-ordinate is as large as possible. The condition to maximise the restoring forces for all displacements simultaneously is achieved through the virial theorem. The balancing condition for minimum potential energy is expressed as a relation.

$$- \frac{\partial E}{\partial \Phi_{ij}} = \sum_{1}^{n} \frac{\partial E}{\partial M_k} \frac{\partial M_k}{\partial \Phi_{ij}} = 0 \quad \ldots (1.45)$$

$i, j = 1 \ldots . n \quad i < j$

connecting the molecular energy E to $\frac{1}{2} n (n-1)$ arbitrary parameters Φ_{ij}. $\frac{\partial E}{\partial M_k}$ is calculated through the virial theorem using the geometrical parameters of the molecule. The method is found to be suitable for obtaining reliable sets of force constants for species with no redundant symmetry co-ordinate.

Wilson has shown that a higher order secular equation can be approximately reduced to one of lower order [3]. The truncated lower order secular equation is solved with the help of additional data such as

Coriolis constants or isotopic frequency shifts. Using the formalism of the 'separation of high and low frequencies', the characteristic high or low group frequency is seperated, reducing the order of the equation by one. The method is particularly useful in $n = 3$ cases and has been successfully applied to different types of molecule [97, 98].

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CHAPTER II

DETERMINATION OF FORCE FIELD FROM ISOTOPIC FREQUENCIES

The graphical method of parametric approach for the determination of exact force field is applied to some XY_4 type molecules and ions. In those cases where a unique force field cannot be determined, methods for arriving at an acceptable force field are outlined. Also a limit of uncertainty in the values of force constants obtained using graphical method is defined. In the latter part of this chapter a strikingly simple but accurate algebraic method is put forward. The theory developed is applied to several molecules and the results obtained are compared with the best known values of force constants so as to bring out the superiority of this algebraic method.

CHAPTER II

DETERMINATION OF FORCE FIELD FROM ISOTOPIC FREQUENCIES

1. Introduction

From the preceding chapter it is clear that, in normal co-ordinate analysis, a unique solution of force constants is not possible, since the number of unknown force constants far exceeds that of vibrational frequencies. Under the Born-Oppenheimer approximation, the molecular force field is unaltered by isotopic substitution, but because of changes in atomic masses, the vibrational frequencies are different. Also the inverse kinetic energy matrix G is altered. This yields additional equations for the force constants in terms of the observed isotopic vibrational frequencies. With the help of these equations the force constants can be evaluated. Several authors have investigated the problem of using isotopic frequencies as additional data in evaluating force constants [1-6].

2. Graphical method

Recently the problem of determination of force

constants using isotopic frequencies in the parameter formalism has been attempted by Ananthakrishnan et.al. [5]. They have formulated a graphical method for evaluating the force constants in n = 2 cases. Making use of the general expression for the parametrized F matrix (1.31), these authors have expressed each force constant F_{ij} as a function of a parameter c

$$F_{ij} = \frac{1}{1+c^2} \left\{ k_{ij} \; c^2 + l_{ij} \; c + m_{ij} \right\} \quad \ldots (2.1)$$

where k_{ij}, l_{ij} and m_{ij} are functions of atomic masses and molecular parameters. For different isotopic species, distinct solutions of the parameter are obtained. For different values of the parameter c of a given isotopic species the F_{ij} (i, j = 1, 2) equations are solved for the parameter c* of another isotopic species. The parameter (c - c*) curves for each pair of isotopic species are plotted and intersections sought. If isotopic invariance is to hold, there should exist a unique point of intersection of all the three parameter curves corresponding to the three Fij elements and the force constants corresponding to this point must be the same for all the isotopic substituents. Because of the quadratic nature of these equations there exists two intersections of which one is found to be in the neighbourhood of the origin (c_A) and the other

far away from it (c_v). The force constants corresponding to the remote intersection c_v yield an inverse assignment of frequencies and hence may be called virtual force constants while the set obtained from the intersection near the origin corresponds to the actual force field. However, in many cases unique intersections of parameter curves do not exist because of the inaccuracies in experimental data. When the curves intersect forming small islands, the force constants have been evaluated as the mean of the values corresponding to the extreme points of the island.

By considering three isotopic species rather than two, an improvement is made over the original approach and is applied to some pyramidal XY_3 type molecules [6]. Parameter curves are plotted in separate two dimensional spaces, taking a pair at a time. With the increase in the number of the isotopic species, a large number of intersections have been obtained. To select the correct point from the multiplicity of intersections near the origin, a principle called the method of equal co-ordinates has been applied. This principle may be stated as follows: If A, B, C, are isotopic species of the same molecule, the intersections of parameter curves for the pairs A - B and B - C should be such that B is represented by equal co-ordinates in the parameter spaces c_A - c_B and c_B - c_C. The acceptable

intersections are those for which the common isotope is represented by equal co-ordinates in the two parameter spaces.

Computational procedure. In the present investigation, the above technique has been applied to the following molecules and ions: $Xe\,O_4$, $C\,F_4$, $Si\,H_4$, $Si\,F_4$, $B\,F_4^-$ and $N\,H_4^+$, all of which have T_d symmetry. The vibrational frequencies are taken from references [3, 7-12]. The symmetry co-ordinates and G matrix elements used in these calculations are the same as those reported by Cyvin [12]. The symmetry co-ordinates of the T_d molecular model are listed as follows:

$$S_{1a}(f_2) = \frac{1}{2}(\Delta r_1 - \Delta r_2 + \Delta r_3 - \Delta r_4)$$

$$S_{2a}(f_2) = \frac{1}{\sqrt{2}} r (\Delta\alpha_{24} - \Delta\alpha_{13})$$

$$S_{1b}(f_2) = \frac{1}{2}(\Delta r_1 + \Delta r_2 - \Delta r_3 - \Delta r_4)$$

$$S_{2b}(f_2) = \frac{1}{\sqrt{2}} r (\Delta\alpha_{34} - \Delta\alpha_{12})$$

$$S_{1c}(f_2) = \frac{1}{2}(-\Delta r_1 + \Delta r_2 + \Delta r_3 - \Delta r_4)$$

$$S_{2c}(f_2) = \frac{1}{\sqrt{2}} r (\Delta\alpha_{14} - \Delta\alpha_{23}) \qquad \ldots (2.2)$$

where Δr and $\Delta\alpha$ are internal co-ordinates which are changes in bond lengths and bond angles. (see Fig.2.1)

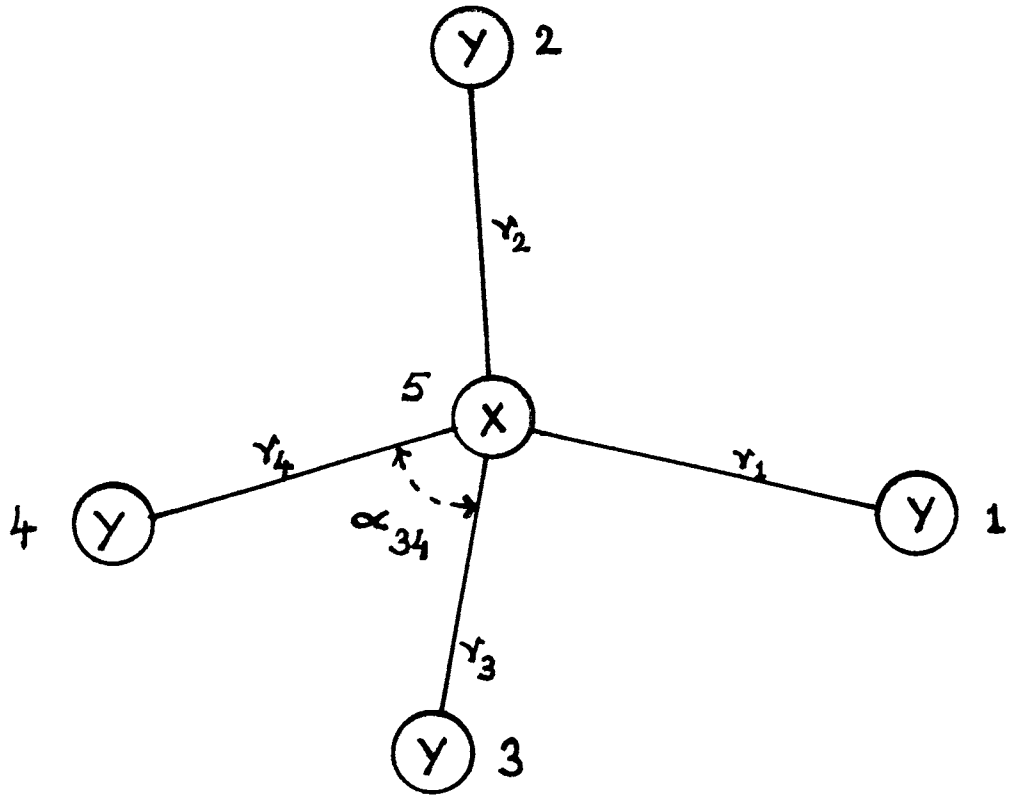

FIG.2.1. Tetrahedral XY_4 model: Molecular geometry

The G matrix elements and the symmetric force constants F, corresponding to the f_2 species vibrations are:

$$G_{11} = \frac{4}{3}\mu_x + \mu_y$$

$$G_{12} = \frac{8}{3}\mu_x$$

$$G_{22} = 2\left(\frac{8}{3}\mu_x + \mu_y\right) \qquad \ldots (2.3)$$

$$F_{11} = f_r - f_{rr}$$

$$F_{12} = -\sqrt{2}\,(f_{r\alpha} - f'_{r\alpha})$$

$$F_{22} = f_\alpha - f_{\alpha\alpha} \qquad \ldots (2.4)$$

Only one parameter space is considered for XeO_4, CF_4 and BF_4^-. With three isotopic species three separate two dimensional parameter spaces are scanned for SiH_4 and SiF_4. In the case of ammonium ion, as the number of isotopic species considered is four, the parameter curves have been plotted in six separate two dimensional spaces. For all isotopic pairs a wide range in parameter space ($-10 \leq c \leq 10$) has been scanned for intersections of parameter curves. The value of the parameter c is systematically varied, from -10 to -1 at steps of 0.5, from -1 to +1 at steps of 0.01 and from +1 to +10 at steps of 0.5.

Figures 2.1 to 2.27 show the parameter curves obtained for these molecules and ions and their isotopic substituents. These graphs are drawn in such a manner that for a pair of isotopic species A and B, the parameter c for A is plotted along the x-axis and that for B along the y-axis. Co-ordinates corresponding to the intersections of c - c* curves are sought. The region near the origin has been plotted separately using a magnified scale to enable clear and exact identification of the intersections. Some of these graphs are shown along with the main graphs. The details regarding the intersections of the parameter curves are presented in tables 2.1 to 2.4. For each intersection, the parameter values are given and the corresponding intersecting curves are identified.

When the number of isotopic species exceeds two there is a multiplicity of intersections. But in a given parameter space, these intersections lie in a small region. As the parameter for the true force field should lie inside this range, the size of this range may be taken as a measure of the uncertainty in fixing the true co-ordinate. With the help of more than two parameter spaces, the extent of uncertainty can be reduced. The minimum value of the uncertainty obtained from an analysis of the graphs corresponds to the smallest range

common to all the parameter spaces. This is also in agreement with the method of equal co-ordinates. The mean of the values for the extreme points of the common range along with the extent of the uncertainties is taken as the true parameter. All points of intersection, whether unique or not, outside the corresponding common range are taken as spurious ones and are automatically eliminated.

Acceptable parameter values for the various molecular species, selected according to the methods explained above, together with the force constants are entered in Table 2.5. The two sets of force constants corresponding to the two solutions are capable of reproducing the vibrational frequencies of the corresponding isotopic species, but only that set obtained from the intersection near the origin has any physical significance. With the predominance of bending mode the second set turns out to be unphysical. The final set of actual force constants is entered in Table 2.6. and compared with values taken from literature.

3. Algebraic method.

Eventhough the graphical method, discussed above, yields good results, the approach is not easy in the sense that it involves too much numerical computation.

Moreover the accuracy of the final selected value of the parameter c varies with the scale used for the graph. As the curves are of irregular shape, the parameter space is to be scanned in regular small steps of the parameter values. A simple algebraic method is suggested below to employ isotopic frequency data in the determination of the molecular force field.

For a vibrational species of the n^{th} order, $N = n(n-1)/2$ parameters $c_1, c_2, \ldots . c_N$ determine the force field. Let $\alpha, \beta, \ldots .$ denote K isotopic species of a molecule $(K \geq 2 \geq N)$. In Wilson's F G matrix formalism, there is the trace relation

$$\text{tr} \quad G^{\alpha} F \quad (c_1^{\alpha}, \ldots ., c_N^{\alpha}) = \sum_i \lambda_i^{\alpha} \qquad \ldots(2.5)$$

where G^{α} is the inverse kinetic energy matrix, $F(c_1^{\alpha}, \ldots . c_N^{\alpha})$ the F matrix parameterised in terms of the N parameters $c_1^{\alpha}, \ldots . c_N^{\alpha}$ and $\lambda_i^{\alpha} = 4\pi c^2 (\omega_i^{\alpha})^2$ for the isotopic species labelled α. Let us introduce the differences

$$\Delta G^{\alpha\beta} = G^{\alpha} - G^{\beta} \qquad \ldots (2.6)$$

and

$$\Delta \lambda_i^{\alpha\beta} = \lambda_i^{\alpha} - \lambda_i^{\beta} \qquad \ldots (2.7)$$

Consequently, from the K equations (2.5), the following set of difference equations is obtained.

$$\text{tr}\ \Delta G^{\alpha\beta} F(c_1^{\alpha}, \ldots . c_N^{\alpha}) = \sum \Delta \wedge_i^{\alpha\beta} \quad \ldots (2.8)$$

These constitute a sufficient set of simultaneous equations for the determination of the parameters $c_1^{\alpha}, \ldots . c_N^{\alpha}$.

In the case $n = 2$, the force constants are expressed in terms of a parameter c, defined in the range $-1 \leq c \leq 1$, as follows:

Factorizing Wilson's G matrix into a triangular matrix T and its transpose, $G = T \tilde{T}$;

The normal co-ordinate transformation matrix L is given by $L = T A$ where A is an orthogonal matrix. Taking A in the form

$$\begin{vmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{vmatrix} \qquad \ldots (2.9)$$

a parameter $c = \tan\theta$ is introduced in the L matrix. From (1.31) $F = \tilde{L}^{-1} \wedge L^{-1}$,

$$F_{11} = \frac{(\wedge_2 |G| + G_{12}^2 \wedge_1) c^2}{G_{11} |G| (1 + c^2)} + \frac{2G_{12} (\wedge_1 - \wedge_2) c}{G_{11} |G|^{1/2} (1 + c^2)} + \frac{\wedge_1 |G| + G_{12}^2 \wedge_2}{G_{11} |G| (1 + c^2)}$$

$$\ldots (2.10)$$

$$F_{12} = \frac{G_{12}\ \Lambda_1\ c^2 + |G|^{1/2}\ (\Lambda_1 - \Lambda_2)c + G_{12}\ \Lambda_2}{(1 + c^2)\ |G|} \qquad \ldots (2.11)$$

$$F_{22} = \frac{G_{11}\ (\Lambda_1\ c^2 + \Lambda_2)}{|G|\ (1 + c^2)} \qquad \ldots (2.12)$$

In the second order case with two isotopic species the trace relation expressed by (2.8) is of the form

$$\Delta G_{11}\ F_{11} + 2\ \Delta G_{12}\ F_{12} + \Delta G_{22}\ F_{22} = \Delta \Lambda_1 + \Delta \Lambda_2 \qquad \ldots (2.13)$$

When the number of isotopic species considered exceeds two, the data corresponding to all the species can be incorporated in the same difference equation. With K isotopic species ($\alpha, \beta, \ldots . K$) the equation is of the form

$$\sum_{k=\beta}^{K} \left[\Delta G_{11}^{\alpha k}\ F_{11} + 2\ \Delta G_{12}^{\alpha k}\ F_{12} + \Delta G_{22}^{\alpha k}\ F_{22} \right] = \sum_{k=\beta}^{K} \left[\Delta \Lambda_1^{\alpha k} + \Delta \Lambda_2^{\alpha k} \right] \qquad \ldots (2.14)$$

Because of the quadratic nature of the expression on the left side of (2.13) or (2.14), there exist two solutions for the parameter c. The solution nearer to zero is

the acceptable one, since the other solution, which often lies outside the natural range of definition of c, invariably leads to unphysical force constants and an inverse assignment.

The algebraic method is applied to all the molecules, studied above graphically. In Table 2.7 the solutions obtained by computation are compared with those obtained by the graphical method. It may be noted that there is excellent agreement between the two sets of values. Using the algebraic approach the force constants of some typical molecules (belonging to the XY_2, XY_3 and XY_4 types) are also evaluated. The results are shown in Table 2.8. Previous results are given in the last column for comparison.

The results obtained in this investigation show that the new algebraic method can be used successfully for the determination of exact force field using isotopic frequencies as additional data. The simplicity of the method coupled with the accuracy of the result obtained is its remarkable feature and in that respect it is superior to all similar methods proposed earlier in the literature.

FIG. 2.2 to 2.27. c - c* parameter curves for different isotopic pairs. In all these figures for an (A - B) pair, parameter c for the isotopic species A is plotted along the x-axis and that for B along the y-axis.

 curve from F_{11}

 curve from F_{12}

 curve from F_{22}

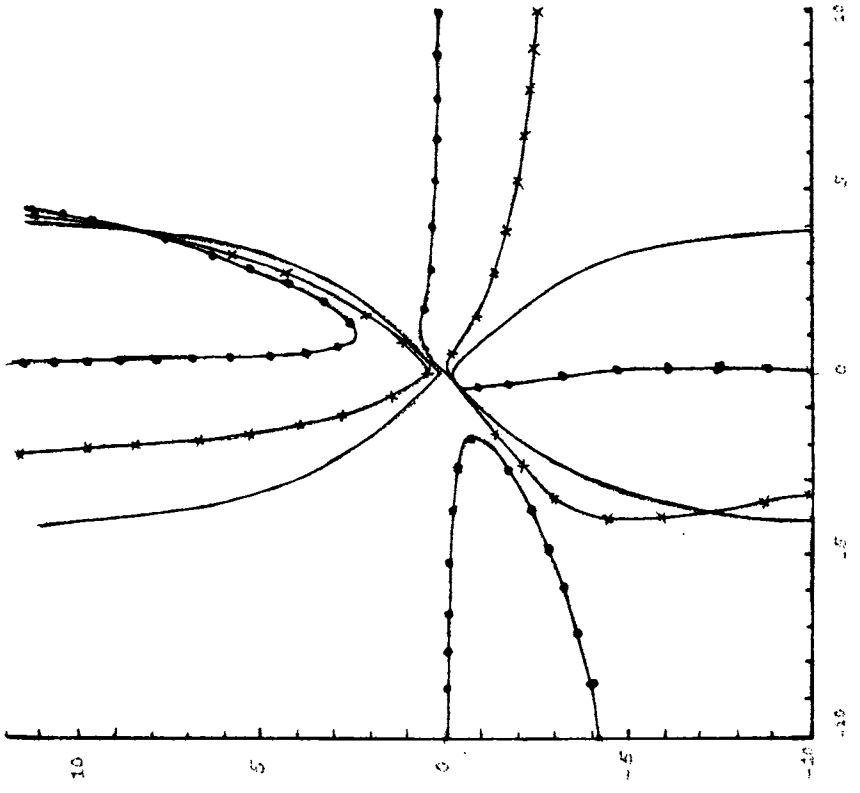

FIG. 2.3. $^{15}NH_4 - ND_4$

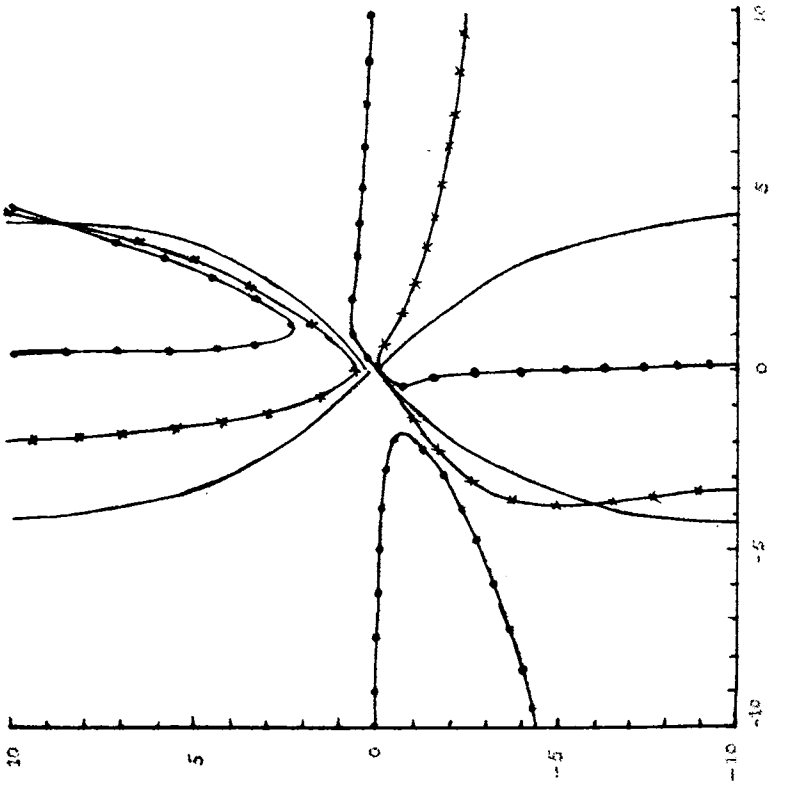

FIG. 2.2. $NH_4 - ND_4$

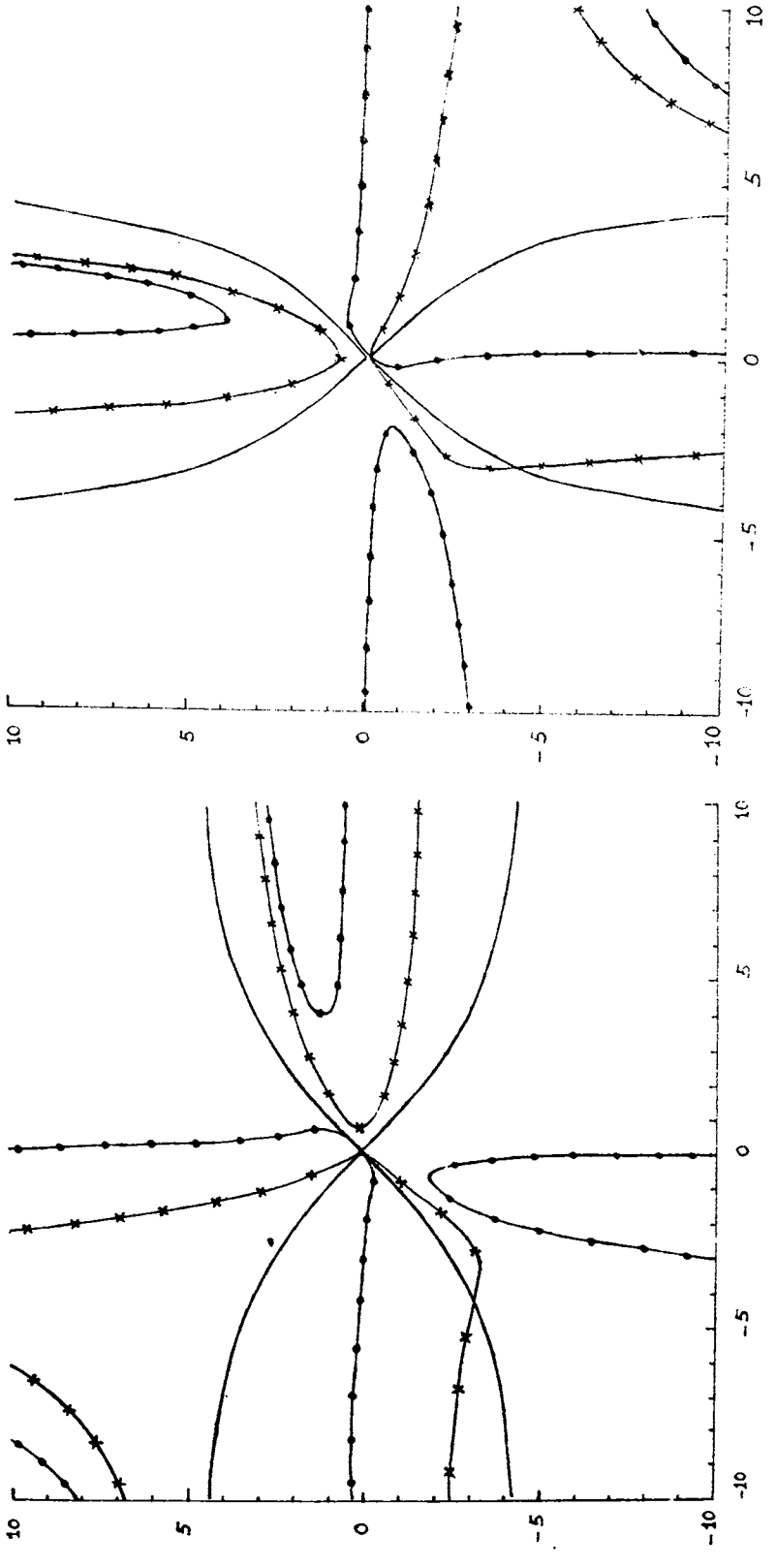

FIG. 2.4. $NT_4 - NH_4$

FIG. 2.5. $^{15}NH_4 - NT_4$

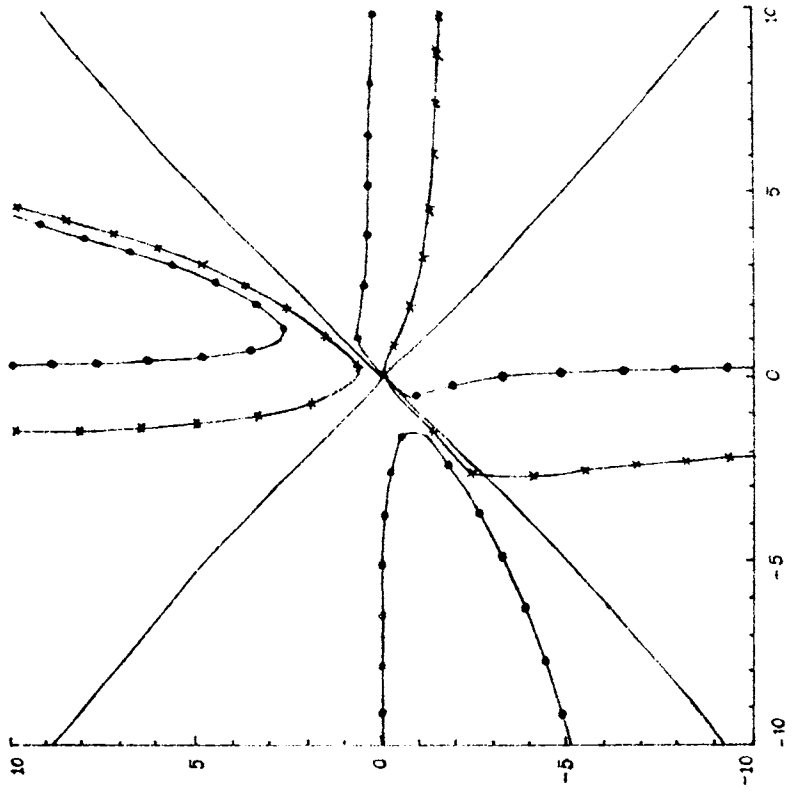

FIG. 2.7. $ND_4 - N^{-}_4$

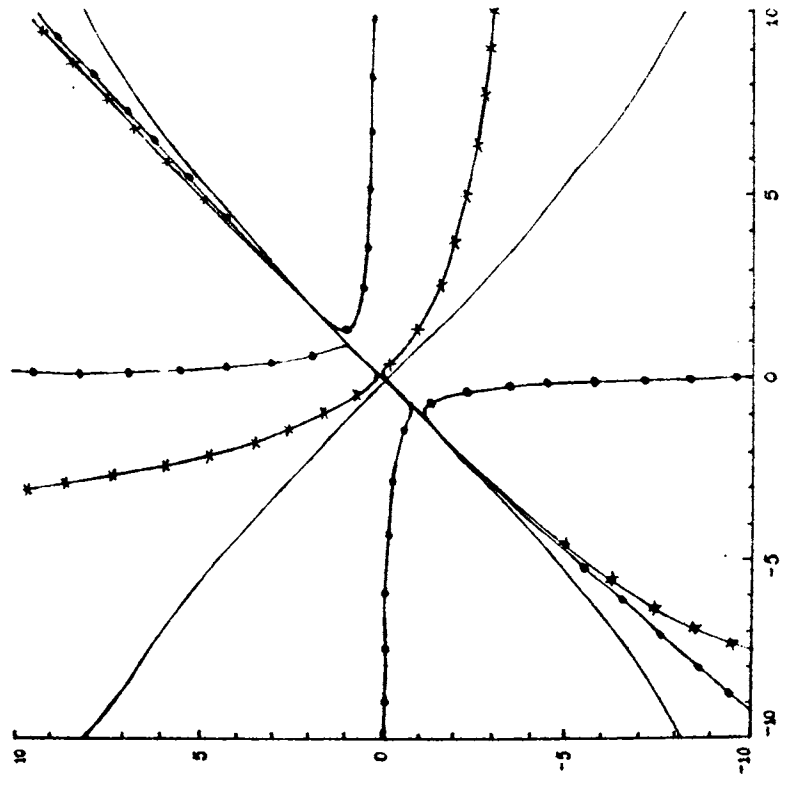

FIG. 2.6. $NH_4 - {}^{15}NH_4$

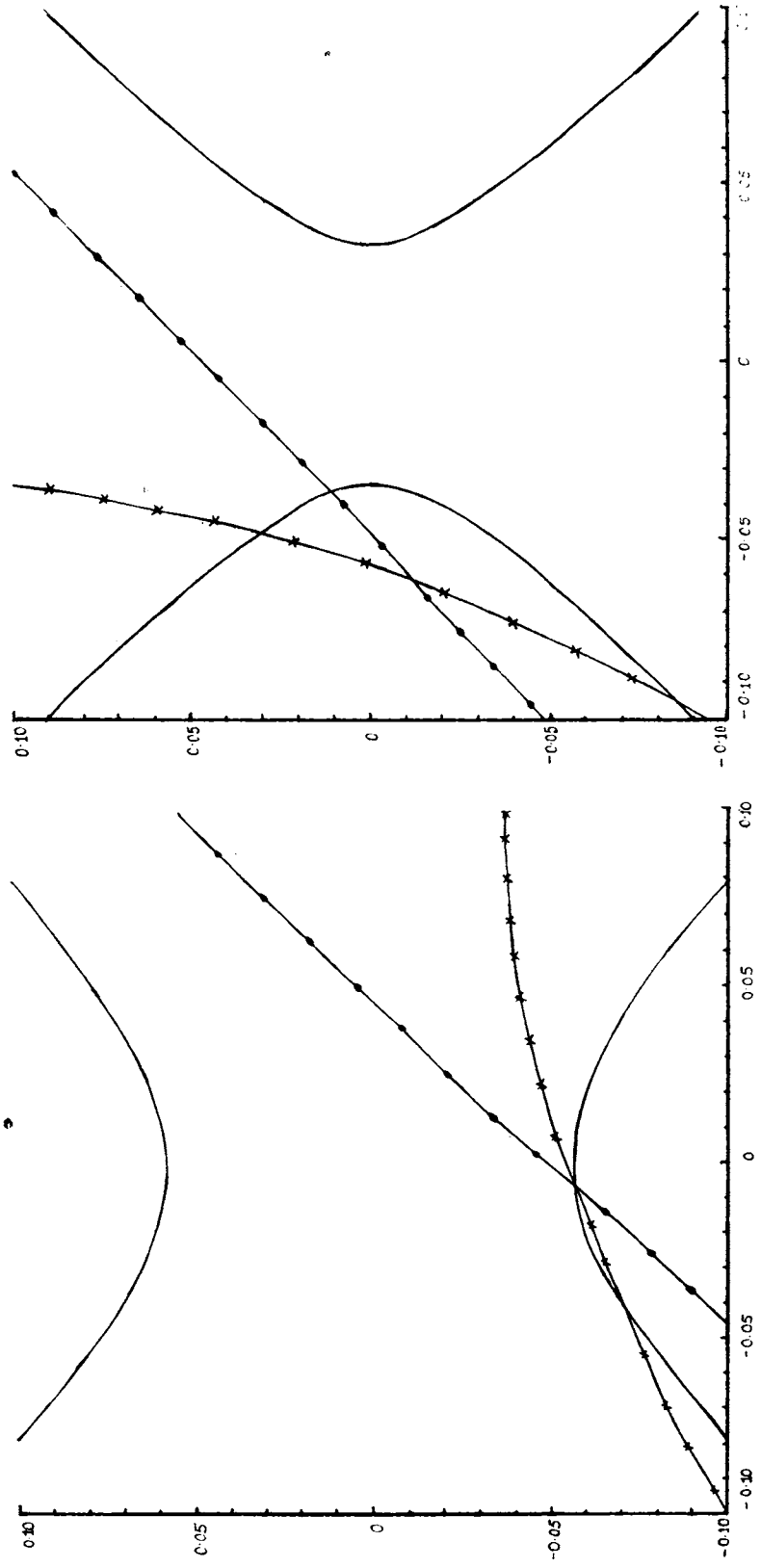

FIG. 2.8. $^{15}NH_4 - NT_4$

FIG. 2.9. $NT_4 - NH_4$

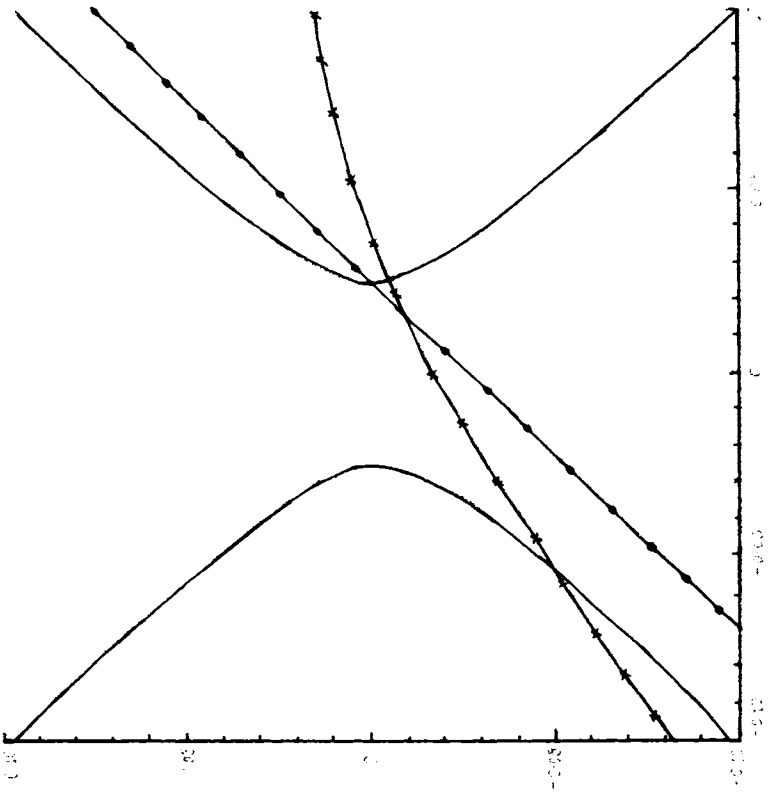

FIG. 2.11. $NH_4 - ND_4$

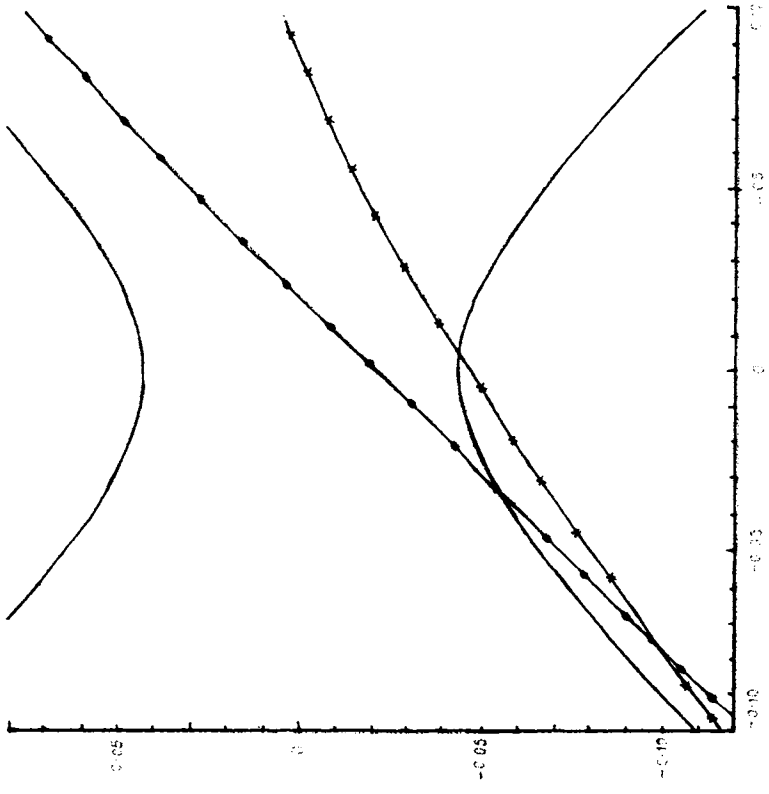

FIG. 2.10. $ND_4 - NT_4$

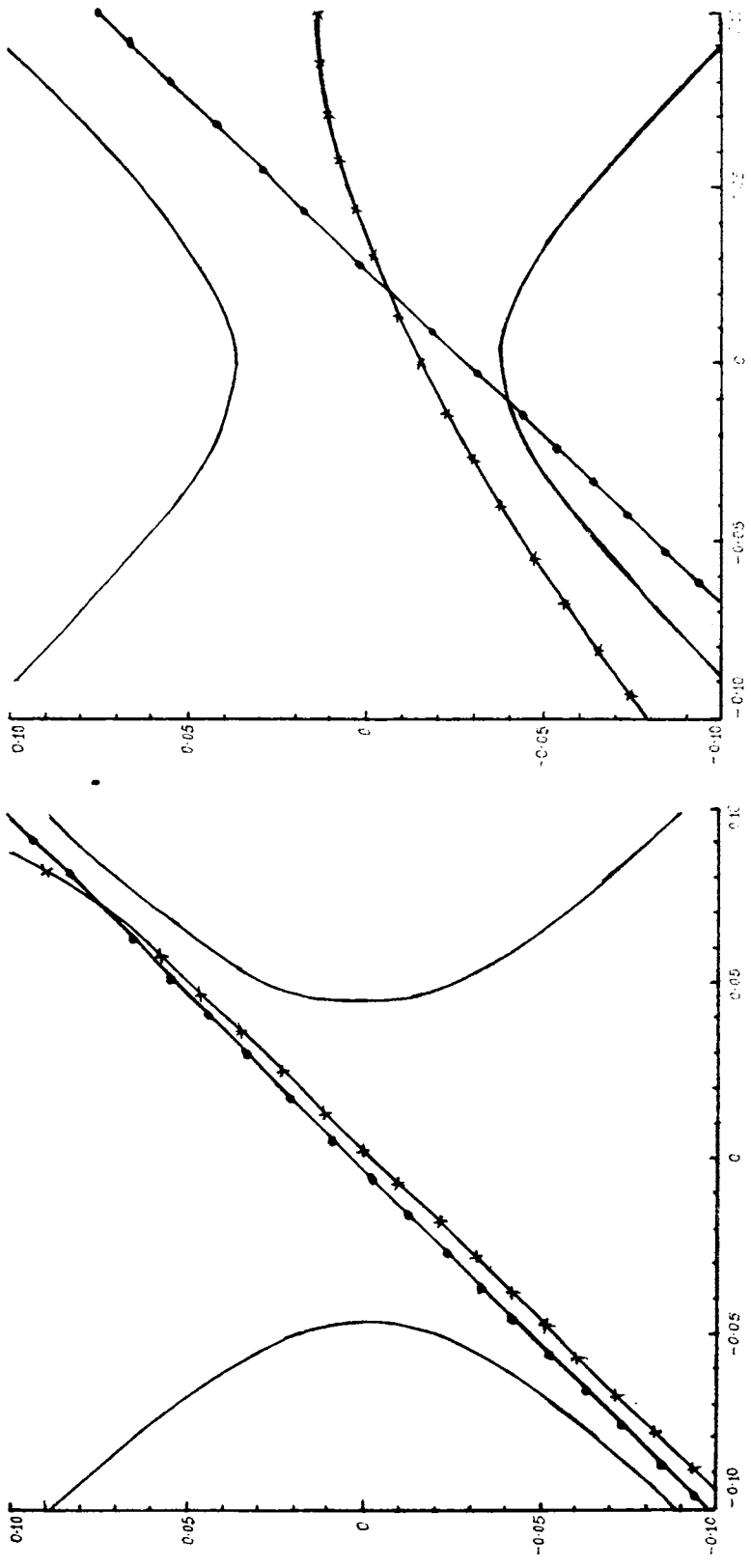

FIG. 2.12. $NH_4 - {}^{15}NH_4$

FIG. 2.13 ${}^{15}NH_4 - ND_4$

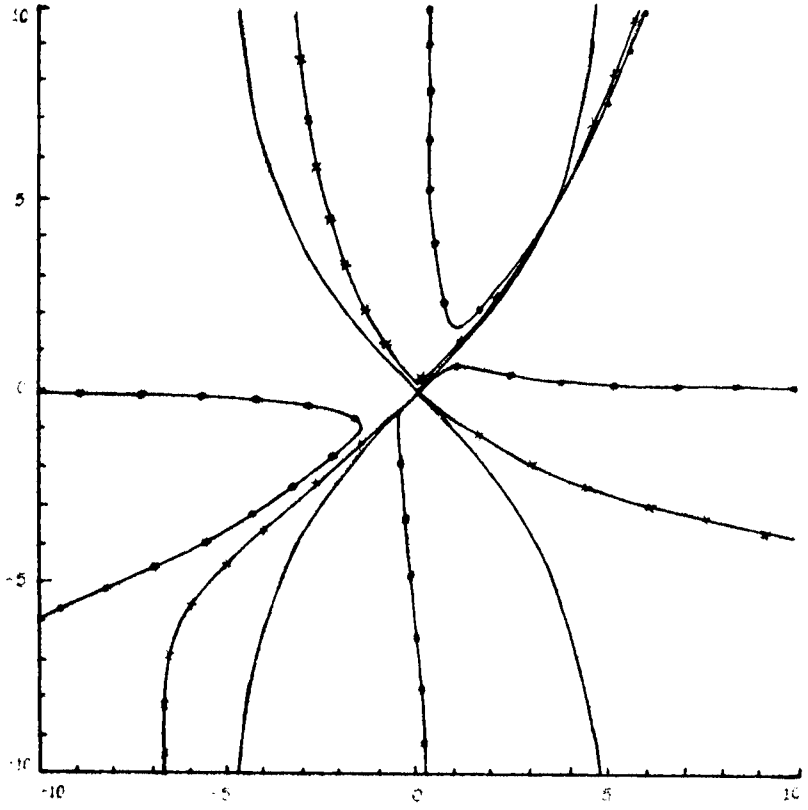

FIG.2.14. $SiH_4 - SiD_4$

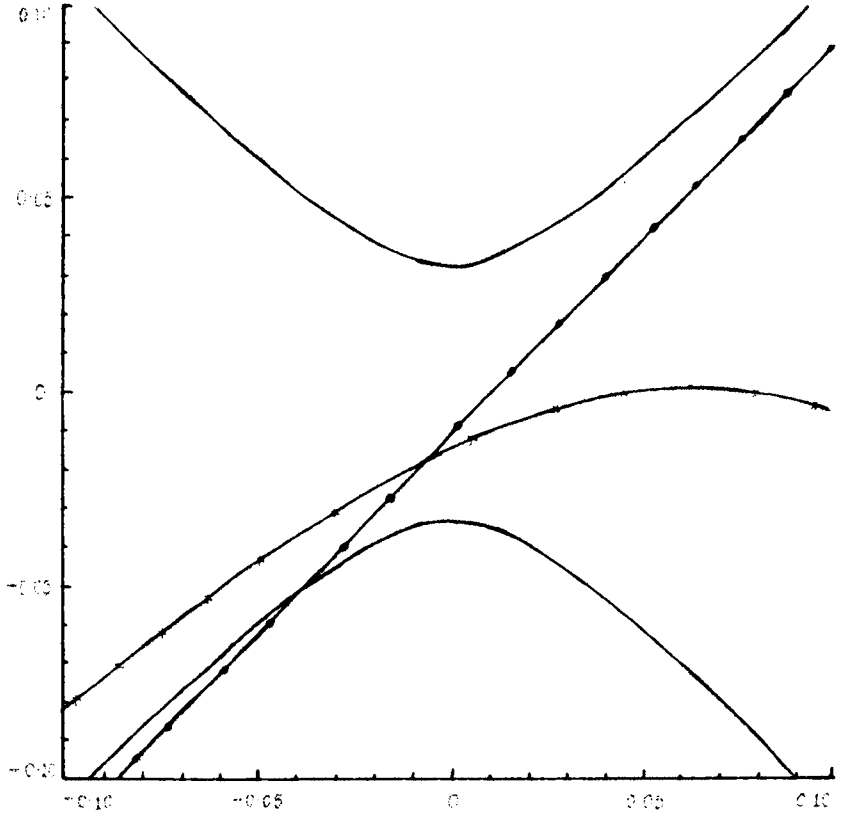

FIG.2.15. $SiH_4 - SiD_4$

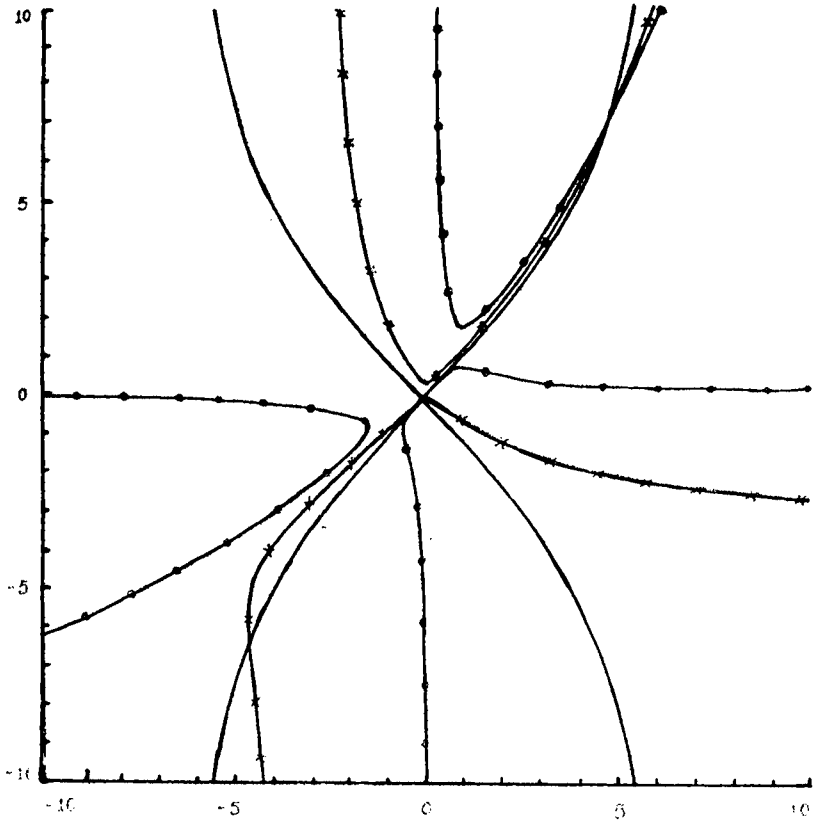

FIG. 2.16. $SiD_4 - SiT_4$

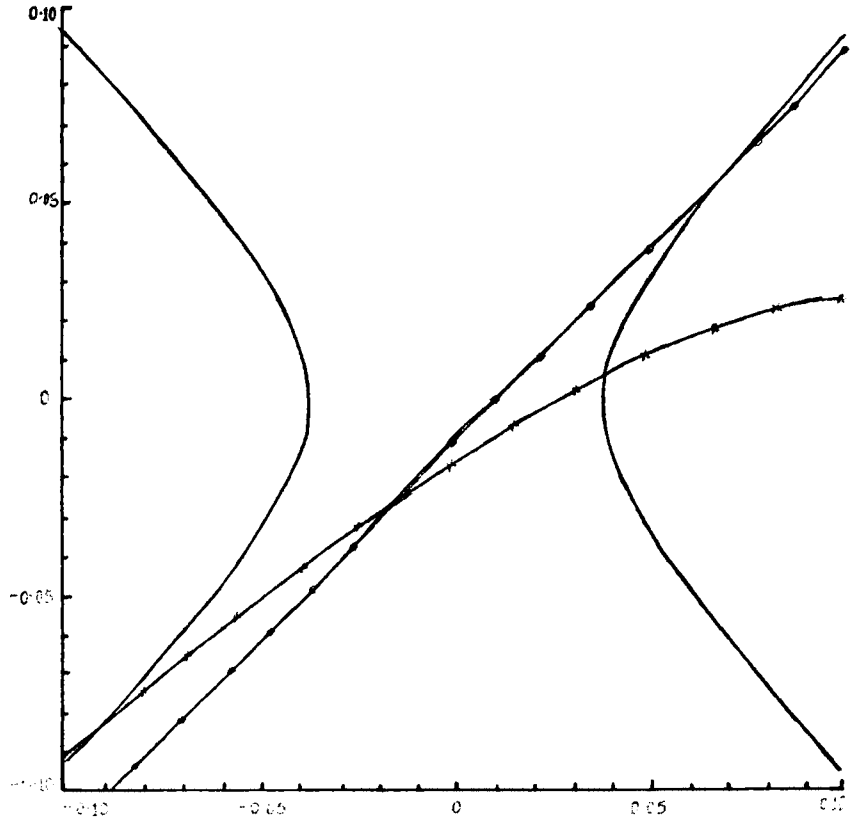

FIG. 2.17. $SiD_4 - SiT_4$

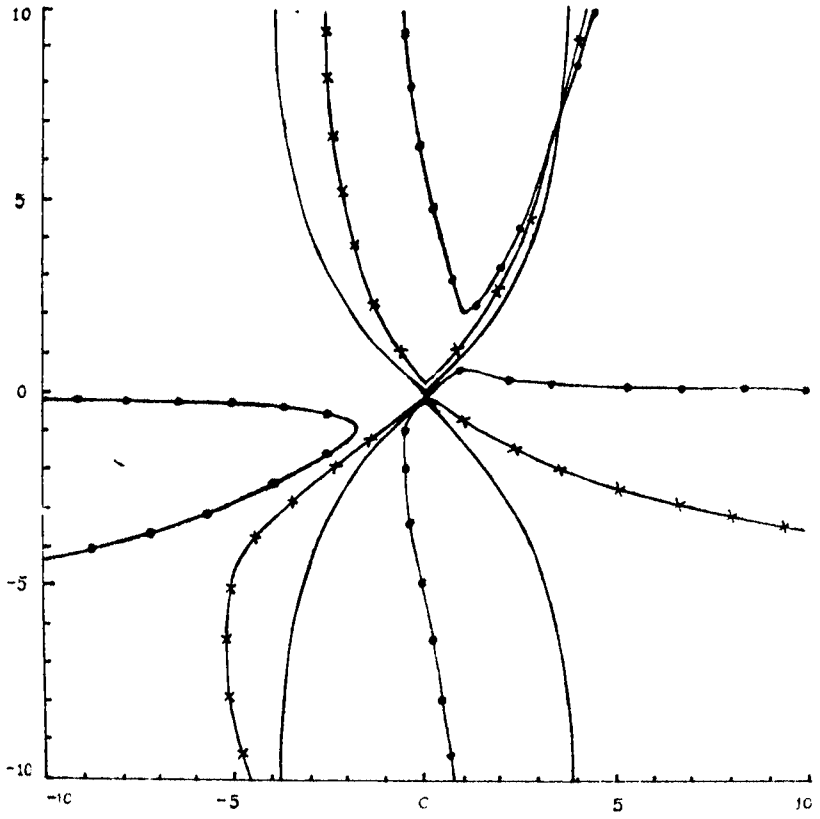

FIG. 2.18. $SiH_4 - SiT_4$

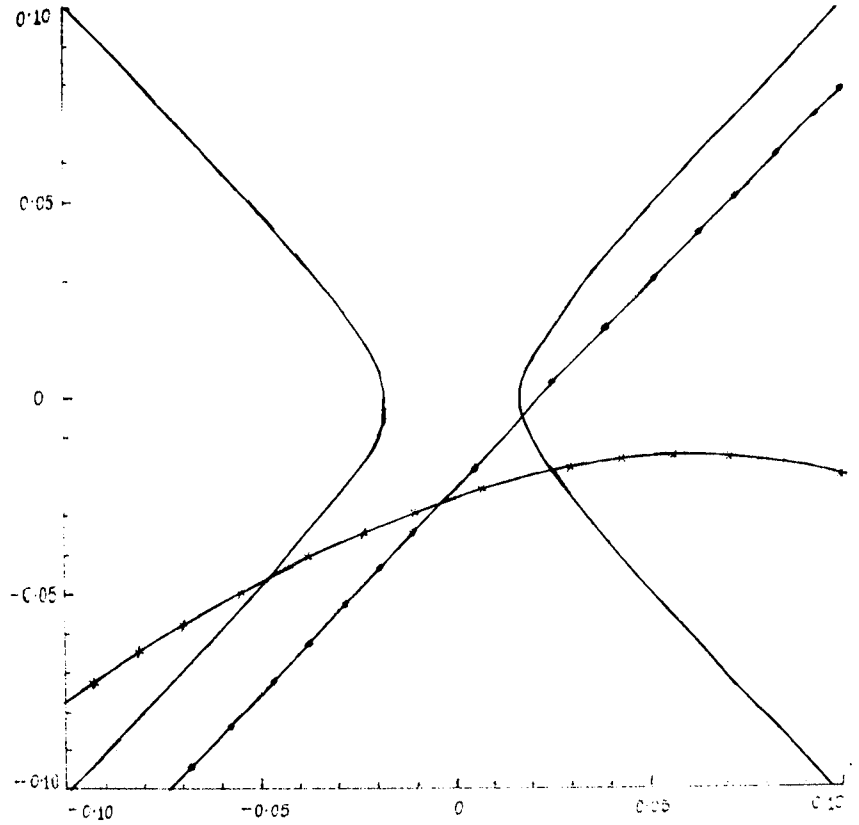

FIG. 2.19. $SiH_4 - SiT_4$

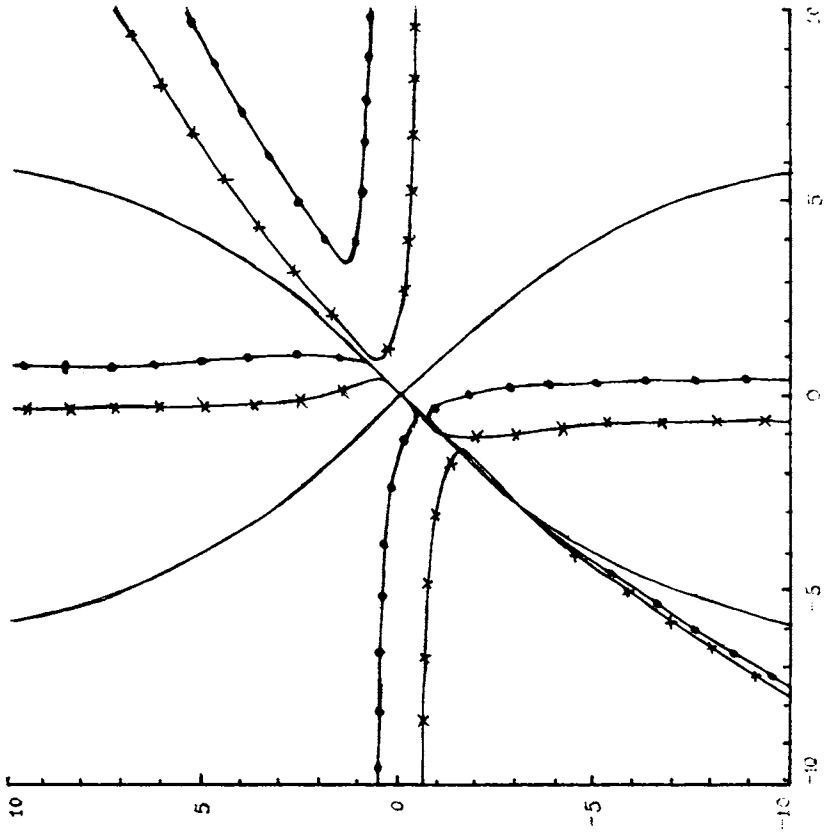

FIG. 2.21. $^{28}SiF_4 - {}^{30}SiF_4$

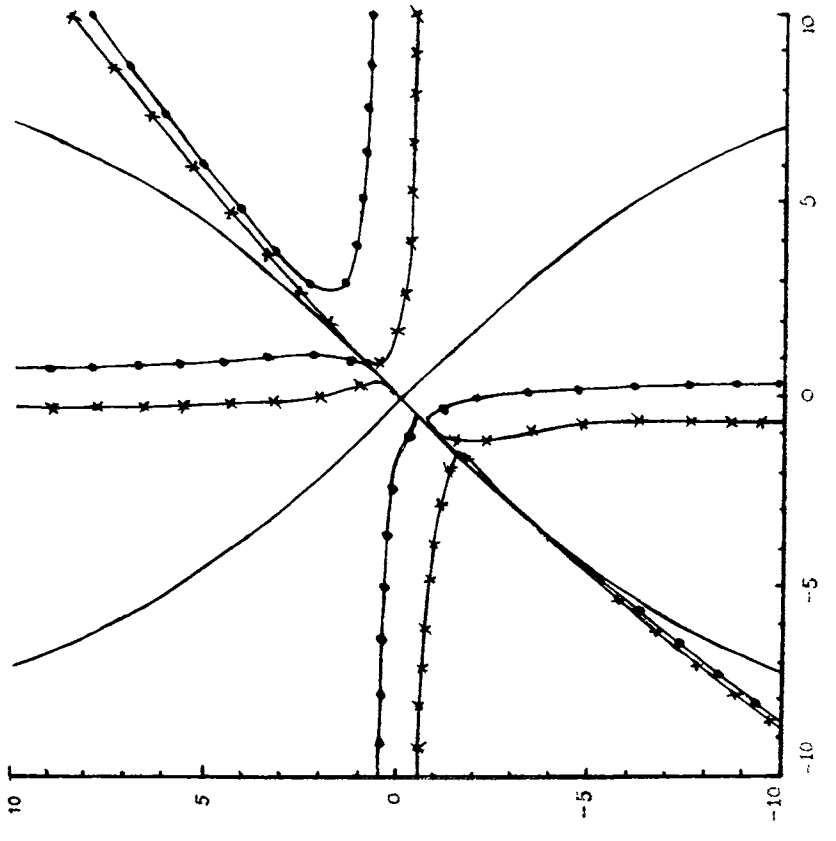

FIG. 2.20. $^{29}SiF_4 - {}^{30}SiF_4$

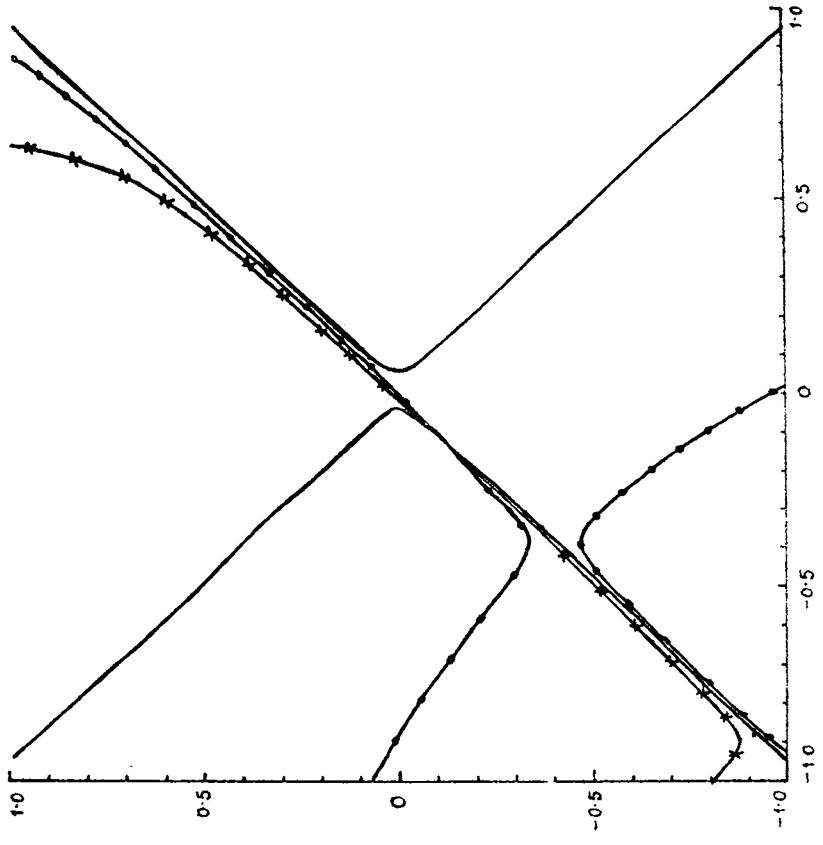

FIG. 2.23. $^{12}CF_4 - {}^{13}CF_4$

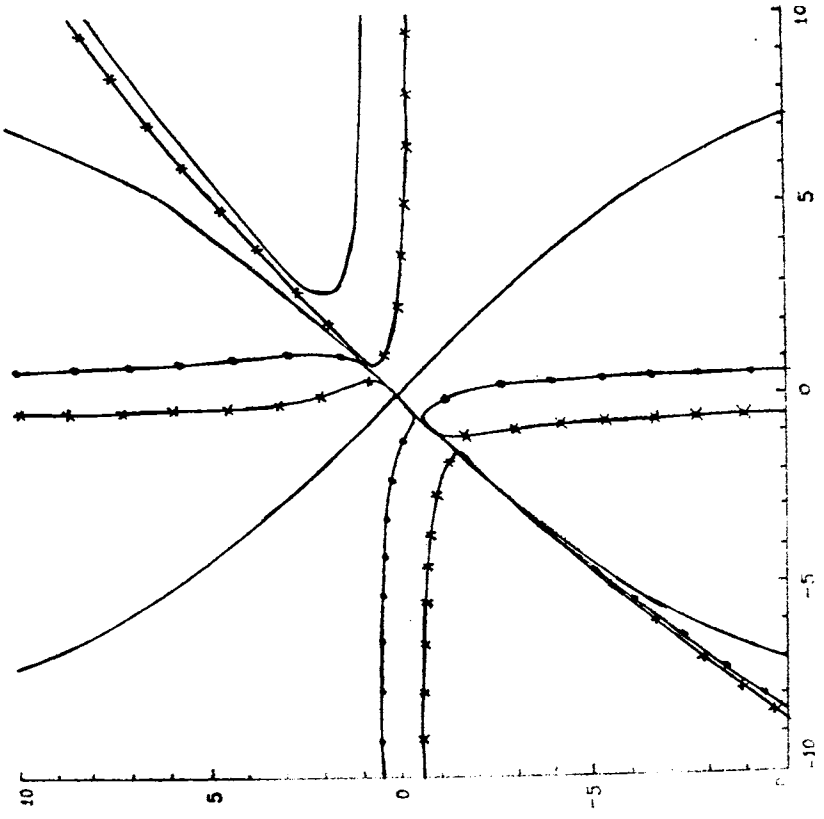

FIG. 2.22. $^{28}SiF_4 - {}^{29}SiF_4$

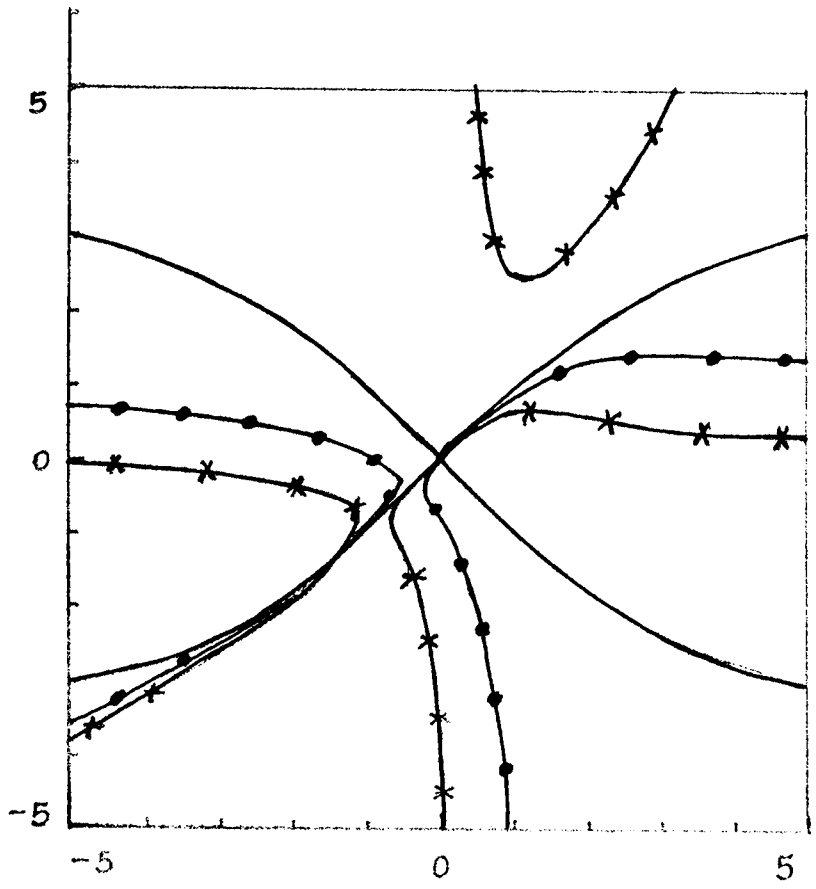

FIG. 2.24. $^{10}BF_4 - {}^{11}BF_4$

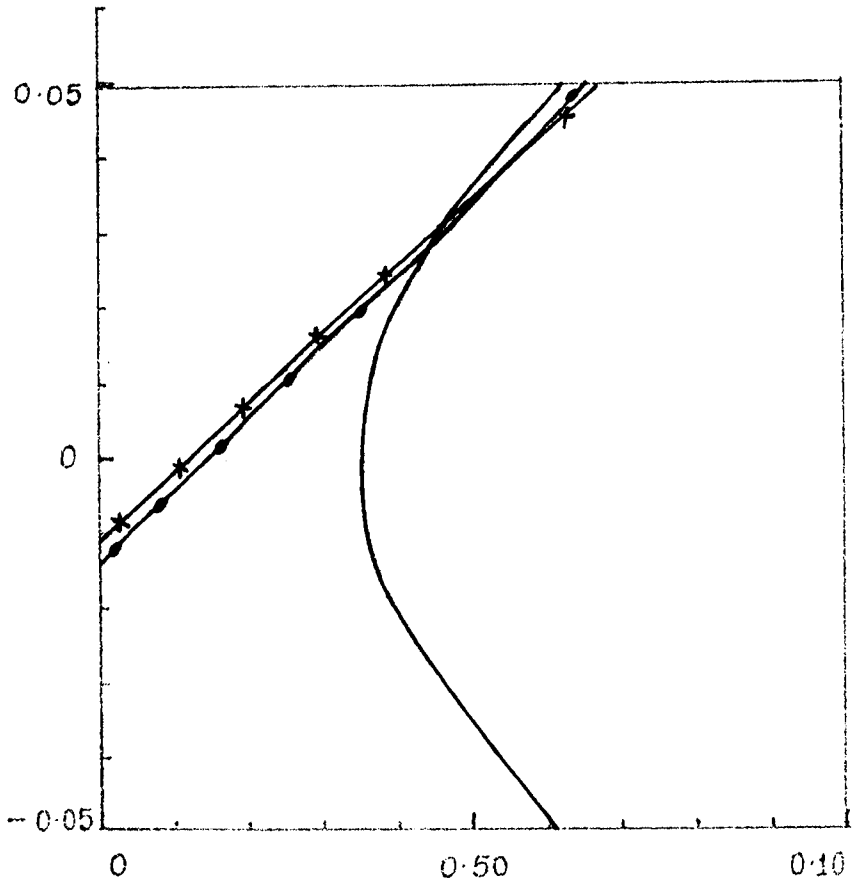

FIG. 2.25. $^{10}BF_4 - {}^{11}BF_4$

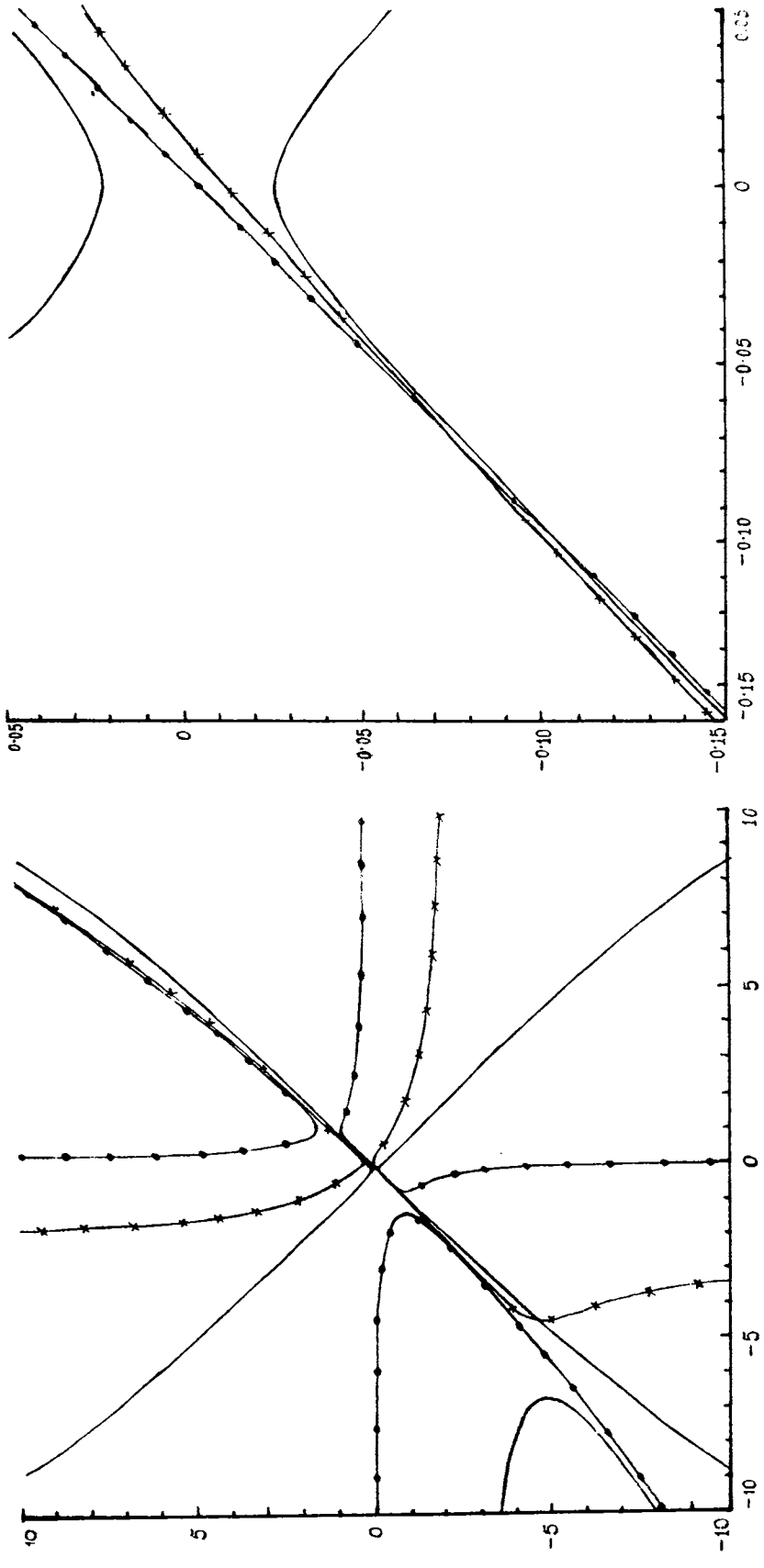

FIG. 2.26. $Xe^{16}O_4 - Xe^{16}O_4$

FIG. 2.27. $Xe^{16}O_4 - Xe^{18}O_4$

TABLE 2.1

DETAILS OF INTERSECTIONS OF c - c* CURVES FOR AMMONIUM ION†

Isotopic pair	Values of parameters corresponding to interesections					
	near origin			away from origin		
	c		c*	c		c*
$NH_4^+ - ND_4^+$	-0.0520	(F_{11}, F_{22})	-0.0480	4.1	(F_{11}, F_{12}, F_{22})	8.5
	+0.0165	(F_{11}, F_{12})	-0.0085			
	+0.0240	(F_{12}, F_{22})	-0.0045			
	+0.0255	(F_{11}, F_{22})	0.0000			
$ND_4^+ - NT_4^+$	+0.005	(F_{11}, F_{22})	-0.043	-		-
	-0.031	(F_{12}, F_{22})	-0.053			
	-0.075	(F_{12}, F_{11})	-0.097			
$^{15}NH_4 - ND_4$	-0.011	(F_{12}, F_{22})	-0.0385	3.9	(F_{11}, F_{12}, F_{22})	8.5
	+0.022	(F_{12}, F_{11})	-0.0050	-3.8	(F_{11}, F_{22})	-7.4

TABLE 2.1 contd.

Isotopic pair	Values of parameters corresponding to intersections					
	near origin			away from origin		
	c		c*	c		c*
$^{15}N\ H_4^+ - N\ T_4^+$	-0.0075	(F_{11}, F_{12}, F_{22})	-0.057	-		-
$N\ H_4^+ - {}^{15}N\ H_4^+$	+0.072	(F_{12}, F_{11})	+0.0720			
	-0.335	(F_{12}, F_{22})	-0.335			
$N\ T_4^+ - N\ H_4^+$	-0.047	(F_{11}, F_{22})	+ 0.031			
	-0.035	(F_{12}, F_{22})	+ 0.011	-4.35	(F_{11}, F_{22})	-3.2
	-0.061	(F_{12}, F_{11})	-0.013			

† Figures 2.2 to 2.13

TABLE 2.2

DETAILS OF INTERSECTIONS OF c - c* CURVES†

	Values of parameters corresponding to intersections			
	near origin		away from origin	
	c	c*	c	c*
	-0.004 (F_{11}, F_{12})	-0.0165	3.65 (F_{11}, F_{12}, F_{22})	4.95
Si H_4-Si D_4	-0.037 (F_{12}, F_{22})	-0.0500		
	- (F_{11}, F_{22})	-		
	-0.0900 (F_{11}, F_{22})	-0.0830		
	-0.0135 (F_{11}, F_{12})	-0.0240	4.00 (F_{11}, F_{12})	5.50
Si D_4-Si T_4	+0.0385 (F_{11}, F_{22})	+0.0070	4.78 (F_{12}, F_{22})	6.95
	+0.0710 (F_{22}, F_{12})	+0.0605	4.85 (F_{11}, F_{22})	7.25
	+0.025 (F_{11}, F_{22})	-0.0180		
	+0.018 (F_{12}, F_{22})	-0.0050	3.60 (F_{11}, F_{22})	7.20
Si H_4-Si T_4	-0.004 (F_{12}, F_{11})	-0.0260	3.45 (F_{11}, F_{12})	6.65
	-0.0465 (F_{11}, F_{22})	-0.0445		

† Figures. 2.14 to 2.19

TABLE 2.3

DETAILS OF INTERSECTIONS OF c - c* CURVES FOR Si F_4 †

Isotopic pair	Values of parameters corresponding to intersections					
	near origin			away from origin		
	c		c*	c		c*
$^{28}Si\ F_4$-$^{29}Si\ F_4$	-0.0366	(F_{11}, F_{12})	-0.0348	-2.80	(F_{11}, F_{12}, F_{22})	-2.90
	-0.0394	(F_{12}, F_{22})	-0.0376			
	-0.0425	(F_{22}, F_{11})	-0.0408			
	-0.0403	(F_{12}, F_{11})	-0.0386			
$^{29}Si\ F_4$-$^{30}Si\ F_4$	-0.0527	(F_{12}, F_{22})	-0.0507	-2.90	(F_{11}, F_{12}, F_{22})	-3.05
	-	(F_{11}, F_{22})	-			
	-0.0390	(F_{12}, F_{11})	-0.0355			
$^{28}Si\ F_4$-$^{30}Si\ F_4$	-0.0493	(F_{22}, F_{12})	-0.0458	-2.80	(F_{11}, F_{12}, F_{22})	-3.05
	-	(F_{11}, F_{22})	-			

† Figures 2.20. to 2.22

TABLE 2.4

DETAILS OF INTERSECTIONS OF c - c* CURVES†

Isotopic pair	Values of parameters corresponding to intersections			
	near origin		away from origin	
	c	c*	c	c*
$^{12}C\ F_4 - {}^{13}C\ F_4$	-0.1460	(F_{11}, F_{12}, F_{22}) -0.1422	-1.055	(F_{11}, F_{12}, F_{22}) -1.13
$Xe^{16}O_4 - Xe^{18}O_4$	-0.102	(F_{12}, F_{22}) -0.105		
	-0.074	(F_{11}, F_{12}) -0.077	-	-
	-	(F_{11}, F_{22}) -		
$^{11}B\ F_4^- - {}^{10}B\ F_4^-$	+0.0505	(F_{12}, F_{11}) +0.0357		
	+0.0470	(F_{22}, F_{11}) +0.0330	-1.5	-1.356
	+0.0460	(F_{22}, F_{12}) +0.0310		

† Figures 2.23 to 2.27

TABLE 2.5

SELECTED PARAMETER VALUES AND CORRESPONDING FORCE CONSTANTS

Molecule or ion	Parameter c		Force constants in mdyn /A		
	c_A	c_V	Actual set (using c_A)		Virtual set (using c_V)
$^{12}C\ F_4$	-0.1460	-1.055	F_{11}	6.4552	3.237
			F_{12}	-0.8206	1.599
			F_{22}	1.0115	2.600
$^{13}C\ F_4$	-0.1423	-1.130	F_{11}	6.4566	3.240
			F_{12}	-0.8209	1.609
			F_{22}	1.0114	2.607
$Xe\ ^{16}O_4$	-0.074 to -0.102		F_{11}	6.3722 $\pm$ 0.0435	
			F_{12}	0.2376 $\pm$ 0.0517	
			F_{22}	0.3723 $\pm$ 0.0064	

TABLE 2.5 contd.

Molecule or ion	Parameter c		Force constants in mdyn / A			
	c_A	c_V	Actual set			Virtual set
$Xe^{18}O_4$	-0.077 to -0.105		F_{11}	6.3679	± 0.0470	
			F_{12}	0.2382	± 0.0514	-
			F_{22}	0.3721	± 0.0066	
$^{11}B F_4^-$	0.0310 to 0.0357	-1.50	F_{11}	4.7939	± 0.0123	2.5703
			F_{12}	-0.9939	± 0.0049	-1.5582
			F_{22}	0.6454	± 0.0004	1.7640
$^{10}B F_4^-$	0.0460 to 0.0505	-1.35	F_{11}	4.7890	± 0.0138	2.5700
			F_{12}	-0.9927	± 0.0052	-1.5581
			F_{22}	0.6453	± 0.0003	1.7638

TABLE 2.5 contd.

$^{28}Si\ F_4$	-0.0425	-2.80	F_{11}	6.3370	1.7312
			F_{12}	-0.2587	-1.4336
			F_{22}	0.4396	2.7575
$^{29}Si\ F_4$	-0.0405	-2.90	F_{11}	6.3391	1.7207
			F_{12}	-0.2593	-1.4204
			F_{22}	0.4396	2.7529
$^{30}Si\ F_4$	-0.0386	-3.05	F_{11}	6.3405	1.7270
			F_{12}	-0.2600	-1.4278
			F_{22}	0.4396	2.7552
$Si\ H_4$	-0.004	3.45 to 3.65	F_{11}	3.0305	0.7814 ± 0.0116
			F_{12}	-0.0149	-0.5824 ± 0.0105
			F_{22}	0.2401	1.3650 ± 0.0046
$Si\ D_4$	-0.015	4.78 to 4.95	F_{11}	3.0320	0.7755 ± 0.0061
			F_{12}	-0.0159	-0.5794 ± 0.0060
			F_{22}	0.2391	1.3669 ± 0.0019
$Si\ T_4$	- 0.025	6.85 to 7.20	F_{11}	3.0315	0.7812 ± 0.0052
			F_{12}	-0.0181	-0.5802 ± 0.0055
			F_{22}	0.2411	1.3662 ± 0.0011

TABLE 2.5 contd

NH_4	-0.013 to -0.0255	4.1	F_{11}	6.0237	± 0.0210	1.8088
			F_{12}	-0.1174	± 0.0629	-1.2259
			F_{22}	0.5565	± 0.0007	2.6758
$^{15}NH_4$	-0.0075	3.9	F_{11}	6.0217		1.8267
			F_{12}	-0.0673		-1.2328
			F_{22}	0.5599		2.6750
ND_4	-0.031 to -0.0385	8.5	F_{11}	5.9844	± 0.0088	1.8164
			F_{12}	-0.0689	± 0.0117	-1.2328
			F_{22}	0.5595	± 0.0006	2.6772
NT_4	-0.057	-	F_{11}	6.0237		
			F_{12}	-0.0664		-
			F_{22}	0.5598		

TABLE 2.6

FORCE CONSTANTS OF SOME XY_4 TYPE MOLECULES AND IONS

Molecule or ion	Force constants in mdyn / A				
	Rresent Result		Previous Result		
C F_4	F_{11}	6.4559	6.489	6.22 ± 0.25	
	F_{12}	-0.8208	-0.827 [3]	0.84	[8]
	F_{22}	1.0115	1.010	1.01	
Xe O_4	F_{11}	6.3701 ± 0.0453	6.480		
	F_{12}	0.2379 ± 0.0516	0.110 [10]		
	F_{22}	0.3722 ± 0.0065	0.359		
Si F_4	F_{11}	6.3388	6.36	6.201	
	F_{12}	-0.2593	-0.269 [9]	0.194	[13]
	F_{22}	0.4396	0.439	0.445	
Si H_4	F_{11}	3.0305	3.032		
	F_{12}	-0.0163	-0.025 [8]		
	F_{22}	0.2401	0.240		
B F_4	F_{11}	4.7915	3.88	5.094	
	F_{12}	-0.9933 ± 0.0050	-0.53 [14]	0.8712	[15]
	F_{22}	0.6454	0.72	0.699	
N H_4	F_{11}	6.0224			
	F_{12}	-0.0667			
	F_{22}	0.5599			

TABLE 2.7

VALUES OF PARAMETER c FOR SOME XY_4 (T_d) MOLECULES.

Molecule	Solution nearer to $c = 0$		Solution outside the natural range	
	Present result	From graphical method	Present result	From graphical method
$^{12}C\ F_4$	-0.14444	-0.146	-1.06900	-1.055
$^{13}C\ F_4$	-0.14082	-0.1423	-1.14025	-1.130
$Xe^{16}\ O_4$	-0.07059	-0.074 to -0.102	12.92785	*
$Xe^{18}\ O_4$	-0.07327	-0.077 to -0.105	18.30733	*
$^{28}Si\ F_4$	-0.03700	-0.0425	-2.79852	-2.80
$^{29}Si\ F_4$	-0.03518	-0.0405	-2.92779	-2.90
$^{30}Si\ F_4$	-0.03343	-0.0386	-3.06144	-3.05
$Si\ H_4$	-0.00390	-0.004	3.58238	3.45 to 3.65
$Si\ D_4$	-0.01341	-0.015	4.79994	4.78 to 4.95
$Si\ T_4$	-0.02882	-0.025	7.20309	6.85 to 7.20

* In grephical method parameter was scanned in the range $-10 \leq c \leq 10$ and no intersection obtained in these cases.

TABLE 2.8

FORCE CONSTANTS USING ALGEBRAIC METHOD (mdyn /A)

Molecule	F_{ij}	Present result	Reported result	
H_2O	F_{11} (A_1)	8.3511	8.356 ± 0.011	8.342 ± 0.012
	F_{12} (A_1)	0.2777	0.366 ± 0.083 [4]	0.283 ± 0.270 [5]
	F_{22} (A_1)	0.7570	0.763 ± 0.002	0.769 ± 0.018
D_2O	F_{11} (A_1)	8.3472		8.389 ± 0.055
	F_{12} (A_1)	0.2784		0.272 ± 0.25 [5]
	F_{22} (A_1)	0.7589		0.764 ± 0.01
$^{10}B F_3$	F_{11} (F_2)	7.2425	7.220	7.120
	F_{12} (F_2)	-0.2899	-0.282 [16]	-0.247 [5]
	F_{22} (F_2)	0.5922	0.594	0.605
$^{11}B F_3$	F_{11} (F_2)	7.2423		7.129
	F_{12} (F_2)	-0.2898		-0.255 [5]
	F_{22} (F_2)	0.5923		0.600

TABLE 2.8 contd.

Molecule	F_{ij}	Present result	Reported result			
	F_{11} (F_2)	5.3804	5.383		5.386	
CH_4	F_{12} (F_2)	-0.2000	-0.206	[8]	-0.194	[5]
	F_{22} (F_2)	0.4577	0.458		0.458	
	F_{11} (F_2)	5.3804			5.388	
CD_4	F_{12} (F_2)	-0.1978			-0.196	[5]
	F_{22} (F_2)	0.4577			0.458	
	F_{11}(F_2)	5.3797				
CT_4	F_{12} (F_2)	-0.2052				
	F_{22} (F_2)	0.4580				

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CHAPTER III

BOND ASYMMETRY PARAMETER - THEORY AND APPLICATION TO BENT XY_2 TYPE MOLECULES

A bond asymmetry parameter η_b is defined in an attempt to study the spatial distribution of bonding forces about a chemical bond. This quantity is expressible in terms of the symmetry force constants. The theory developed is applied to bent XY_2 molecular model. Numerical results are obtained in a number of cases. Bond angle versus η_b and η_b versus percentage p-character curves are smooth. The force fields of some molecules are evaluated on the basis of the η_b value, determined from the η_b -bond angle graph and are found to be in good agreement with calculations previously reported in the literature.

CHAPTER III

BOND ASYMMETRY PARAMETER - THEORY AND APPLICATION TO BENT XY_2 TYPE MOLECULES

1. Introduction

Normal co-ordinate analysis provides a convenient method for the calculation of strengths of chemical bonds. Such analyses do not, however, reveal any kind of asymmetry that might be present in the constitution of bonds. Quantum mechanical studies of the electronic structure of molecules [1,2] indicate that the chemical bond is not, after all, a homogeneous geometrical entity, but is to be interpreted from a probability stand point that favours a heterogeneous composition. Typical among the factors affecting the bond homogeneity are electronegativity, π bonding and hybridization. Because of the enormous complexity of *ab initio* calculations using molecular orbitals, the information currently available regarding the force fields of even simple molecules is incomplete and consequently, asymmetries in bond strength in a plane at right angles to a bond are not obtained by this approach. However, a study of the directional asymmetry in bond strength is feasible within the framework of cartesian force constants. Introducing an asymmetry

parameter, a study of the spatial distribution of bonding forces between atoms in a molecule has been attempted. In the present chapter as well as in the succeeding ones the theory of the asymmetry parameter is applied to several simple molecular models.

2. Theory of asymmetry parameter

In Wilson's FG matrix formalism, the general expression for the vibrational potential energy of a molecule, in symmetry co-ordinates S, is of the form $2V = \tilde{S}FS$ (1.11). The symmetry co-ordinates S can be transformed into a set of cartesian displacement co-ordinates $\mathfrak{X}$ referred to the atom-fixed co-ordinate system which is oriented parallel to the principal axes through the relation

$$S = B\mathfrak{X} \qquad \ldots (3.1)$$

where B is the transformation matrix which depends on the geometry of the molecule and is constructed in terms of Wilson's s vectors [3]. The B matrix elements are the components of the s vectors. Using the transformation relation (3.1), the potential energy of the molecule is written in terms of the cartesian displacement co-ordinates as

$$2V = \tilde{\mathfrak{X}}\,\Phi\,\mathfrak{X} \qquad \ldots (3.2)$$

Here Φ given by

$$\Phi = \tilde{B} F B \qquad \ldots(3.3)$$

defines a symmetric force tensor of 3N x 3N cartesian force constants in the case of an N-atomic molecule. From the matrix representation of the force tensor Φ, blocks associated with each of the atoms, and blocks connecting one atom with another can be extracted separately. The block corresponding to any atom X and the block connecting an atom X with another atom Y have the following structure.

$$\Phi^X = \begin{vmatrix} \Phi^X_{z'z'} & \Phi^X_{z'x'} & \Phi^X_{z'y'} \\ \Phi^X_{x'z'} & \Phi^X_{x'x'} & \Phi^X_{x'y'} \\ \Phi^X_{y'z'} & \Phi^X_{y'x'} & \Phi^X_{y'y'} \end{vmatrix} \qquad \ldots(3.4)$$

$$\Phi^{XY} = \begin{vmatrix} \Phi^{XY}_{z'z''} & \Phi^{XY}_{z'x''} & \Phi^{XY}_{z'y''} \\ \Phi^{XY}_{x'z''} & \Phi^{XY}_{x'x''} & \Phi^{XY}_{x'y''} \\ \Phi^{XY}_{y'z''} & \Phi^{XY}_{y'x''} & \Phi^{XY}_{y'y''} \end{vmatrix} \qquad \ldots (3.5)$$

The labelling is such that Φ^X_{zz} is the z component of

the force tensor associated with atom X. '___ and "___ co-ordinate systems are associated with atoms X and Y.

These cartesian force constants are thus linear combinations of the generalised valence force constants and they represent the spatial distribution of bonding forces around atoms in a molecule. For a given atom, the spherically symmetric potential environment is indicated by $\Phi_{zz} = \Phi_{xx} = \Phi_{yy}$. For an asymmetrical environment, the components may not be of equal magnitude and the differences may be taken as a measure of the deviation from spherical symmetry.

The Φ matrix can be transformed tensorially with a rotation matrix R into a form referred to a bond based set of axes with the Z axis along the bond. R is constructed in block form by giving a common rotation to all atom-fixed axes so as to orient them parallel to the bond-based set of axes under consideration. The force tensor in a system with the z axis along the bond XY is given by

$$\mathcal{F} = \tilde{R}\,\Phi\,R \qquad \ldots (3.6)$$

$\mathcal{F}$ is called the bond force tensor. Thus for each bond there is an $\mathcal{F}$ matrix such that $\mathcal{F}^{X}_{zz}$ is the tensor component along the bond at X atom and $\mathcal{F}^{X}_{yy}$ and $\mathcal{F}^{X}_{xx}$ are the corresponding perpendicular components. The component along the bond is, naturally, the largest one.

In the theory of nuclear quadrupole resonance [4-6], an electric field gradient q is assumed to be existing at a nucleus, due to the asymmetrical distribution of electrons. Referred to an arbitrary set of axes, the components of q can be arranged in tensor form:

$$\begin{vmatrix} q_{x'x'} & q_{x'y'} & q_{x'z'} \\ q_{y'x'} & q_{y'y'} & q_{y'z'} \\ q_{z'x'} & q_{z'y'} & q_{z'z'} \end{vmatrix} \qquad \ldots (3.7)$$

Here $q_{x'x'}$ represents the field gradient along the x' axis given by $q_{x'x'} = -\frac{\partial^2 V}{\partial x'^2}$, V being the electric potential. Transforming to the principal system of axes, the three principal components, which are ordered as $q_{zz} \geq q_{yy} \geq q_{xx}$, are obtained. From these components an asymmetry parameter η is defined for the field gradient at the nucleus:

$$\eta = \frac{q_{xx} - q_{yy}}{q_{zz}} \qquad \ldots (3.8)$$

such that $0 \leq \eta \leq 1$.

By a similar approach, an asymmetry parameter is introduced for the distribution of bonding forces within a molecule. The cartesian force const-

ants $\mathcal{F}_{\alpha\beta}$ (α , β = x, y, z), being the second derivatives of the vibrational potential energy V, can be taken to be the components of a tensor similar to q. Therefore, a bond asymmetry parameter η_b is defined to characterise the non-symmetric spatial distribution of bonding forces around the centre of a bond b between two atoms X and Y as:

$$\eta_b = \frac{\frac{1}{2}\left\{\mathcal{F}^X_{xx} + \mathcal{F}^Y_{xx}\right\} - \frac{1}{2}\left\{\mathcal{F}^X_{yy} + \mathcal{F}^Y_{yy}\right\}}{\frac{1}{2}\left\{\mathcal{F}^X_{zz} + \mathcal{F}^Y_{zz}\right\}}$$

$$= \frac{\left\{\mathcal{F}^X_{xx} + \mathcal{F}^Y_{xx}\right\} - \left\{\mathcal{F}^X_{yy} + \mathcal{F}^Y_{yy}\right\}}{\left\{\mathcal{F}^X_{zz} + \mathcal{F}^Y_{zz}\right\}} \quad \ldots (3.9)$$

From the definition it is clear that limits of

$\eta_b = -1 \leq \eta_b \leq 1.$

3. Application to Bent XY_2 type Molecules

Bent symmetric XY_2 type molecules belong to the point group C_{2V}. The molecular geometry and the principal system of axes are shown in Fig. 3.1. The y-axis is taken to be normal to the molecular plane and z direction is along the C_2 axis. The three possible

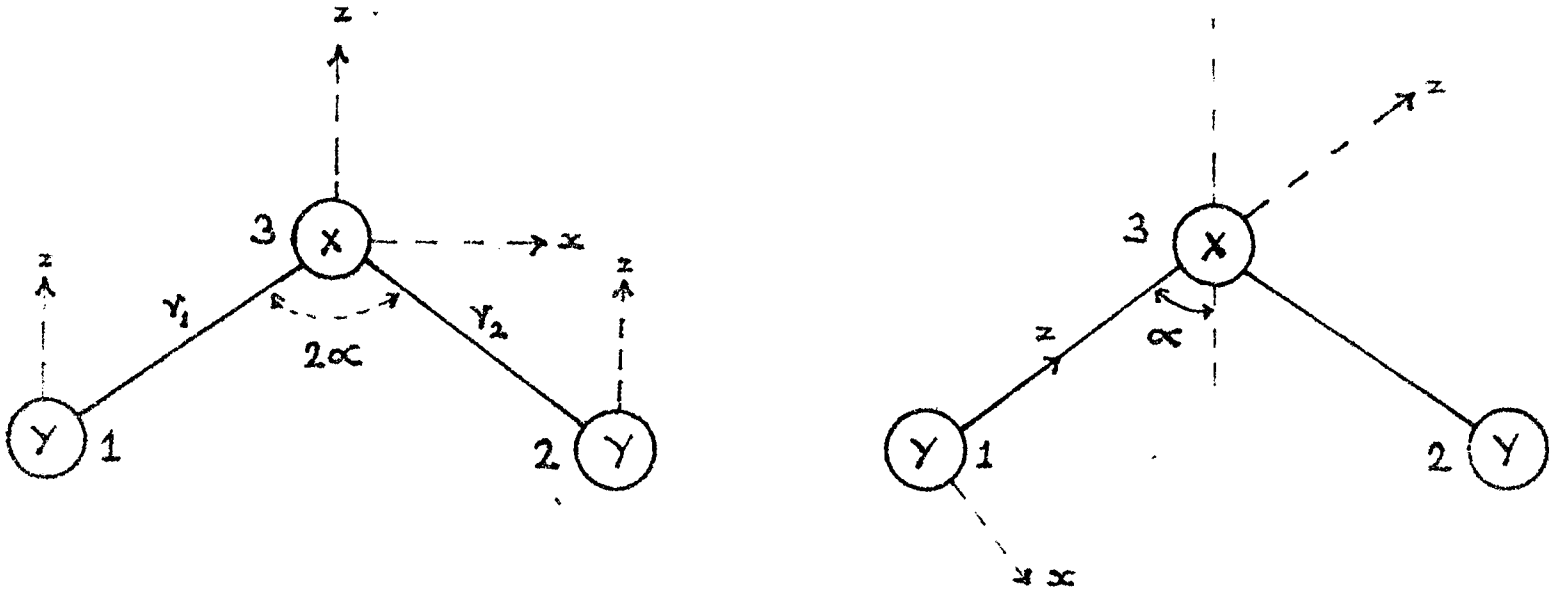

FIG.3.1. XY_2 (C_{2v}) molecular model: Internal co-ordinates and system of axes (a) Principal axes (b) Bond based axes.

fundamental modes of vibrations are classified as $2a_1 + b_1$. The corresponding symmetry co-ordinates [7] are:

a_1 species:

$$S_1 = \frac{1}{\sqrt{2}} (\Delta r_1 + \Delta r_2)$$

$$S_2 = r \Delta \alpha$$

b_1 species:

$$S_3 = \frac{1}{\sqrt{2}} (- \Delta r_1 + \Delta r_2) \qquad \ldots (3.10)$$

where Δr_1 and Δr_2 refer to changes in $X - Y_1$ and $X-Y_2$ bond lengths and $\Delta\alpha$ to change in the interbond angle YXY. The symmetry F matrix elements in terms of valence force constants are written as

a_1 species:

$$F_{11} = f_r + f_{rr}$$

$$F_{12} = \sqrt{2} \; f_{r\alpha}$$

$$F_{22} = f_\alpha$$

b_1 species:

$$F_{33} = f_r - f_{rr} \qquad \ldots (3.11)$$

Here f_r is stretching force constant and f_α the bending constant. f_{rr} and $f_{r\alpha}$ are the interaction force constants.

B matrix

For each symmetry co-ordinates, the components of the s vectors, which constitute the B matrix are given below:

S_1

Atom	x	y	z
1	$-\frac{\sin\alpha}{\sqrt{2}}$	0	$-\frac{\cos\alpha}{\sqrt{2}}$
2	$\frac{\sin\alpha}{\sqrt{2}}$	0	$-\frac{\cos\alpha}{\sqrt{2}}$
3	0	0	$\sqrt{2}\cos\alpha$

S_2

Atom	x	y	z
1	$-\cos\alpha$	0	$\sin\alpha$
2	$\cos\alpha$	0	$\sin\alpha$
3	0	0	$-2\sin\alpha$

S_3

Atom	x	y	z
1	$\frac{\sin\alpha}{\sqrt{2}}$	0	$\frac{\cos\alpha}{\sqrt{2}}$
2	$\frac{\sin\alpha}{\sqrt{2}}$	0	$-\frac{\cos\alpha}{\sqrt{2}}$
3	$-\sqrt{2}\sin\alpha$	0	0

...(3.12)

The elements of the inverse kinetic energy matrix G are

$$G_{11} = 2\mu_x \cos^2\alpha + \mu_y$$

$$G_{12} = -\sqrt{2}\mu_x \sin\alpha$$

$$G_{22} = 4\mu_x \sin^2\alpha + 2\mu_y$$

$$G_{aa} = 2\mu_x \sin^2\alpha + \mu_y \qquad \ldots (3.13)$$

where μ_x and μ_y are the reciprocal masses of atoms X and Y respectively.

The force tensor Φ referred to the principal system of axes is obtained from the F and B matrices. Components of Φ belonging to the block corresponding to atom 1 are of the form:

$$\Phi^1_{xx} = \frac{1}{2}(F_{11} + F_{33}) \sin^2\alpha + F_{22} \cos^2\alpha + \sqrt{2}\, F_{12} \sin\alpha \cos\alpha .$$

$$\Phi^1_{zz} = \frac{1}{2}(F_{11} + F_{33}) \cos^2\alpha + F_{22} \sin^2\alpha - \sqrt{2}\, F_{12} \sin\alpha \cos\alpha$$

$$\Phi^1_{xz} = \left\{\frac{1}{2}(F_{11} + F_{33}) - F_{22}\right\} \sin\alpha \cos\alpha + \frac{1}{\sqrt{2}} F_{12} \cos 2\alpha$$

$$\Phi^1_{yy} = 0$$

$$\Phi^1_{xy} = 0$$

$$\Phi^1_{yz} = 0 \qquad \ldots (3.14)$$

All the force tensor components for atom 2 are identically equal to the corresponding components for atom 1 except Φ^2_{xz} which is the negative of Φ^1_{xz}. This is in accordance with expectation, since identical cartesian force components indicate the same type of potential environment

for symmetrically equivalent atoms in the molecule.

For atom 3 only two components are different from zero. They are:

$$\Phi^3_{xx} = 2 \sin^2\alpha . F_{33}$$

$$\Phi^3_{zz} = 2 \cos^2\alpha . F_{11} + 4 F_{22} \sin^2\alpha$$

$$-2\sqrt{2} F_{12} \sin 2\alpha . \qquad \ldots (3.15)$$

The transformation of Φ to a co-ordinate system with the z-axis along the bond connecting atoms 1 and 3 is accomplished by an anticlockwise rotation through $(2\pi - \alpha)$ about the y-axis. For an atom, if the Φ components are arranged in the form

$$\Phi = \begin{vmatrix} \Phi_{zz} & \Phi_{zx} & \Phi_{zy} \\ \Phi_{xz} & \Phi_{xx} & \Phi_{xy} \\ \Phi_{yz} & \Phi_{yx} & \Phi_{yy} \end{vmatrix}$$

the relevant block of the rotation matrix R is

$$\begin{vmatrix} \cos(2\pi - \alpha) & \sin(2\pi - \alpha) & 0 \\ -\sin(2\pi - \alpha) & \cos(2\pi - \alpha) & 0 \\ 0 & 0 & 1 \end{vmatrix} \qquad \ldots (3.16)$$

The resultant force tensor $\mathcal{F}$ referred to the bond - based set of axes is given by (3.6). The components of $\mathcal{F}$ along

the three mutually perpendicular directions are

$$\mathcal{F}_{zz} = \Phi_{zz}\cos^2\alpha + \Phi_{xx}\sin^2\alpha + \Phi_{xz}\sin 2\alpha$$

$$\mathcal{F}_{yy} = \Phi_{yy}$$

$$\mathcal{F}_{xx} = \Phi_{zz}\sin^2\alpha + \Phi_{xx}\cos^2\alpha - \Phi_{xz}\sin 2\alpha$$

... (3.17)

The force tensor components for atoms 1 and 3 are given by the relations

$$\mathcal{F}^1_{xx} = 2(F_{11} + F_{33})\sin^2\alpha\cos^2\alpha + 4F_{22}\sin^4\alpha - 4\sqrt{2}\sin^3\alpha \cdot \cos\alpha \cdot F_{12}.$$

$$\mathcal{F}^1_{yy} = 0$$

$$\mathcal{F}^1_{zz} = 2F_{11}\cos^4\alpha + 2F_{33}\sin^4\alpha + \sin^2 2\alpha \cdot F_{22} - 4\sqrt{2}F_{12}\sin\alpha\cos^3\alpha .$$

... (3.18)

$$\mathcal{F}^3_{xx} = F_{22}$$

$$\mathcal{F}^3_{yy} = 0$$

$$\mathcal{F}^3_{zz} = \frac{1}{2}(F_{11} + F_{33})$$ ... (3.19)

The bond asymmetry parameter η_b is expressed as

$$\eta_b = \frac{\left\{\mathcal{F}^1_{xx} + \mathcal{F}^3_{xx}\right\} - \left\{\mathcal{F}^1_{yy} + \mathcal{F}^3_{yy}\right\}}{\left\{\mathcal{F}^1_{zz} + \mathcal{F}^3_{zz}\right\}}$$

substituting the relations (3.18) and 3.19)

$$\eta_b = \left\{ 4\,(F_{11} + F_{33})\,\sin^2\alpha\,\cos^2\alpha + 2\,F_{22}\,(4\sin^4\alpha + 1) - 8\sqrt{2}\,F_{12}\sin^3\alpha\,\cos\alpha \right\} \Big/ \left\{ F_{11}\,(4\cos^4\alpha + 1) + F_{33}\,(4\sin^4\alpha + 1) + 8\sin\alpha\,\cos^2\alpha\,(\sin\alpha\,.\,F_{22} - F_{12}\sqrt{2}\,\cos\alpha) \right\} \quad \ldots (3.20)$$

Results and discussion

The theory developed above is applied to a number of XY_2 molecules for which established valence force fields exist [8-18] . The data used in the investigation are given in Table 3.1. The bond asymmetry parameter and cartesian force constants refered to atom-fixed axis are listed in Table 3.2. The cartesian force constants have been found to be in agreement with the King - Zelano square sum rule [19],

$$\sum_i \nu_i^2 = \frac{N_o}{(2\pi c)^2} \sum_a \mu_a \nabla_a^2 V \qquad \ldots (3.21)$$

where ν_i denotes the i^{th} frequency; μ_a the reciprocal mass of atom a; ∇_a^2 the Laplacian for atom a; N_o the Avogadro number and V the potential energy of the molecule.

The magnitude of η_b is within the proposed limits (o, 1) and is found to be decreasing with increase of bond angle (Fig.3.2), which is a clear indication of the effect of hybridization on the distribution of bonding forces. To investigate this dependence further, η_b is plotted against percentage p-character (Fig.3.3). The latter quantity is given by the formula [1]

$$\% \text{ p character} = \frac{-100}{\cos 2\alpha - 1} \qquad \ldots (3.22)$$

where 2α is the bond angle. The η_b versus percentage p-character curve is a smooth one. It registers first an increase in η_b and then a gradual flattening with increase of percentage p-character. Increase of η_b with p-character is suggestive of the fact that with the greater mixing of p orbitals in the molecular orbitals, the bonding strength increases in the region away from the bond axis.

Though the $\eta_b - 2\alpha$ curve must in principle intersect the axis at 180° corresponding to cylindrical symmetry about the bond axis, the actual intersection point could not be precisely determined owing to paucity of data relating to large bond angle values.

The smooth graphical relations, bond angle versus η_b and percentage p-character versus η_b, suggest η_b may be yet another characteristic parameter for molecules. With

a view to ascertaining this, force fields of several molecules are evaluated using η_b values estimated from the $\eta_b - 2\alpha$ graph. The calculation makes use of the parametric representation of force constants (2.10 to 2.12) which yields the following expression for η_b :

$$\eta_b = \frac{P c^2 + Qe + R}{P' c^2 + Q' c + P'} \qquad \ldots (3.23)$$

where

$$P = 2\Lambda_1 \left\{ \frac{G_{11}}{|G|} + 2k^2 \sin^2 \alpha \right\} + (\sin 2\alpha)^2 \left\{ \frac{\Lambda_2}{G_{11}} + F_{33} \right\}$$

$$Q = \frac{4k (\Lambda_2 - \Lambda_1) \sin \alpha \sin 2\alpha}{\sqrt{G_{11}}}$$

$$R = 2\Lambda_2 \left\{ \frac{G_{11}}{|G|} + 2k^2 \sin^2 \alpha \right\} + (\sin 2\alpha)^2 \left\{ \frac{\Lambda_1}{G_{11}} + F_{33} \right\}$$

$$P' = \Lambda_1 \left\{ 4k^2 \cos^2 \alpha + \frac{G_{12}^2}{G_{11} |G|} \right\} + \frac{\Lambda_2}{G_{11}} (4 \cos^4 \alpha + 1) + F_{33} (4 \sin^4 \alpha + 1)$$

$$Q' = \frac{8\cos^3\alpha \quad k(\lambda_2 - \lambda_1)}{\sqrt{G_{11}}} - \frac{2G_{12} \quad (\lambda_2 - \lambda_1)}{G_{11} \quad |G|^{1/2}}$$

$$R' = \lambda_2 \left\{ 4k^2 \cos^2\alpha + \frac{G_{12}^2}{G_{11}|G|} \right\} + \frac{\lambda_1}{G_{11}}$$

$$(4\cos^4\alpha + 1) + F_{33}(4\sin^4\alpha + 1).$$

$$k = -\frac{\sqrt{2G_{11}} \quad \sin\alpha}{|G|^{1/2}} - \frac{G_{12} \quad \cos\alpha}{\sqrt{G_{11}} \quad |G|^{1/2}}$$

With the η_b value obtained from the graph, (3.23) can be solved for the parameter c, from which the force constants are calculated. The results are entered in Table 3.3. and compared with values reported earlier. Reasonable agreement between the two sets of values indicates that η_b is another molecular parameter that can be used with advantage in molecular force field problems.

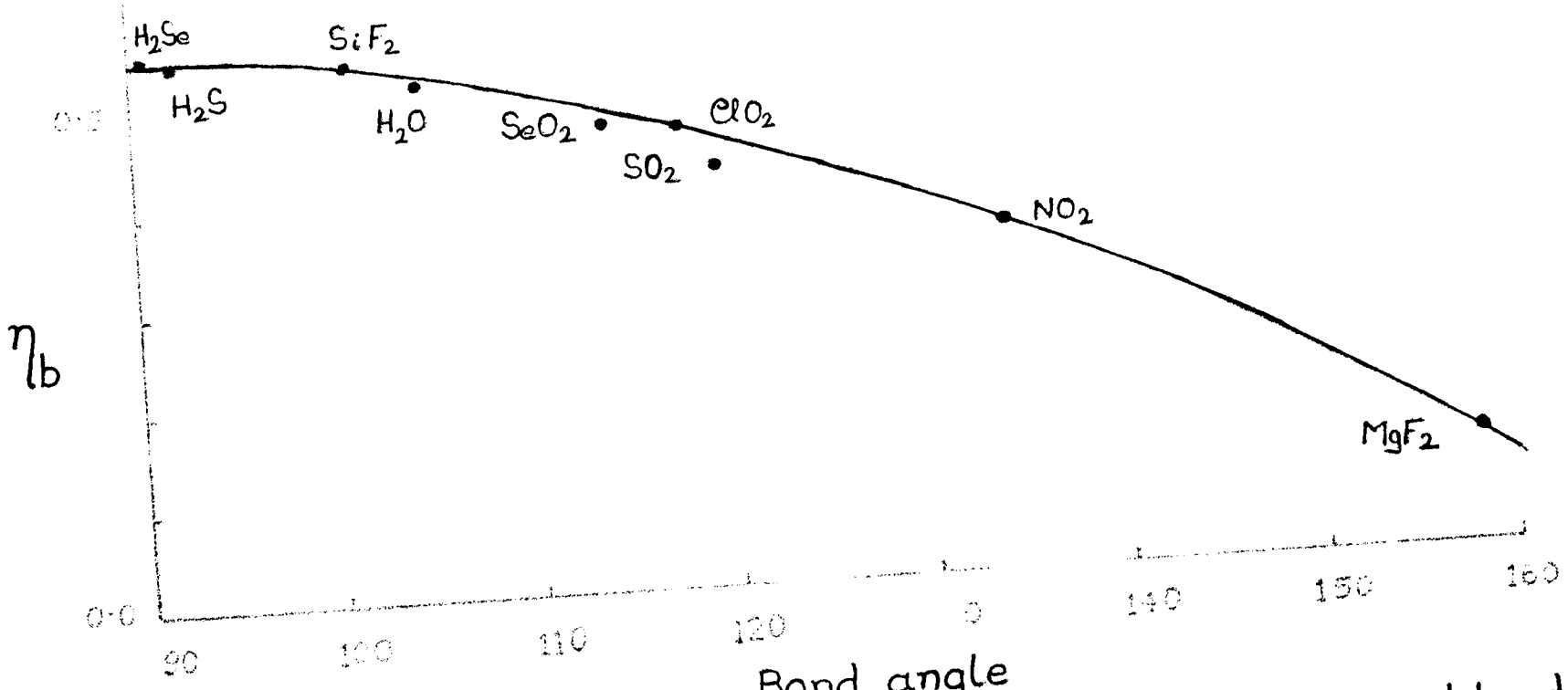

FIG. 3.2. Relation between bond asymmetry parameter η_b and bond angle 2α for XY_2 (C_{2v}) type molecules

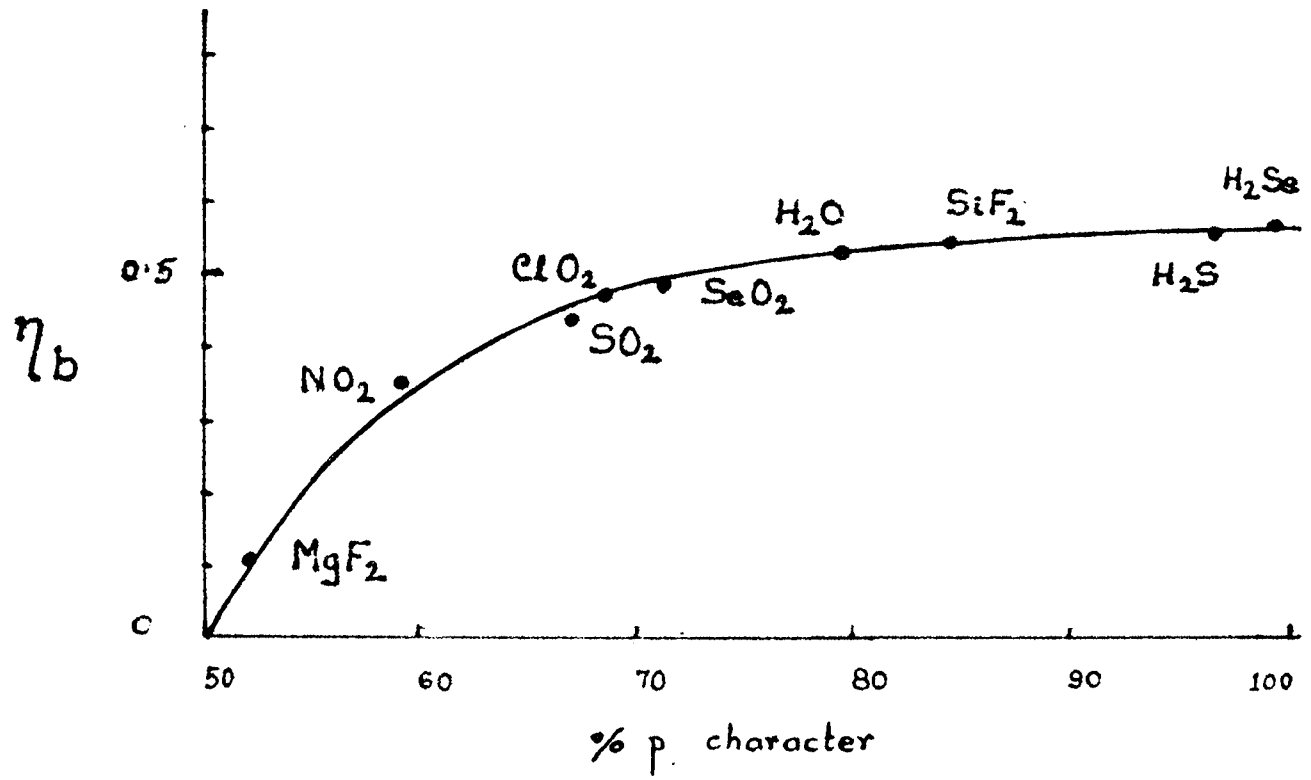

FIG.3.3. Relation between bond asymmetry parameter η_b and percentage p-character for XY_2 (C_{2V}) type molecules.

TABLE 3.1

BOND ANGLE AND SYMMETRY FORCE CONSTANTS

Molecule	Angle	Symmetry force constants md/Å				Ref.
		F_{11}	F_{12}	F_{22}	F_{33}	
H_2 Se	90° 34'	3.480	0.1386	0.334	3.530	8, 9
H_2 S	92° 12'	4.246	0.3096	0.449	4.296	8, 10
H_2 O	104° 31'	8.356	0.3478	0.762	8.554	8, 11
S O_2	119° 19'	10.413	0.3210	0.815	10.251	12
N O_2	134° 4'	13.183	0.6801	1.109	8.903	13
Cl O_2	117° 36'	6.848	0.0085	0.651	7.188	14, 15
Si F_2	100° 53'	5.329	0.1736	0.440	4.709	16
Mg F_2	158°	2.46	0.02	0.14	3.16	17
Se O_2	113° 50'	6.93	0.0131	0.488	6.80	18

TABLE 3.2

CARTESIAN FORCE CONSTANTS AND ASYMMETRY PARAMETER

Molecule	Percentage p-character	Cartesian force constants md/A				η_b
		Φ^x_{xx}	Φ^x_{yy}	Φ^y_{xx}	Φ^y_{yy}	
H_2 Se	99.00	3.564	3.730	2.033	1.8065	0.5568
H_2 S	96.30	4.462	4.142	2.653	2.068	0.5531
Si F_2	84.12	5.560	4.884	3.273	2.175	0.5437
H_2 O	79.96	10.696	7.218	5.810	3.407	0.5200
Se O_2	71.24	9.548	5.466	4.973	2.380	0.4719
Cl O_2	68.34	10.520	5.562	5.316	2.355	0.4671
S O_2	67.14	15.274	6.946	8.103	3.043	0.4210
N O_2	59.00	15.092	6.388	9.873	2.274	0.3555
Mg F_2	51.89	6.089	0.697	2.718	0.232	0.1163

TABLE 3.3

SYMMETRY FORCE CONSTANTS

Molecule	η_b from graph.	Symmetry force constants mdyn/A°					
		Present result		Previous result			
Ge F_2	0.5525	F_{11}	4.3740	4.3704			
		F_{12}	0.0504	0.0407	[20]		
		F_{22}	0.3135	0.3139			
S Cl_2	0.5425	F_{11}	2.9733				
		F_{12}	0.1507				
		F_{22}	0.2683				
O F_2	0.5350	F_{11}	6.118	5.56		6.475	
		F_{12}	0.983	0.60	[21]	1.396	[22]
		F_{22}	0.713	0.68		0.825	
O Cl_2	0.5000	F_{11}	4.086	3.96			
		F_{12}	0.493	0.47	[21]		
		F_{22}	0.416	0.40			

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CHAPTER IV

BOND ASYMMETRY PARAMETER - APPLICATION TO PLANAR XY_3 TYPE MOLECULES

The theory of bond asymmetry parameter introduced in Chapter III to characterise inhomogeneities associated with chemical bonds, is applied to planar XY_3 type molecules. Numerical calculations show that this molecular type has a constant value (0.48) for the bond asymmetry parameter η_b.

CHAPTER IV

BOND ASYMMETRY PARAMETER - APPLICATION TO PLANAR XY_3 TYPE MOLECULES

Planar symmetrical XY_3 type molecules belong to the point group D_{3h}. The molecular geometry and the principal system of axes are shown in Fig. 4.1. The y-axis is taken to be normal to the molecular plane and the z-axis lies along the bond connecting atoms 4 and 1. With three species of normal vibrations, the fundamental modes are classified as $1a' + 1a'' + 2e'$. The symmetry co-ordinates used are:

a_1 species:

$$S_1 = \frac{1}{\sqrt{3}} (\Delta r_1 + \Delta r_2 + \Delta r_3)$$

a_2 species:

$$S_2 = \Delta y_1 + \Delta y_2 + \Delta y_3 - 3 \Delta y_4$$

e' species:

$$S_{3a} = \frac{1}{\sqrt{6}} (2 \Delta r_1 - \Delta r_2 - \Delta r_3)$$

$$S_{4a} = \frac{1}{\sqrt{6}} r (2 \Delta \alpha_{23} - \Delta \alpha_{13} - \Delta \alpha_{12})$$

$$S_{3b} = \frac{1}{\sqrt{2}} (\Delta r_2 - \Delta r_3)$$

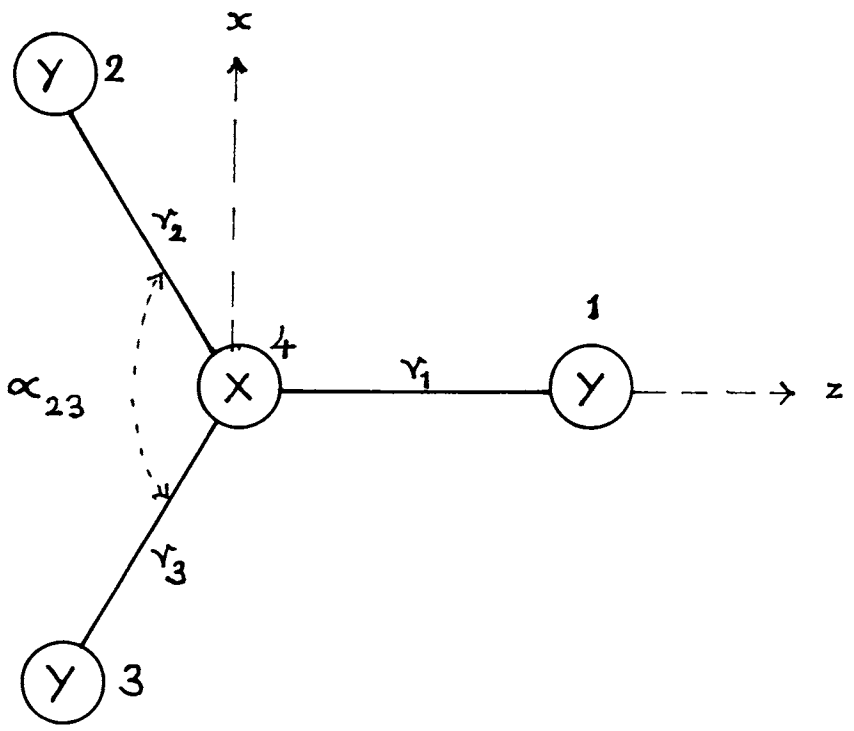

FIG. 4.1. Planar XY_3 molecular model: Internal co-ordinates and system of axes

$$S_{4b} = \frac{1}{\sqrt{2}} r \left(\Delta \alpha_{13} - \Delta \alpha_{12} \right) \qquad \ldots(4.1)$$

where Δr_1, Δr_2 and Δr_3 refer to changes in bond lengths and $\Delta \alpha_{12}$, $\Delta \alpha_{13}$ and $\Delta \alpha_{23}$ to changes in bond angles. Being a kind of out of plane bending, the symmetry co-ordinates S_2 (a''_2) is expressed in terms of cartesian displacements.

The symmetry F matrix elements are given by the following expressions:

a' species:

$F_{11} = fr + 2\, frr$

a'' species:

$F_{22} = f_\gamma$

e' species:

$F_{33} = f_r - f_{rr}$

$F_{34} = f_{r\alpha} - f'_{r\alpha}$

$F_{44} = f_\alpha - f_{\alpha\alpha}$ ... (4.2)

Here f_γ is the out-of plane bending force constant and f_r is the stretching force constant, f_α the bending force constant and the rest are interaction constants.

The interaction constant $f_{r\alpha}$ involves an angle and a bond which does not form one side of the angle and $f'_{r\alpha}$ involves an angle and a side which forms one side of the angle.

ß matrix

The s vectors, connecting the cartesian displacement co-ordinates and the symmetry co-ordinates, which constitute the ß matrix are given below:

S_1

Atom	x	y	z
1	0	0	$\frac{1}{\sqrt{3}}$
2	$\frac{1}{2}$	0	$-\frac{1}{2\sqrt{3}}$
3	$-\frac{1}{2}$	0	$-\frac{1}{2\sqrt{3}}$
4	0	0	0

S_2

Atom	x	y	z
1	0	1	0
2	0	1	0
3	0	1	0
4	0	-3	0

S_{3a}

Atom	x	y	z
1	0	0	$\frac{\sqrt{2}}{\sqrt{3}}$
2	$-\frac{1}{2\sqrt{2}}$	0	$\frac{1}{2\sqrt{6}}$
3	$\frac{1}{2\sqrt{2}}$	0	$\frac{1}{2\sqrt{6}}$
4	0	0	$-\frac{\sqrt{3}}{\sqrt{2}}$

S_{4a}

Atom	x	y	z
1	0	0	0
2	$\frac{\sqrt{3}}{2\sqrt{2}}$	0	$\frac{3}{2\sqrt{2}}$
3	$-\frac{\sqrt{3}}{2\sqrt{2}}$	0	$\frac{3}{2\sqrt{2}}$
4	0	0	$-\frac{3}{\sqrt{2}}$

S_{3b}

Atom	x	y	z
1	0	0	0
2	$\frac{\sqrt{3}}{2\sqrt{2}}$	0	$-\frac{1}{2\sqrt{2}}$
3	$\frac{\sqrt{3}}{2\sqrt{2}}$	0	$\frac{1}{2\sqrt{2}}$
4	$-\frac{\sqrt{3}}{\sqrt{2}}$	0	0

S_{4b}

Atom	x	y	z
1	$\sqrt{2}$	0	0
2	$\frac{1}{2\sqrt{2}}$	0	$\frac{\sqrt{3}}{2\sqrt{2}}$
3	$\frac{1}{2\sqrt{2}}$	0	$-\frac{\sqrt{3}}{2\sqrt{2}}$
4	$-\frac{3}{\sqrt{2}}$	0	0

... (4.3)

The G matrix elements are

a_1' species:

$$G_{11} = \mu_y$$

a_2'' species:

$$G_{22} = 3 (3\mu_x + \mu_y)$$

e' species:

$$G_{33} = \frac{3}{2}\mu_x + \mu_y$$

$$G_{34} = \frac{3\sqrt{3}}{2}\mu_x$$

$$G_{44} = \frac{9}{2}\mu_x + 3\mu_y \qquad \ldots(4.4)$$

where μ_x and μ_y are the reciprocal masses of the central atom X and the end atom Y respectively.

The force tensor Φ referred to the principal system of axes is derived from the F and β matrices. Here as the principal z-direction is taken along one of the bonds, XY_1 (Fig. 4.1), the bond force tensor $\mathcal{F}$ is the same as cartesian force tensor Φ.

The cartesian force tensor components for the atoms 4 and 1 are given by the relations:

$$\Phi^1_{xx} = 2 F_{44}$$

$$\Phi^1_{yy} = F_{22}$$

$$\Phi^1_{zz} = \frac{1}{3} F_{11} + \frac{2}{3} F_{33}$$

$$\Phi^4_{xx} = \frac{3}{2} F_{33} + \frac{9}{2} F_{44} + 3\sqrt{3}\, F_{34}$$

$$\Phi^4_{yy} = 9 F_{22}$$

$$\Phi^4_{zz} = \frac{3}{2} F_{33} + \frac{9}{2} F_{44} + 3\sqrt{3}\, F_{34} \qquad \ldots(4.5)$$

All the other components of Φ are zero. Using these relations the bond asymmetry parameter η_b is expressed as

$$\eta_b = 3\left\{13\,F_{44} + 3\,F_{33} + 6\sqrt{3}\,F_{34} - 20\,F_{22}\right\} \Big/ \left\{2F_{11} + 13\,F_{33} + 18\sqrt{3}\,F_{34} + 27\,F_{44}\right\} \quad \ldots(4.6)$$

Results and discussion

The expression for the bond asymmetry parameter derived above is utilised to calculate this quantity for some molecules for which established valence force fields exist. The data used in the investigation are given in Table 4.1. The calculated values of the cartesian force constants and the asymmetry parameter are tabulated in Table 4.2. It can be seen from the table that the η_b value remains constant for all the molecules belonging to the planar XY_3 model. The average of the last column is 0.48 and it can be taken as the characteristic value of η_b for molecules of XY_3 type belonging to D_{3h} point group. Such a constant value of η_b is in accordance with expectation since all planar XY_3 molecules have the same bond angle.

Making use of the characteristic constant value 0.48 for η_b, the force constants of some planar XY_3 molecules have been evaluated. With the aid of the parametric representation of force constants (2.10 to 2.12) and inserting the constant value into the expression for η_b a quadratic equation is obtained:

$$k\,c^2 + l\,c + m = 0 \qquad \ldots(4.7)$$

where

$$k = \frac{2.76\,\Lambda_4}{G_{33}} + \Lambda_3(\mu - 0.48\,\delta) - \frac{60\,\Lambda_2}{G_{22}} - \frac{0.96\,\Lambda_1}{G_{11}}$$

$$l = (\Lambda_3 - \Lambda_4)\left\{\frac{5.52\,G_{34}}{G_{33}\,|G|^{1/2}} - \frac{9.36\sqrt{3}}{|G|^{1/2}}\right\}$$

$$m = \frac{2.76\,\Lambda_3}{G_{33}} + \Lambda_4(\mu - 0.48\,\delta) - \frac{60\,\Lambda_2}{G_{22}} - \frac{0.96\,\Lambda_1}{G_{11}}$$

$$\mu = \frac{9\,G_{34}^2 - 18\sqrt{3}\,G_{34}\,G_{33} + 39\,G_{33}^2}{G_{33}\,|G|}$$

$$\delta = \frac{13\ G_{34}^{2} - 18\sqrt{3}\ G_{34}\ G_{33} + 27\ G_{33}^{2}}{G_{33}\ |G|}$$

Of the two values of c, the one which is within the acceptable range (-1, 1), is used to calculate the force constants. The results are tabulated in Table 4.3.

TABLE 4.1

SYMMETRY FORCE CONSTANTS

Molecule	Force constants mdyn. /A.					Ref.
	F_{11}*	F_{22}*	F_{33}	F_{34}	F_{44}	
B F_3	8.8223	0.2885	6.683	- 0.37	0.5095	1
B Cl_3	4.0318	0.1349	3.47	- 0.25	0.247	2
B Br_3	3.6369	0.0955	2.79	- 0.195	0.191	2
B I_3	2.6982	0.0653	2.25	- 0.17	0.130	3

* Present calculations. Frys. are taken from refs. [4 - 6].

TABLE 4.2

CARTESIAN FORCE CONSTANTS AND BOND ASYMMETRY PARAMETER η_b .

Molecule	Cartesian force constants (mdyn / A).						η_b
	Φ^4_{xx}	Φ^4_{yy}	Φ^4_{zz}	Φ^1_{xx}	Φ^1_{yy}	Φ^1_{zz}	
B F_3	10.3946	2.5965	10.3946	1.0190	0.2885	7.3961	0.4794
B Cl_3	5.0174	1.2141	5.0174	0.4940	0.1349	3.6572	0.4798
B Br_3	4.0312	0.8595	4.0312	0.3820	0.0955	3.0723	0.4868
B I_3	3.0766	0.5877	3.0766	0.2600	0.0653	2.3994	0.4649

TABLE 4.3

SYMMETRY FORCE CONSTANTS (mdyn./A).

Molecule	Symmetry force constants		
	F_{33}	F_{34}	F_{44}
$^{10}BF_3$	6.6499	- 0.3622	0.5106
$^{10}BCl_3$	3.4844	- 0.2590	0.2514
$^{10}BBr_3$	2.9059	- 0.2280	0.1880
$^{10}BI_3$	2.3220	- 0.1993	0.1278
$GeCl_3$	2.6165	- 0.1899	0.0867
CS_3^-	2.8915	0.2732	0.3918

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CHAPTER V

BOND ASYMMETRY PARAMETER - APPLICATION TO PYRAMIDAL XY_3 TYPE MOLECULES

The theory of bond asymmetry parameter developed in Chapter III is applied to pyramidal XY_3 type molecules. Numerical results are obtained in a number of cases for which established valence force fields exist. There is smooth relationship between η_b and hybridisation as brought out by the graph between η_b and percentage p-character.

CHAPTER V

BOND ASYMMETRY PARAMETER - APPLICATION TO PYRAMIDAL XY_3 TYPE MOLECULES

Pyramidal XY_3 type molecules belong to the point group C_{3V}. There are two species of normal vibrations which are classified into $2a_1 + 2e$. The geometry of this model and the principal system of axes are shown in Fig. 5.1a and Fig. 5.1b. The following symmetry co-ordinates are used in the analysis of the vibrations:

a_1 species:

$$S_1 = \frac{1}{\sqrt{3}} (\Delta r_1 + \Delta r_2 + \Delta r_3)$$

$$S_2 = \frac{r}{\sqrt{3}} (\Delta \alpha_{12} + \Delta \alpha_{23} + \Delta \alpha_{13})$$

e species:

$$S_{3a} = \frac{1}{\sqrt{6}} (2\Delta r_1 - \Delta r_2 - \Delta r_3)$$

$$S_{4a} = \frac{r}{\sqrt{6}} (2\Delta \alpha_{23} - \Delta \alpha_{13} - \Delta \alpha_{12})$$

$$S_{3b} = \frac{1}{\sqrt{2}} (\Delta r_2 - \Delta r_3)$$

$$S_{4b} = \frac{r}{\sqrt{2}} (\Delta \alpha_{13} - \Delta \alpha_{12}) \qquad \ldots(5.1)$$

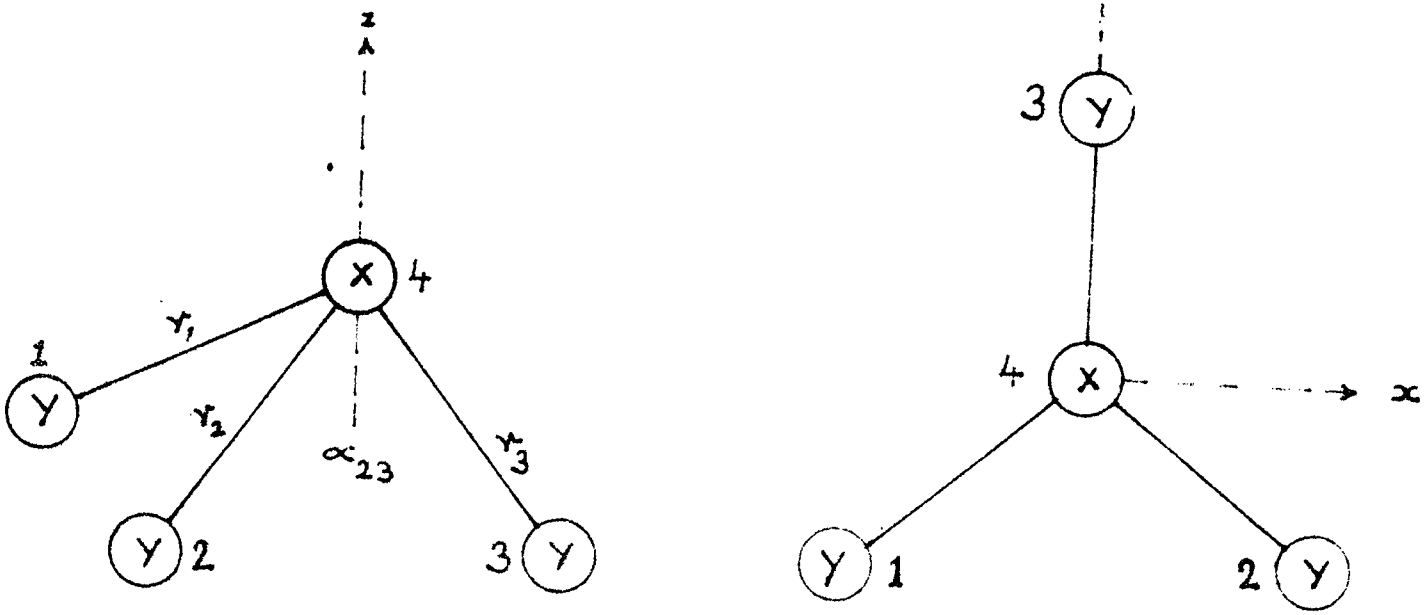

FIG.5.1a. and 5.1b. Pyramidal XY_3 molecular model: Internal co-ordinates and system of axes.

where r represents the equilibrium distance X - Y. Δr_1, Δr_2 and Δr_3 are changes in bond lengths and $\Delta\alpha_{12}$, $\Delta\alpha_{23}$ and $\Delta\alpha_{13}$ changes in bond angles. The symmetry F elements corresponding to these symmetry co-ordinates are given by

a_1 species:

$$F_{11} = f_r + 2f_{rr}$$

$$F_{12} = 2f_{r\alpha} + f'_{r\alpha}$$

$$F_{22} = f_\alpha + 2f_{\alpha\alpha}$$

e species:

$$F_{33} = f_r - f_{rr}$$

$$F_{34} = f'_{r\alpha} - f_{r\alpha}$$

$$F_{44} = f_\alpha - f_{\alpha\alpha} \qquad \ldots(5.2)$$

Here f_r is the stretching force constant, f_α the bending constant and all the rest are interaction constants.

B matrix

The following components of s vectors constitute the B matrix:

S_1

Atom	x	y	z
1	$-\frac{1}{2}\sin\beta$	$-\frac{1}{2\sqrt{3}}\sin\beta - \frac{1}{\sqrt{3}}\cos\beta$	
2	$\frac{1}{2}\sin\beta$	$-\frac{1}{2\sqrt{3}}\sin\beta - \frac{1}{\sqrt{3}}\cos\beta$	
3	0	$\frac{1}{\sqrt{3}}\sin\beta - \frac{1}{\sqrt{3}}\cos\beta$	
4	0	0	$\sqrt{3}\cos\beta$

S_2

Atom	x	y	z
1	$-\ell$	$-\frac{1}{\sqrt{3}}\ell$	$\frac{2}{\sqrt{3}}H$
2	ℓ	$-\frac{1}{\sqrt{3}}\ell$	$\frac{2}{\sqrt{3}}H$
3	0	$\frac{2}{\sqrt{3}}\ell$	$\frac{2}{\sqrt{3}}H$
4	0	0	$-2\sqrt{3}H$

S_{3a}

Atom	x	y	z
1	$-\frac{1}{\sqrt{2}}\sin\beta$	$-\frac{1}{\sqrt{6}}\sin\beta$	$-\frac{\sqrt{2}}{\sqrt{3}}\cos\beta$
2	$-\frac{1}{2\sqrt{2}}\sin\beta$	$\frac{1}{2\sqrt{6}}\sin\beta$	$\frac{1}{\sqrt{6}}\cos\beta$
3	0	$-\frac{1}{\sqrt{6}}\sin\beta$	$\frac{1}{\sqrt{6}}\cos\beta$
4	$\frac{3}{2\sqrt{2}}\sin\beta$	$\frac{\sqrt{3}}{2\sqrt{2}}\sin\beta$	0

S_{4a}

Atom	x	y	z
1	$\frac{1}{\sqrt{2}}$ $\mathcal{G}$	$\frac{1}{\sqrt{6}}$ $\mathcal{G}$	$-\frac{\sqrt{2}}{\sqrt{3}}$ H
2	-J	T	$\frac{1}{\sqrt{6}}$ H
3	$-\sqrt{3}$ K	$\frac{1}{\sqrt{6}}$ $\mathcal{G}$	$\frac{1}{\sqrt{6}}$ H
4	3J	$\sqrt{3}$ J	0

S_{3b}

Atom	x	y	z
1	0	0	0
2	$\frac{\sqrt{3}}{2\sqrt{2}}\sin\beta$	$-\frac{1}{2\sqrt{2}}\sin\beta$	$-\frac{1}{\sqrt{2}}\cos\beta$
3	0	$-\frac{1}{\sqrt{2}}\sin\beta$	$\frac{1}{\sqrt{2}}\cos\beta$
4	$-\frac{\sqrt{3}}{2\sqrt{2}}\sin\beta$	$\frac{3}{2\sqrt{2}}\sin\beta$	0

S_{4b}

Atom	x	y	z
1	K	$-\sqrt{3}K$	0
2	U	$-$ J	$-\frac{1}{\sqrt{2}}$ H
3	K	$\frac{1}{\sqrt{2}}$ ℓ	$\frac{1}{\sqrt{2}}$ H
4	$-\sqrt{3}J$	3J	0

... (5.3)

where β is the acute angle that the bond makes with the z-axis and it is given by $\sin\beta = \frac{2}{\sqrt{3}} \sin\frac{\alpha}{2}$

and

$$\ell_y = \frac{\sin\beta\ (1 + 2\cos\alpha\ )}{2\sin\alpha}$$

$$H = \frac{\cos\beta\ (1 - \cos\alpha\ )}{\sin\alpha}$$

$$J = \frac{\sin\beta\ (1 - \cos\alpha\ )}{2\sqrt{2}\ \sin\alpha}$$

$$K = \frac{\sqrt{3}\ \sin\beta}{2\sqrt{2}\ \sin\alpha}$$

$$T = \frac{\sin\beta\ (5 + \cos\alpha\ )}{2\sqrt{6}\ \sin\alpha}$$

$$U = \frac{\sqrt{3}\ \sin\beta\ (1 + \cos\alpha\ )}{2\sqrt{2}\ \sin\alpha}$$

The G matrix elements are of the following form:

a_1 species:

$$G_{11} = \mu_y + \mu_x\ (1 + 2\cos\alpha\ )$$

$$G_{12} = -2\mu_x \frac{(1 + 2\cos\alpha\ )\ (1 - \cos\alpha\ )}{\sin\alpha}$$

$$G_{22} = 2\ (1 - \cos\alpha\ )\ (2\cos\alpha + 1)\ \frac{1}{\sin^2\alpha}$$

$$\times\ [2\ (1 - \cos\alpha\ )\ \mu_x + \mu_y]$$

e species:

$$G_{33} = \mu_y + \mu_x (1 - \cos\alpha)$$

$$G_{34} = \frac{\mu_x (1 - \cos\alpha)^2}{\sin\alpha}$$

$$G_{44} = \frac{(2 + \cos\alpha)\ \mu_y + (1 - \cos\alpha)^2 \mu_x}{(1 + \cos\alpha)}$$

... (5.4)

where μ_x and μ_y denote the reciprocal masses of the atom X and Y respectively.

The force tensor Φ given by $\Phi = \tilde{B} F B$ is constructed from the F and B matrices and its elements are of the form:

$$\Phi^3_{xx} = 4 K^2 F_{44}$$

$$\Phi^3_{yy} = \frac{1}{3}(F_{11} + 2F_{33}) \sin^2\beta + \frac{2}{3} g^2 (2 F_{22} + F_{44})$$

$$+ \frac{4}{3} g (F_{12} - F_{34}) \sin\beta$$

$$\Phi^3_{zz} = \frac{1}{3}(F_{11} + 2F_{33}) \cos^2\beta + \frac{2}{3} H^2 (2F_{22} + F_{44})$$

$$+ \frac{4}{3} H (F_{34} - F_{12}) \cos\beta$$

...(5.5)

$$\Phi^4_{xx} = \frac{3}{2} F_{33} \sin^2\beta + J^2 F_{44}$$

$$+ 6\sqrt{2}\ F_{34} J \sin\beta \qquad = \Phi^4_{yy}$$

$$\Phi^4_{zz} = 2 F_{11} \cos^2\beta + 12 H^2 F_{22} - 12 H F_{12} \cos\beta \qquad \ldots(5.6)$$

To get an idea of the directional asymmetry of bonding forces, the force tensor Φ referred to principal axes is transformed into a bond-based co-ordinate system. In the present investigation, the z-axis is oriented along the bond connecting atoms 3 and 4. Φ is transformed into the new co-ordinate system by giving an anticlockwise rotation about the x axis, through an angle β. The resulting bond force tensor $\mathcal{F}$ can be expressed in block form for each atom. Components of $\mathcal{F}$ along and perpendicular to the bond for a given atom are

$$\mathcal{F}_{zz} = \Phi_{zz} \cos^2\beta - \Phi_{zy} \sin 2\beta + \Phi_{yy} \sin^2\beta$$

$$\mathcal{F}_{yy} = \Phi_{zz} \sin^2\beta + \Phi_{zy} \sin 2\beta + \Phi_{yy} \cos^2\beta$$

$$\mathcal{F}_{xx} = \Phi_{xx} \qquad \ldots(5.7)$$

The bond asymmetry parameter η_b is defined by

$$\eta_b = \frac{\left\{ \mathcal{F}^3_{xx} + \mathcal{F}^4_{xx} \right\} - \left\{ \mathcal{F}^3_{yy} + \mathcal{F}^4_{yy} \right\}}{\left\{ \mathcal{F}^3_{zz} + \mathcal{F}^4_{zz} \right\}} \qquad \ldots(5.8)$$

With the help of (5.6) and (5.7) this can be expressed as

$$\eta_b = \left\{ \frac{3}{2} E F_{33} + 3 R F_{34} + \frac{3}{2} (L + N) F_{44} - 3 A F_{11} + 12 B F_{12} - (12 D + 3 M) F_{22} \right\} \Big/ \left\{ \left(\frac{2}{3} + \frac{3}{2} E \right) F_{33} + 3 R F_{34} + \frac{3}{2} L F_{44} + \left(\frac{1}{3} + 3 V \right) F_{11} - 12 P F_{12} + 12 Q F_{22} \right\} \quad \ldots(5.9)$$

where

$$A = \sin^2\beta \cos^2\beta$$

$$B = \sin^2\beta \cos^2\beta \tan \frac{\alpha}{2}$$

$$D = \sin^2\beta \cos^2\beta \tan^2 \frac{\alpha}{2}$$

$$E = \sin^4\beta$$

$$R = \sin^4\beta \tan \frac{\alpha}{2}$$

$$L = \sin^4\beta \tan^2 \frac{\alpha}{2}$$

$$M = \frac{\sin^2\beta \cos^2\beta}{\sin^2\alpha}$$

$$N = \frac{\sin^4\beta}{\sin^2\alpha}$$

$$V = \cos^4\beta$$

$$P = \cos^4\beta \tan \frac{\alpha}{2}$$

$$Q = \cos^4\beta \tan^2 \frac{\alpha}{2}$$

Results and discussion

Using the general valence force constants reported earlier, the theory developed above has been applied to several molecules belonging to the pyramidal XY_3 model. The data taken from the literature are given in Tables 5.1a and 5.1b. The force constant data given in Table 5.1a are based on additional experimental information while the values listed in Table 5.1b have only the vibrational frequencies as their calculational basis. The cartesian force components of the molecules are calculated and tabulated in Table 5.2. The η_b values have been evaluated and are reported in Table 5.3. It is noted that the η_b value varies with the bond angle. A graphical study of the variation of η_b with bond angle α is presented in Figs. 5.2 and 5.3. The points are easily fitted into two distinct straight lines. This seems to suggest a grouping of pyramidal XY_3 molecules into hydrides and non-hydrides. The linear relationships between η_b and α may be expressed as

$$\eta_b = m\alpha_\theta + l \qquad \ldots(5.10)$$

where m and l are constants, characteristic of the straight line. With η_b in arbitrary units and α_θ in

radian measure, for hydrides,

$$m = 2.192$$

and

$$l = -3.663 \qquad \ldots(5.11)$$

For non-hydrides the constants are

$$m = 1.179$$

and

$$l = -2.053 \qquad \ldots(5.12)$$

η_b value of any pyramidal XY_3 type molecule can be calculated from the empirical relation (5.10). As η_b varies with bond angle, its dependence on the percentage p-character is studied and shown in Figs. 5.4 and 5.5.

Unlike XY_2 systems, a direct evaluation of the force constants of a pyramidal XY_3 type molecule is not possible from the η_b value alone. Since there are two second order vibrational species, two independent parameters c_1 and c_2 are to be used in the parameter representation for the evaluation of the force constants. However, if, in additions to the η_b value, one more datum other then the experimental frequencies is made use of, the force field can be fixed completely.

In the present investigation an attempt has been made to evaluate the force fields of NF_3 and AsF_3,

using the experimentally observed coriolis coupling constant ζ_{33} [6,7]. In this approach the symmetry force constants of the e species are determined first. These values are then used in conjunction with the η_b value in (5.9) to evaluate the force constants of the a_1 species. The results of this calculation are given in Table 5.4 and Table 5.5 together with the previously reported values. Using the present results mean amplitudes of vibration for bonded distances are also obtained. For NF_3 the calculated value of the mean amplitude is 0.04798 A° and this is in good agreement with the reported value 0.049 A° [8]. In the case of AsF_3 too, the calculated value 0.0423 A° is very close to the observed value 0.0433 A° [9].

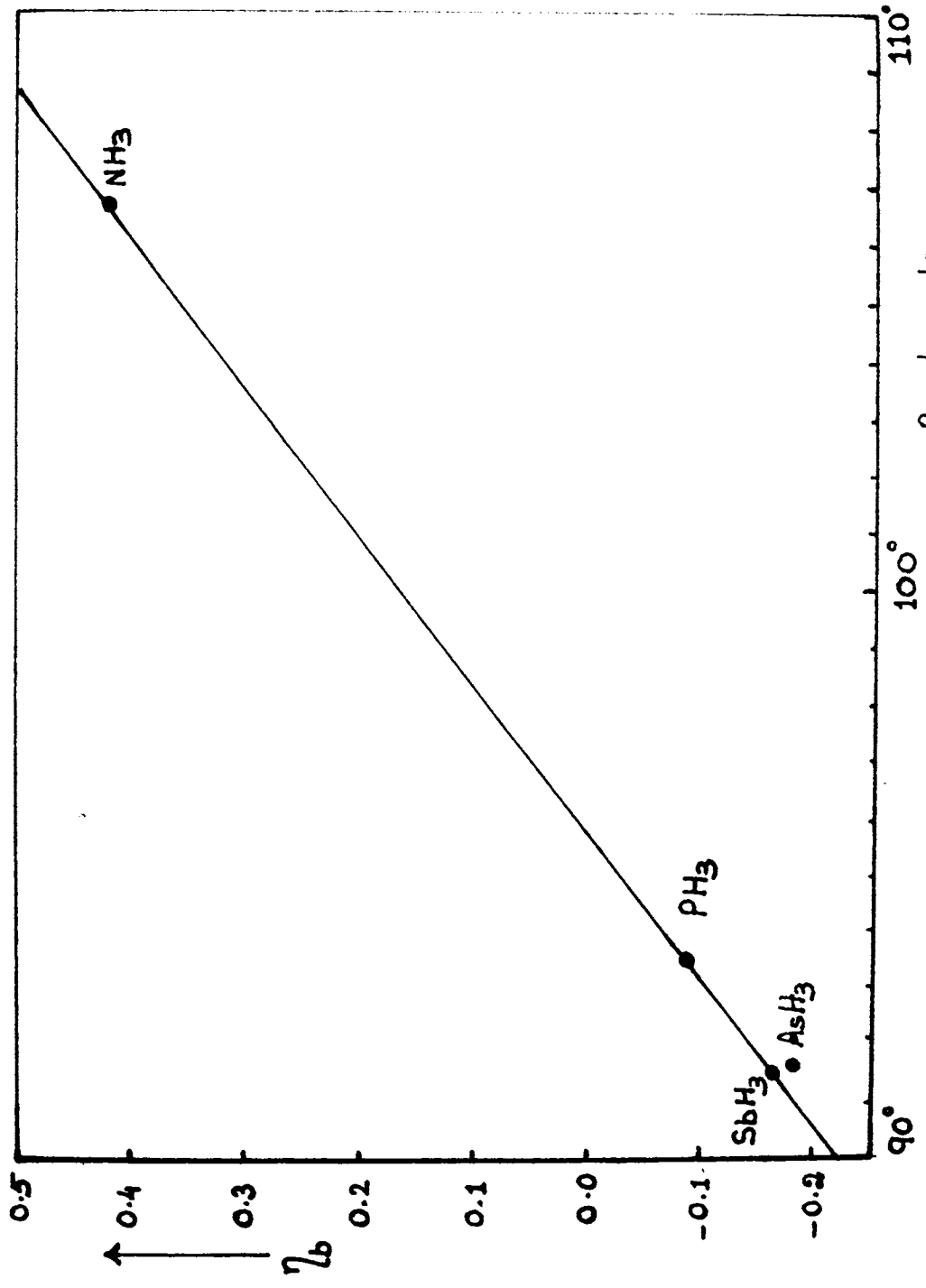

FIG.5.2. Relation between bond asymmetry parameter η_b and bond angle for pyramidal XY_3 type hydrides.

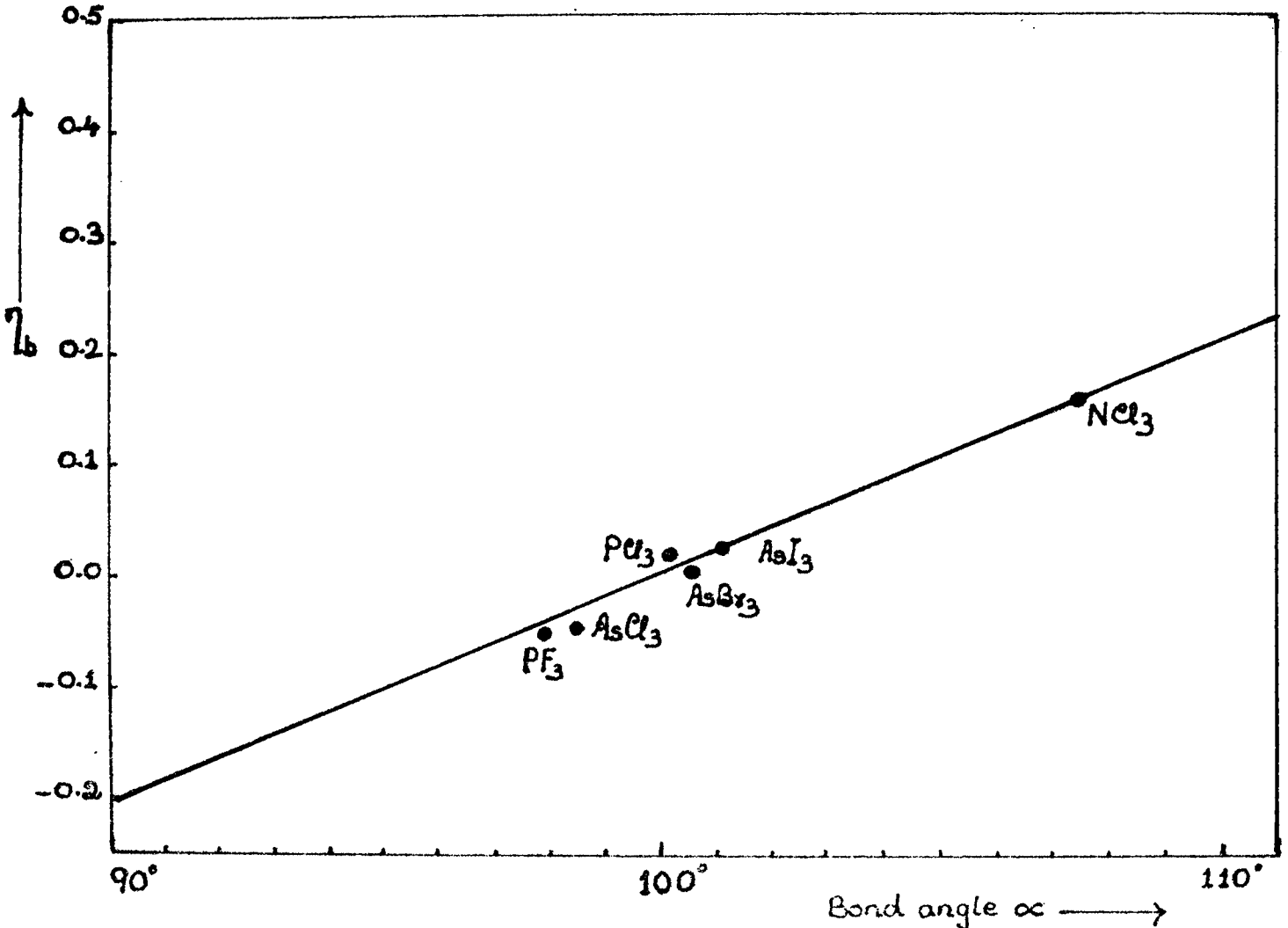

FIG.5.3. Relation between bond asymmetry parameter η_b and bond angle for pyramidal XY_3 type non hydrides.

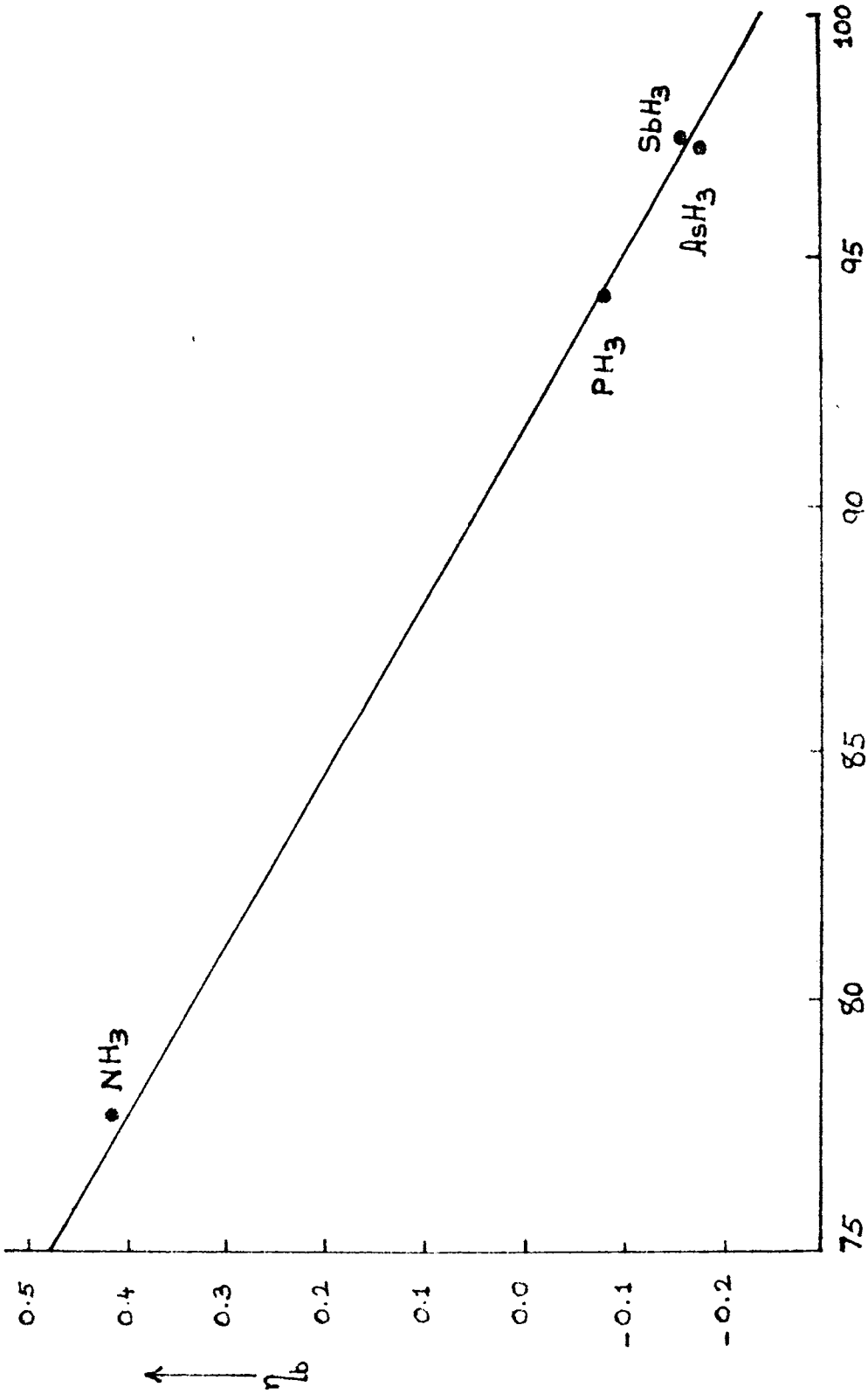

FIG.5.4. Relation between bond asymmetry parameter η_b and percentage p-character for pyramidal XY_3 type hydrides.

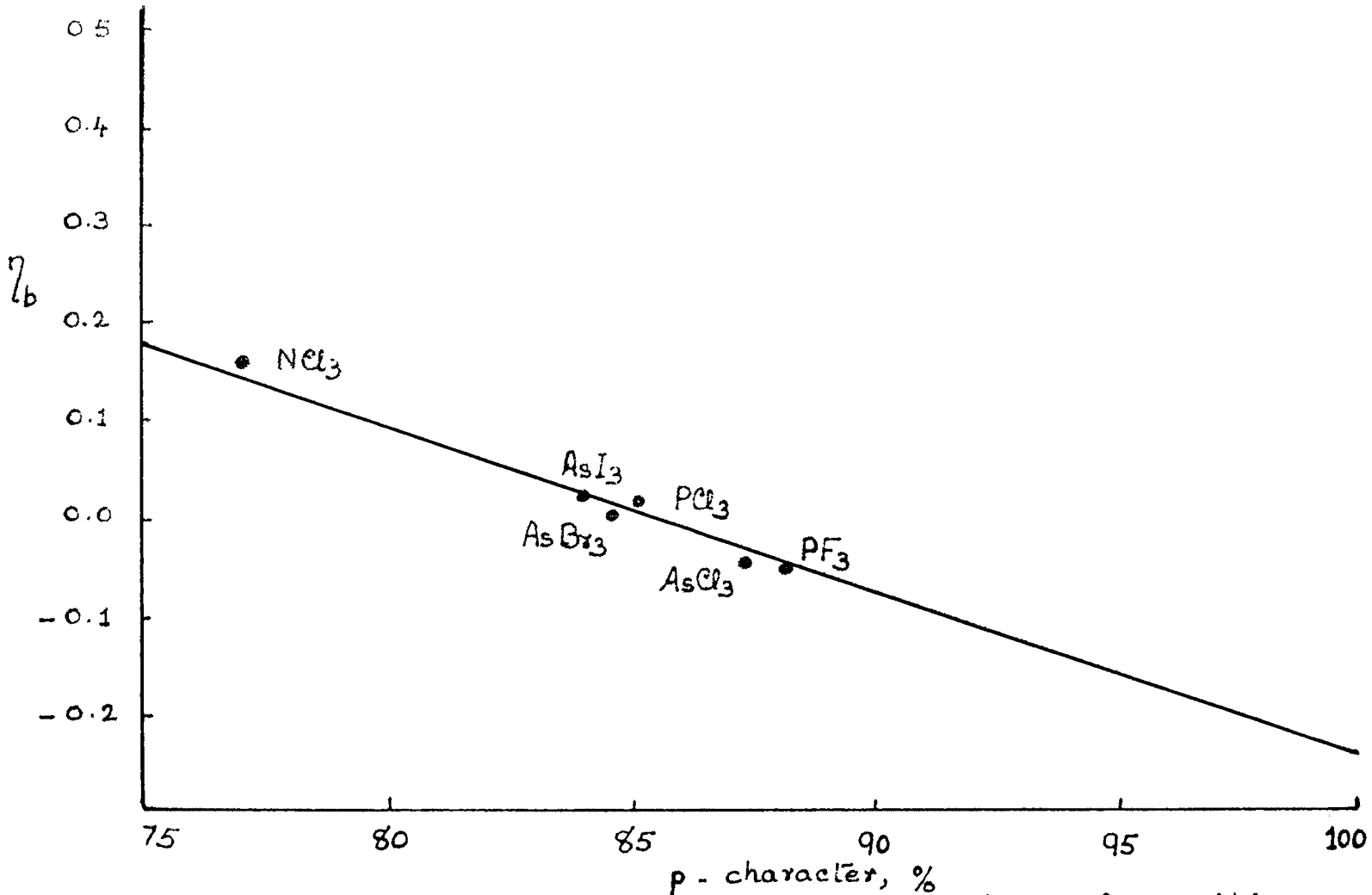

FIG.5.5. Relation between bond asymmetry parameter η_b and percentage p-character for pyramidal XY_3 type non hydrides.

TABLE 5.1a

BOND ANGLE AND SYMMETRY FORCE CONSTANTS

Molecule	Bond angle	Force constants md/A						Ref.
		F_{11}	F_{12}	F_{22}	F_{33}	F_{34}	F_{44}	
NCl_3	107°22'	2.925	0.4612	0.6030	2.374	-0.3611	0.3575	1
NH_3	106°42'	7.075	0.780	0.532	7.038	-0.174	0.665	2
PCl_3	100°6'	3.11	0.1958	0.3642	2.25	-0.083	0.242	1
PF_3	97°48'	6.146	0.312	0.819	4.962	-0.205	0.491	3
PH_3	93°30'	3.402	-0.200	0.340	3.466	-0.040	0.376	2
AsH_3	91°36'	2.778	-0.250	0.310	2.892	-0.100	0.301	2
SbH_3	91°30'	2.267	-0.200	0.215	2.297	-0.020	0.208	2

TABLE 5.1b

BOND ANGLE AND SYMMETRY FORCE CONSTANTS

Molecule	Bond angle	Force constants md/A						Ref.
		F_{11}	F_{12}	F_{22}	F_{33}	F_{34}	F_{44}	
$AsCl_3$	98° 24'	2.5109	0.0000	0.2713	1.8122	0.0000	0.2044	4
$AsBr_3$	100° 30'	1.9574	0.0000	0.2255	1.5005	0.0000	0.1589	4
AsI_3	101° 0'	1.3230	0.0000	0.1879	1.1200	0.0000	0.1231	5

TABLE 5.2

CARTESIAN FORCE CONSTANTS

Molecule	Cartesian force constants md/A°.					
	Φ^3_{xx}	Φ^3_{yy}	Φ^3_{zz}	Φ^4_{xx}	Φ^4_{yy}	Φ^4_{zz}
NCl_3	0.5096	2.4546	0.4024	2.6660	2.6660	1.9666
NH_3	0.8645	5.7139	1.0365	9.2048	9.2048	3.2473
PCl_3	0.2934	2.1389	0.6524	2.8165	2.8165	2.7602
PF_3	0.5680	4.3941	1.5614	5.1634	5.1634	6.5684
PH_3	0.4004	2.4666	1.3072	4.0382	4.0382	5.0824
AsH_3	0.3096	1.9853	1.1680	3.0885	3.0885	4.8397
SbH_3	0.2136	1.5521	0.9418	2.5399	2.5399	3.7853

TABLE 5.3

BOND ASYMMETRY PARAMETER η_b .

Molecule	η_b
NH_3	0.41339
PH_3	-0.08581
AsH_3	-0.18340
SbH_3	-0.16208
NCl_3	0.15915
PCl_3	0.01547
PF_3	-0.05159
$AsCl_3$	-0.04825
$AsBr_3$	0.00432
AsI_3	0.02283

TABLE 5.4

SYMMETRY FORCE CONSTANTS OF NF_3 (mdyn/A°)

Fij	Present result	Previous result		
		[10]	[11]	[12]
F_{11}	7.3295	6.131	8.00	6.90
F_{12}	0.9541	0.630	0.88	0.81
F_{22}	1.1475	1.29	0.60	1.18
F_{33}	3.3974	3.404	3.96	3.55
F_{34}	-0.3264	-0.33	-0.63	-0.40
F_{44}	0.8987	0.90	0.84	0.88

TABLE 5.5

SYMMETRY FORCE CONSTANTS OF AsF_3 (md/A)

Fij	Present result	Previous result	
		[13]	[14]
F_{11}	5.016	5.080	4.800
F_{12}	0.0164	0.205	-0.281
F_{22}	0.4910	0.496	0.568
F_{33}	4.3849	4.350	4.340
F_{34}	-0.2033	-0.105	-0.134
F_{44}	0.3280	0.318	0.314

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CHAPTER VI

BOND ASYMMETRY PARAMETER - APPLICATION TO TETRAHEDRAL XY_4 TYPE MOLECULES

Theoretical expression for the bond asymmetry parameter η_b is derived with particular reference to the tetrahedral XY_4 type molecular model. The calculation of η_b values of a number of molecules shows an approximate invariance of this quantity for this molecular model. There is a very small difference in η_b values between hydrides and non-hydrides. The force fields of a number of molecules are evaluated making use of the characteristic value (-0.24) for non-hydrides.

CHAPTER VI

BOND ASYMMETRY PARAMETER - APPLICATION TO TETRAHEDRAL XY_4 TYPE MOLECULES

Tetrahedral XY_4 type molecules belong to the point group T_d. The internal co-ordinates and the orientation of the axes are shown in Fig. 6.1. According to the irreducible representations of the point group T_d, the normal vibrations are classified as a_1, e and f_2. Of these f_2 alone is of second order, while a_1 and e are of first order. Let r be the equilibrium X-Y distance and α_{12} the angle between the bonds r_1 and r_2. The symmetry co-ordinates employed in this investigation are listed as follows:

a_1 species:

$$S_1 = \frac{1}{2} (\Delta r_1 + \Delta r_2 + \Delta r_3 + \Delta r_4)$$

e species:

$$S_{2a} = \frac{r}{2\sqrt{3}} (2 \Delta\alpha_{14} + 2 \Delta\alpha_{23} - \Delta\alpha_{12} - \Delta\alpha_{13} - \Delta\alpha_{34} - \Delta\alpha_{24})$$

$$S_{2b} = \frac{r}{2} (\Delta\alpha_{13} - \Delta\alpha_{12} + \Delta\alpha_{24} - \Delta\alpha_{34})$$

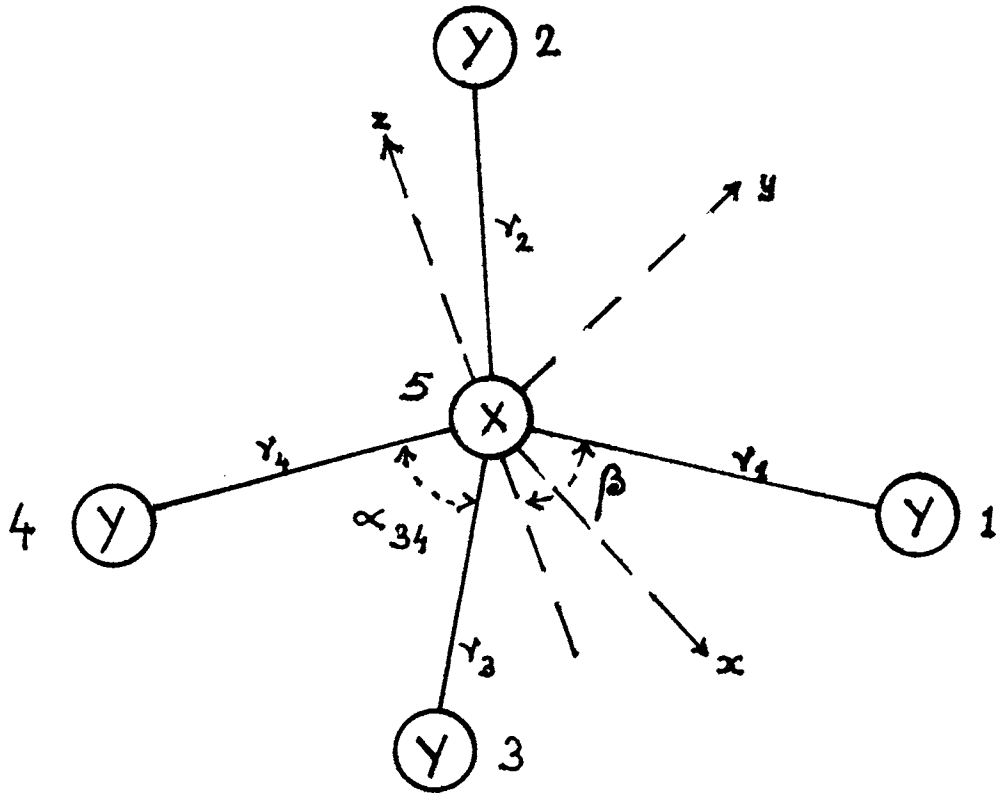

FIG.6.1. Tetrahedral XY_4 molecular model: Internal co-ordinates and system of axes

f_2 species:

$$S_{3a} = \frac{1}{2} (\Delta r_1 - \Delta r_2 + \Delta r_3 - \Delta r_4)$$

$$S_{4a} = \frac{r}{\sqrt{2}} (\Delta \alpha_{24} - \Delta \alpha_{13})$$

$$S_{3b} = \frac{1}{2} (\Delta r_1 + \Delta r_2 - \Delta r_3 - \Delta r_4)$$

$$S_{4b} = \frac{r}{\sqrt{2}} (\Delta \alpha_{34} - \Delta \alpha_{12})$$

$$S_{3c} = \frac{1}{2} (\Delta r_2 + \Delta r_3 - \Delta r_1 - \Delta r_4)$$

$$S_{4c} = \frac{r}{\sqrt{2}} (\Delta \alpha_{14} - \Delta \alpha_{23}) \qquad \ldots (6.1)$$

where Δr and $\Delta \alpha$ are the changes in bond lengths and bond angles. The symmetry F elements are given by

a_1 species:

$$F_{11} = f_r + 3 f_{rr}$$

e species:

$$F_{22} = f_\alpha - 2f_{\alpha\alpha} + f'_{\alpha\alpha}$$

f_2 species:

$$F_{33} = f_r - f_{rr}$$

$$F_{34} = -\sqrt{2} (f_{r\alpha} - f'_{r\alpha})$$

$$F_{44} = f_\alpha - f'_{\alpha\alpha}$$

$$\ldots (6.2)$$

where f_r is the stretching force constant and f_α the bending and the remaining constants are interaction force constants. The primed quantities represent the interaction between opposite co-ordinates and the unprimed ones, the interaction between adjacent co-ordinates. Thus, for instance, $f'_{r\alpha}$ represents the interaction between r_1 and α_{23} and $f_{r\alpha}$ stands for the $r_1 - \alpha_{12}$ interaction.

B matrix

The B matrix elements for each symmetry co-ordinate are displayed in the following form:

S_1

Atom	x	y	z
1	1	1	-1
2	-1	1	1
3	1	-1	1
4	-1	-1	-1
5	0	0	0

$\times \frac{1}{2\sqrt{3}}$

S_{2a}

Atom	x	y	z	
1	1	1	2	
2	-1	1	-2	
3	1	-1	-2	$\times \frac{1}{2\sqrt{2}}$
4	-1	-1	2	
5	0	0	0	

S_{2b}

Atom	x	y	z	
1	$-\sqrt{3}$	$\sqrt{3}$	0	
2	$\sqrt{3}$	$\sqrt{3}$	0	
3	$-\sqrt{3}$	$-\sqrt{3}$	0	$\times \frac{1}{2\sqrt{2}}$
4	$\sqrt{3}$	$-\sqrt{3}$	0	
5	0	0	0	

S_{3a}

Atom	x	y	z	
1	1	1	-1	
2	1	-1	-1	
3	1	-1	1	$\times \frac{1}{2\sqrt{3}}$
4	1	1	1	
5	-4	0	0	

S_{4a}

Atom	x	y	z	
1	2	-1	1	
2	2	1	1	
3	2	1	-1	$\times \frac{1}{2\sqrt{3}}$
4	2	-1	-1	
5	-8	0	0	

S_{3b}

Atom	x	y	z	
1	1	1	-1	
2	-1	1	1	
3	-1	1	-1	$\times \frac{-1}{2\sqrt{3}}$
4	1	1	1	
5	0	-4	0	

S_{4b}

Atom	x	y	z	
1	-1	2	1	
2	1	2	-1	
3	1	2	1	$\times \frac{1}{2\sqrt{3}}$
4	-1	2	-1	
5	0	-8	0	

S_{3c}

Atom	x	y	z	
1	-1	-1	1	
2	-1	1	1	
3	1	-1	1	$\times \frac{1}{2\sqrt{3}}$
4	1	1	1	
5	0	0	-4	

S_{4c}

Atom	x	y	z	
1	1	1	2	
2	1	-1	2	
3	-1	1	2	$\times \frac{1}{2\sqrt{3}}$
4	-1	-1	2	
5	0	0	-8	

...(6.3)

The G matrix elements are:

a_1 species:

$$G_{11} = \mu_Y$$

e species:

$$G_{22} = 3\ \mu_Y$$

f_2 species:

$$G_{33} = \frac{4}{3}\ \mu_x + \mu_Y$$

$$G_{34} = \frac{8}{3}\ \mu_x$$

$$G_{44} = 2\left\{\frac{8}{3}\ \mu_x + \mu_Y\right\} \qquad \ldots(6.4)$$

where μ_x and μ_Y are the reciprocal masses of the X and Y atoms respectively.

The components of the force tensor Φ belonging to the blocks corresponding to atoms 1 to 4 are equal in magnitude, indicating an identical potential environment for symmetrically equivalent atoms. The force components for atom 1 are:

$$\Phi^1_{\alpha\alpha} = \frac{1}{12}\ F_{11} + \frac{1}{2}\ (F_{22} + \frac{1}{2}\ F_{33} + F_{44})$$

$$\Phi^1_{xy} = \frac{1}{12} F_{11} - \frac{1}{8} (F_{22} - F_{33} + F_{44})$$

$$\Phi^1_{xz} = -\frac{1}{12} F_{11} + \frac{1}{4} (F_{22} - F_{33} + F_{44})$$

$$\Phi^1_{yy} = \frac{1}{12} F_{11} + \frac{1}{2} (F_{22} + \frac{1}{2} F_{33} + F_{44})$$

$$\Phi^1_{yz} = -\frac{1}{12} F_{11} + \frac{1}{4} (F_{22} - F_{33} + F_{44})$$

$$\Phi^1_{zz} = \frac{1}{12} F_{11} + \frac{1}{2} (F_{22} + \frac{1}{2} F_{33} + F_{44})$$

... (6.5)

For the central atom numbered as 5 only three components are different from zero and all the three are identically equal. They are

$$\Phi^5_{xx} = \Phi^5_{yy} = \Phi^5_{zz}$$

$$= \frac{4}{3} F_{33} + \frac{16}{3} (F_{34} + F_{44}) \qquad \ldots(6.6)$$

The equality of the three components of Φ indicates the existence of a spherically symmetric potential environment for atom 5 and this is consistent with the fact that in tetrahedral symmetry, atom 5 is at the geometrical centre of the molecule.

The transformation of Φ to a co-ordinate system with the z axis along the bond connecting atoms 1 and 5 is accomplished by means of two rotations. The first one is an anticlockwise rotation through 45° about the z-axis and the second is through an angle β in clockwise direction about the y-axis where β is the acute angle between the bond and the z direction.

For an atom the component along the bond to which it is attached, of the bond force tensor $\mathfrak{F}$ (formulated in block form) is given by

$$\mathfrak{F}_{zz} = \frac{1}{3}\left(\Phi_{xx} + \Phi_{yy} + \Phi_{zz}\right) - \frac{2}{3}\left(\Phi_{xy} + \Phi_{xz} - \Phi_{yz}\right) \qquad \ldots(6.7)$$

The corresponding perpendicular components are of the form

$$\mathfrak{F}_{yy} = \frac{1}{2}\left(\Phi_{xx} + \Phi_{yy}\right) + \Phi_{xy}$$

$$= \frac{1}{6}\left(\Phi_{xx} + \Phi_{yy}\right) + \frac{2}{3}\Phi_{zz}$$

$$- \frac{1}{3}\Phi_{xy} + \frac{2}{3}\left(\Phi_{xz} - \Phi_{yz}\right) \qquad \ldots(6.8)$$

The bond force tensor components for atoms 1 and 5 are then given by

$$\mathcal{F}^{1}_{xx} = \frac{1}{18} F_{11} + \frac{7}{12} F_{22} + \frac{1}{6} F_{33} + \frac{7}{12} F_{44}$$

$$\mathcal{F}^{1}_{yy} = \frac{1}{6} F_{11} + \frac{1}{4} F_{22} + \frac{1}{2} F_{33} + \frac{1}{4} F_{44}$$

$$\mathcal{F}^{1}_{zz} = \frac{1}{36} F_{11} + \frac{2}{3} F_{22} + \frac{1}{12} F_{33} + \frac{2}{3} F_{44} \quad \ldots(6.9)$$

For the central atom 5, only the three components $\mathcal{F}_{xx}$, $\mathcal{F}_{yy}$ and $\mathcal{F}_{zz}$ are different from zero and are identically equal.

$$\mathcal{F}^{5}_{xx} = \frac{4}{3} F_{33} + \frac{16}{3} (F_{34} + F_{44})$$

$$= \mathcal{F}^{5}_{yy} = \mathcal{F}^{5}_{zz} \quad \ldots(6.10)$$

Accordingly, the asymmetry parameter η_b for the bond is written as

$$\eta_b = \left\{12 (F_{44} - F_{33} + F_{22}) - 4 F_{11}\right\} \Big/ \left\{F_{11} + 24 F_{22} + 51 F_{33} + 192 F_{34} + 216 F_{44}\right\}$$

$$\ldots (6.11)$$

Results and discussion

The theory developed in the previous section is applied to a number of molecules, for which force constant values are available in the literature. The data employed

are given in Table 6.1. The calculated values of the cartesian force constants and the bond asymmetry parameter η_b are tabulated in Table 6.2. It may be noted from the table that for non-hydrides η_b value is approximately - 0.24 while for hydrides it is around - 0.20. Thus hydrides and non-hydrides, it seems, form two separate classes with different characteristic η_b values.

Using the η_b value, the force constants of several XY_4 type molecules are evaluated. For non-hydride molecules of tetrahedral symmetry, taking the specific value - 0.24 for η_b , the expression (6.11) is rewritten as

$$46.08\ F_{34} + 63.84\ F_{44} + 0.24\ F_{33} - 3.76\ F_{11} + 17.76\ F_{22} = 0 \qquad \ldots (6.12)$$

F_{11} and F_{22}, can be evaluated directly from the corresponding vibrational frequencies and the one dimensional G matrices. The remaining three force constants are evaluated in terms of a parameter c, using the relations (2.10) through (2.12). The parameter c is obtained as a solution of (6.12) which is now of the form

$$\left\{ \frac{\Lambda_3 \mu}{|G|} + \delta + \frac{0.24\,\Lambda_4}{G_{33}} \right\} c^2 + \delta$$

$$+ \frac{0.24\,\Lambda_3}{G_{33}} + \frac{\Lambda_4 \mu}{|G|} + \frac{46.08\,(\Lambda_3 - \Lambda_4)\,c}{|G|^{1/2}}$$

$$+ \frac{0.48\,G_{34}}{G_{33}} \frac{(\Lambda_3 - \Lambda_4)\,c}{|G|^{1/2}} = 0 \qquad \ldots (6.13)$$

where

$$\delta = \frac{17.76\,\Lambda_2}{G_{22}} - \frac{3.76\,\Lambda_1}{G_{11}}$$

and

$$\mu = \frac{0.24\,G_{34}^2}{G_{33}} - 46.08\,G_{34} + 63.84\,G_{33}$$

The results are reported in Table 6.3, along with other published values for comparison. The agreement between the two sets of values points to the fact that the value of $\eta_b = -0.24$ is characteristic of XY_4 tetrahedral non-hydride molecules and this value of η_b can be used as an additional datum for the evaluation of force fields in these molecules.

TABLE 6.1

SYMMETRY FORCE CONSTANTS (mdyn / A)

Molecule	Symmetry force constants					Ref.
	F_{11}	F_{22}	F_{33}	F_{34}	F_{44}	
$C F_4$	9.25	0.71	6.907	-0.938	0.971	1
$Si F_4$	7.178	0.257	6.338	-0.259	0.439	1
$C Cl_4$	4.393	0.328	2.649	-0.394	0.441	2
$C Br_4$	3.355	0.233	2.098	-0.285	0.324	2
$C I_4$	2.368	0.202	1.460	-0.206	0.235	2
$Ru O_4$	7.311	0.34	6.49	-0.07	0.381	3
$Os O_4$	8.85	0.37	8.01	+0.012	0.454	4
$Ge F_4$	6.093	0.1567	5.79	-0.005	0.270	5
$V Cl_4$	3.063	0.1140	2.40	+0.04	0.10	5

TABLE 6.1 Contd.

Molecule	Symmetry force constants					Ref.
	F_{11}	F_{22}	F_{33}	F_{34}	F_{44}	
$C H_4$	5.8416	0.4858	5.383	-0.206	0.458	6
$Ge H_4$	2.808	0.183	2.807	-0.083	0.208	6
$Si H_4$	3.1457	0.2097	3.0305	-0.0163	0.2401	7
$N H_4^+$	6.834	0.5960	6.0224	-0.0667	0.5599	7

TABLE 6.2

CARTESIAN FORCE CONSTANTS AND BOND ASYMMETRY PARAMETER η_b.

Molecule	Cartesian force constants (md/A)		η_b
	$\Phi^1_{xx} = \Phi^1_{yy} = \Phi^1_{zz}$	$\Phi^5_{xx} = \Phi^5_{yy} = \Phi^5_{zz}$	
CF_4	3.3380	9.3853	-0.2442
SiF_4	2.5311	9.4133	-0.2524
CCl_4	1.4128	3.7826	-0.2404
CBr_4	1.0826	3.0053	-0.2432
CI_4	0.7808	2.1013	-0.2341
RuO_4	2.5922	11.4067	-0.2371
OsO_4	3.1520	13.1653	-0.2330
GeF_4	2.1686	9.1333	-0.2359
VCl_4	0.9622	3.9467	-0.2443
CH_4	2.3044	8.5213	-0.2180
SiH_4	1.2447	5.2343	-0.2242
GeH_4	1.1313	4.4093	-0.2060
NH_4^+	2.6530	10.6603	-0.1965

TABLE 6.3

SYMMETRY FORCE CONSTANTS FOR XY_4 (Td) TYPE MOLECULES

Molecule		Symmetry force constants mdyn/A							
		Present result				Previous result			
$SiCl_4$	F_{33}	2.8547	2.96	± 0.09		2.83		2.84	
	F_{34}	-0.1063	-0.14	± 0.03	[8]	-0.10	[4]	-0.14	[5]
	F_{44}	0.2435	0.236	± 0.005		0.24		0.24	
$SnCl_4$	F_{33}	2.3587				2.41		2.11	
	F_{34}	-0.0326				-0.02	[9]	-0.17	[11]
	F_{44}	0.1116				0.12		0.15	
$GeCl_4$	F_{33}	2.6286	2.63	± 0.30		2.57		2.73	± 0.13
	F_{34}	-0.0386	-0.12	± 0.20	[10]	-0.06	[5]	-0.13	± 0.08 [8]
	F_{44}	0.1771	0.18	± 0.01		0.18		0.17	± 0.003

TABLE 6.3 Contd

Molecule	Symmetry force constants mdyn. /A				
	Present result		Previous result		
$Si\ Br_4$	F_{33}	2.1043	1.919	2.31	
	F_{34}	-0.0893	-0.048 [2]	-0.14	[9]
	F_{44}	0.1930	0.208	0.18	
$Ge\ Br_4$	F_{33}	1.9002	1.84	2.03	
	F_{34}	0.0020	-0.02 [11]	-0.08	[9]
	F_{44}	0.1172	0.15	0.14	
$Si\ I_4$	F_{33}	1.5401	1.357		
	F_{34}	-0.0686	-0.030 [2]		
	F_{44}	0.1405	0.157		

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CHAPTER VII
BOND ASYMMETRY PARAMETER - GENERAL DISCUSSION

The results obtained from the application of the theory of bond asymmetry parameter to several XY_n type molecular models are reviewed and discussed.

CHAPTER VII

BOND ASYMMETRY PARAMETER - GENERAL DISCUSSION

In Chapter III a bond asymmetry parameter η_b has been defined in an attempt to study the variation of bonding forces about a chemical bond. Strictly speaking, η_b refers to the centre of a bond b between two atoms X and Y and is defined by

$$\eta_b = \frac{\left\{ \mathcal{F}^X_{xx} + \mathcal{F}^Y_{xx} \right\} - \left\{ \mathcal{F}^X_{yy} + \mathcal{F}^Y_{yy} \right\}}{\left\{ \mathcal{F}^X_{zz} + \mathcal{F}^Y_{zz} \right\}}$$

where the $\mathcal{F}_{ij}$ are the cartesian force constants with the z axis oriented in the direction $\overrightarrow{XY}$. This parameter η_b is expressible in terms of the symmetry force constants. The theory developed has been applied to bent XY_2, planar and pyramidal XY_3 and tetrahedral XY_4 systems. The following conclusions are arrived at from such a study.

1. The bond asymmetry parameter η_b is intimately connected with molecular structure. There exists a smooth relationship between the asymmetry parameter η_b and the hybridization of atomic orbitals involved in bond formation. In planar XY_3 and tetrahedral XY_4 type molecules, the central atom uses sp^2 and sp^3 hybridised orbitals respectively. As a result in these molecules the bond angles have the

fixed values of 120° in XY_3 and 109°28' in XY_4 type molecules. The calculation of η_b values of a number of molecules having these structures shows that each of these molecular types has a constant value for the bond asymmetry parameter. The fact that in tetrahedral molecules there is a very small difference in η_b values between hydrides and non-hydrides suggests that this parameter depends also to a small extent on the overlap of atomic orbitals. In bent XY_2 and pyramidal XY_3 molecules also there is a smooth relationship between η_b and hybridisation, as brought out by the graph between η_b and percentage p - character (Fig. 3.3, Fig. 5.4 and Fig. 5.5.)

2. It has been noted in the case of pyramidal XY_3 type molecules, that all the hydrides fall on a straight line and the non-hydrides on another straight line. (Figs. 5.2, page 131 and 5.3, page 132). These straight lines are analytically represented by the equation

$$\eta_b = m \alpha_\theta + l$$

where α_θ is in radians and m and l are constants having distinct values for the hydride and non-hydride groups of molecules belonging to the pyramidal XY_3 model. This implies the fact that in hydrides

hybridization is more than that indicated by the bond angle [G.R. Bird and C.H. Townes. Phy. Rev. 94, 1203 (1954)] .

For non-hydride molecules m = 1.179, l = -2.053. If η_b is calculated using these values for $\alpha_\theta = 2\pi/3$ radian ($\alpha = 120°$), the value 0.416 is obtained. In Chapter IV it has been noted that for planar XY_3 type non-hydrides, η_b has the characteristic value of 0.48. Since η_b depends on the bond angle, it is interesting to compare these values for the two XY_3 configurations. This establishes a correspondence between the pyramidal and planar configurations of the XY_3 type. The small difference in the two values, namely 0.064 (13% of the η_b value for the planar model), may be explained on the basis that in the pyramidal configuration there is a lone pair orbital while there is none in the planar configuration. Further, it may be observed that for SO_2 with a bond angle of 119° 19' and having unpaired electrons, η_b has been found to be equal to 0.421 (Table 3.2, page 97).

Another observation from Table 5.3 is that in the case of some pyramidal XY_3 type molecules η_b is positive while in others, it is negative. It can also be noted that η_b is positive for molecules in which the

bond angle is less than 100°. If pure p orbitals are used in bond formation the bond angle would be 90°. For ideal sp^3 hybridisation the bond angle is 109° 28'. It is interesting to note that at about the middle of this range the bond asymmetry parameter η_b is nearly zero.

3. In all the XY_4 type molecules studied the bond angles are tetrahedral and hence η_b must have the same value. Eventhough there is only a small difference in the η_b values for hydrides and non-hydrides, it calls for an explanation. The spatial disposition of bonds around the central atom is determined by the hybridization of the atomic orbitals of the central atom. This being the same, the angles are tetrahedral in all the molecules. The strength of chemical bonds depends on the overlap of the bonding orbitals. In hydrides these are the hybridised orbitals of the central atom and the spherically symmetrical is orbitals of the hydrogen atoms. On the other hand in non-hydrides, in place of the spherically symmetrical s obbitals, there exists a p orbital of the halogen or oxygen atom. This difference in the nature of the bonding orbitals may be the reason for the very small difference in η_b values between hydrides and non-hydrides in tetrahedral XY_4 molecules.

4. The asymmetry parameter is proposed to be as an additional datum to be used along with vibrational frequencies for the determination of force constants. The extent of usefulness of this parameter has been investigated by calculating the force constants of molecules belonging to different symmetry types. In all the cases studied the results are found to be satisfactory.

The bond asymmetry parameter η_b characterises the potential environment about the centre of a bond. Since the potential is generated by the electron distribution, η_b turns out to be a useful index of the symmetry of this distribution. η_b is mass independent and is found to depend only on the bond angle in the XY_n type of molecules investigated in this thesis. Besides being an index characteristic of the molecular structure, the bond asymmetry parameter provides an additional input useful in normal co-ordinate analysis.

CHAPTER VIII

INFRARED SPECTRUM OF COUMARIN

Infrared spectra of coumarin in the solid state and in polar and non-polar solvents are recorded. An attempt to explain the observed splitting of the C = O frequency is made. Of the two strong components of the C = O band, one is assigned as a combination and the other as C = O frequency.

CHAPTER VIII

INFRARED SPECTRUM OF COUMARIN

1. Introduction

Raman spectrum of coumarin in the solid state was studied by Venkateswaran [1] and Girijavallabhan and Venkateswarlu [2]. Murti and Seshadri [3] investigated the Raman spectrum of this substance in the solid state as well as in various solvents. They observed that C = C bond frequencies of the benzene and pyron rings are fairly constant. On the other hand the C = O frequency was considerably lower in solids as compared to its value in polar solvents. All the previous workers observed a splitting of the C = O frequency in solid. Since the splitting was absent in the spectra of solutions, Murti and Seshadri explained this splitting as due to intermolecular effects rather than resonance. With a view to finding out the exact reason for the splitting of the C = O frequency, a study of the infrared spectrum of the substance was undertaken and the results obtained are presented here.

2. Results and Discussion

All the spectra were recorded on Beckman IR 20 infrared spectrophotometer. The infrared spectrum compared

well with Raman spectrum and in Table 8.1 the frequencies of prominent lines are given. It may be noted that a few additional lines are observed in the infrared spectrum.

In Table 8.2 the C = O frequencies in the solid and solution states are given along with the values obtained by other workers. From this Table as well as from Fig. 8.1a through 8.1e, it may be seen that the C = O frequency splits in solid as well as in solutions. In all cases as many as four components can be identified. Of these, two components seem to be more intense. In non-polar solvents the lines at 1758 cm^{-1} and 1740 cm^{-1} are very strong while the lines at 1708 cm^{-1} and 1728 cm^{-1} are very weak. In polar solvents the intense line is at 1728 cm^{-1}. Other components at 1708 cm^{-1}, 1740 cm^{-1} and 1758 cm^{-1} are weak. In the solid state the maximum intense line is at 1708 cm^{-1}, and the line at 1758 cm^{-1}, even though weak, resolves out. The component at 1740 cm^{-1} is absent.

From these observations, the following conclusions may be drawn. In non-polar solvents one can expect the C = O bond to be almost free from external influences that try to weaken the bond. Hence it is reasonable to assume that the frequency in non-polar solvents corresponds to the free chemical bond. If we assume that the line at

1758 cm^{-1} is a combination (of the lines at 930 cm^{-1} and 830 cm^{-1}) line, then the C = O frequency may be taken as 1740 cm^{-1}. There is good reason to believe that the line at 1758 cm^{-1} is either an overtone or a combination since it is present at the same position in all the spectra, unaffected by the nature of the solvent. In polar solvents the C = O bond is weakened through co-ordination and the C = O frequency moves to 1728 cm^{-1}. In the solid state the lattice field effect further weakens this bond and the frequency shifts to 1708 cm^{-1}. The line at 1758 cm^{-1} has maximum intensity in non-polar solvents in which the C = O frequency is at 1740 cm^{-1} and is very close to 1758 cm^{-1}. In the case of solid the C = O frequency is at 1708 cm^{-1} and it is well separated from 1758 cm^{-1} which now has only a minimum intensity. Therefore the variation in the intensity of the 1758 cm^{-1} line is in accord with the assumption that it is an overtone or a combination.

Infrared spectrum of coumarin was recorded in the gaseous phase by Hartwell [4] and he reports 1776 cm^{-1} as the frequency of the C = O bond. Eventhough this value seems to be a bit high, the result is in agreement with the conclusions of this investigation. Finally the presence of multiple components may be a result of resonance that exists in the molecule as was shown by

Govinda Rao [5]. Splitting of fundamental frequencies resulting from resonance has been reported earlier [6-8].

FIG. 8.1a through 8.1e. THE C = O frequency region in the infrared spectra of coumarin

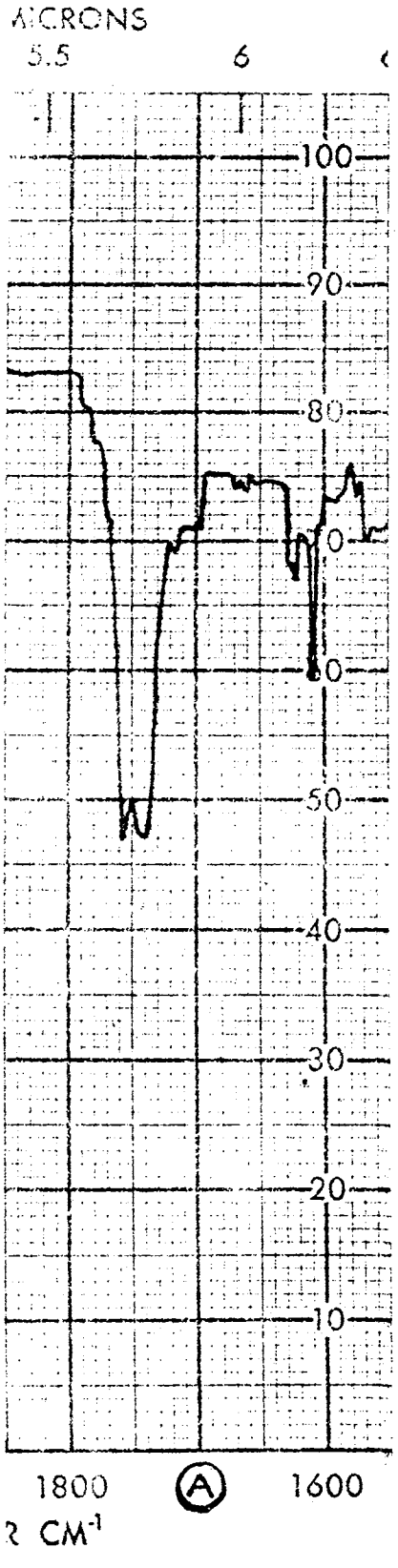
(A) in $C Cl_4$

(B) in $C_6 H_6$

(C) in $C H_3 O H$

(D) in $C H Cl_3$

(E) in solid.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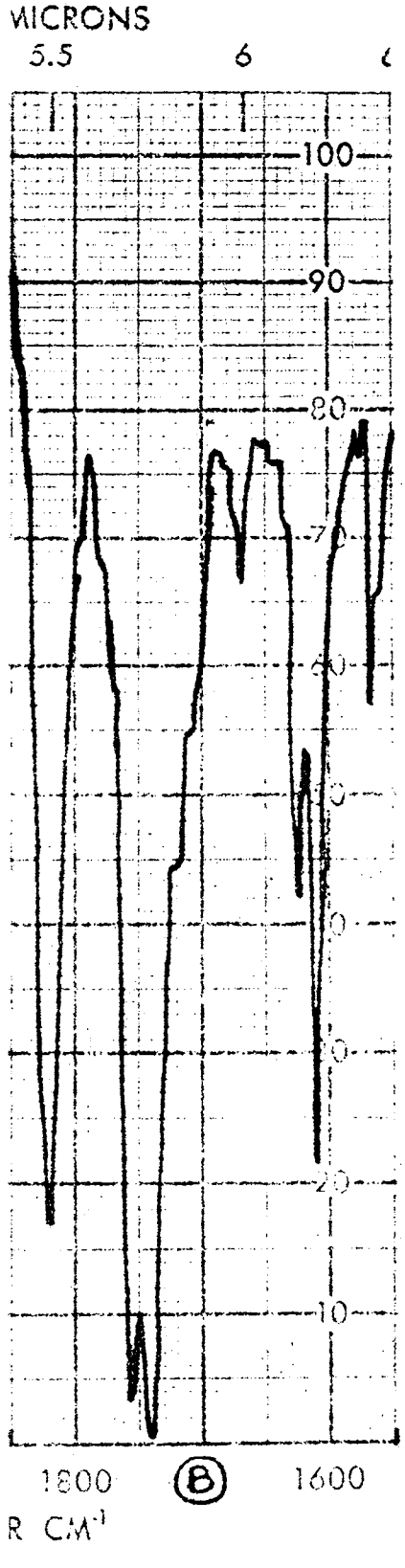
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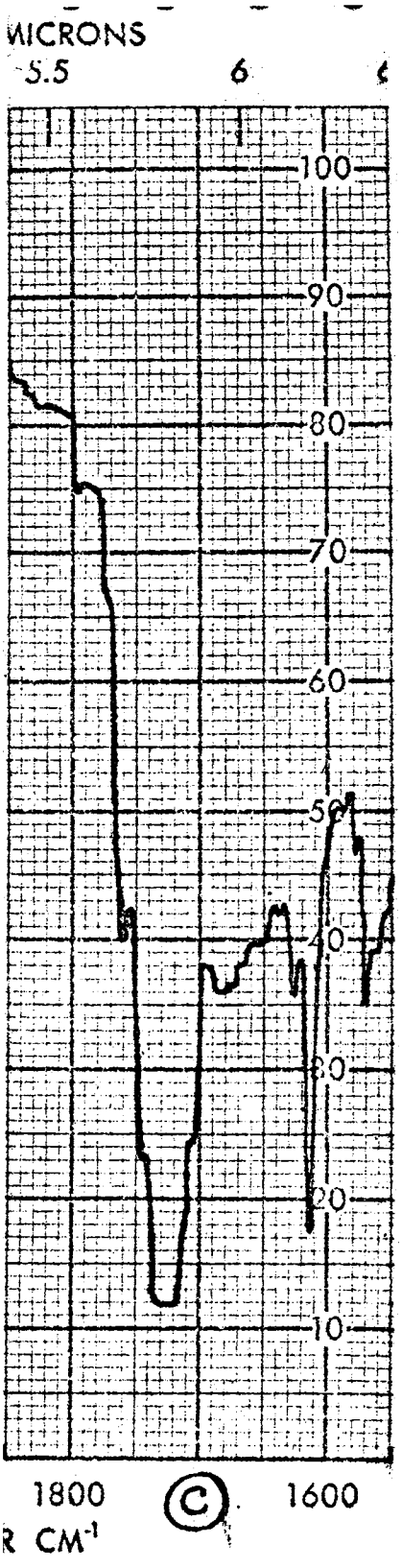
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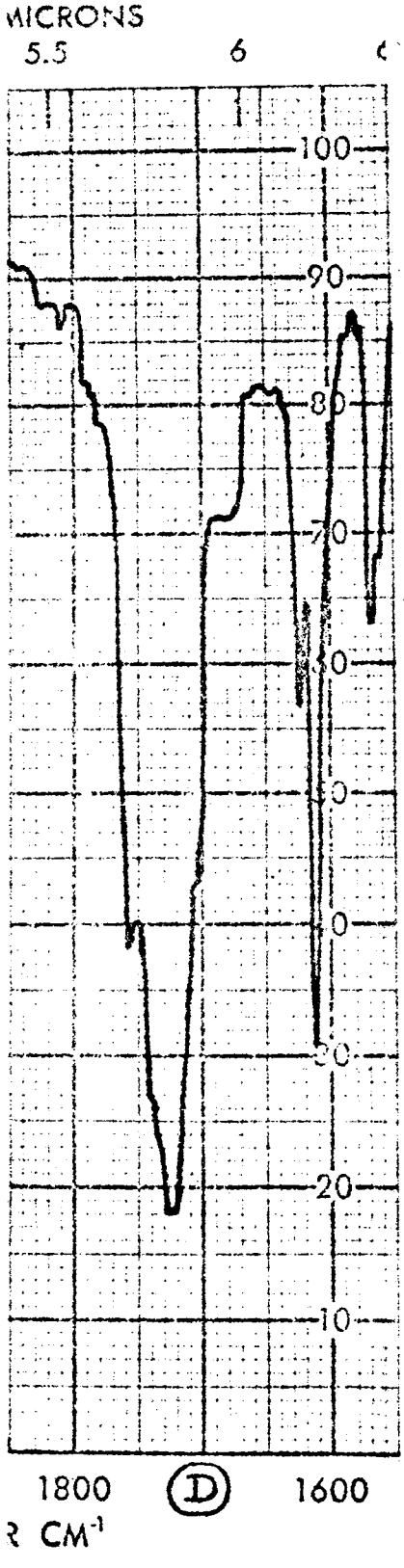
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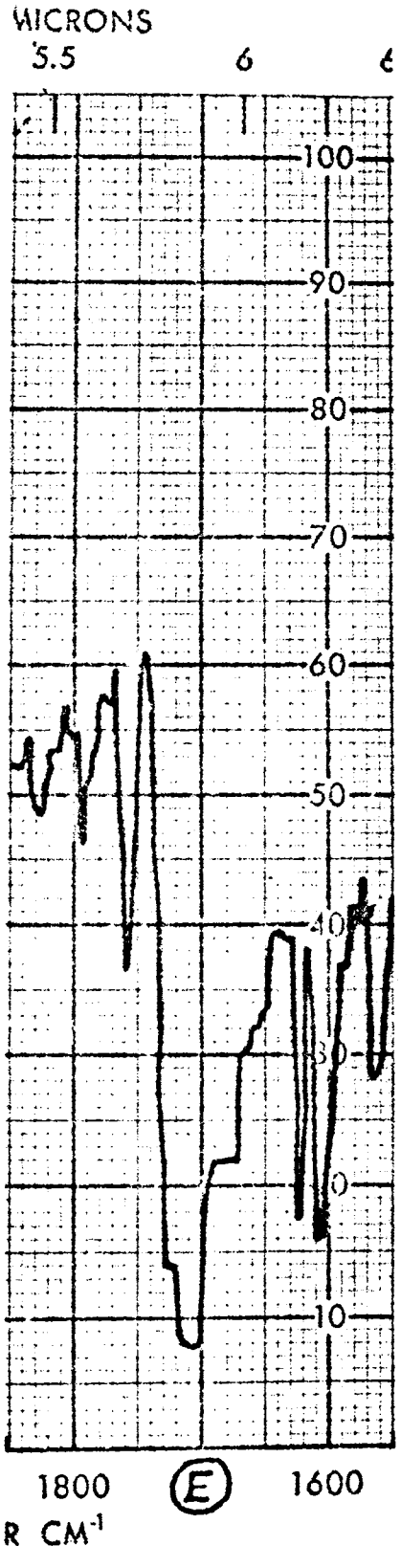
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TABLE 8.1

INFRARED AND RAMAN FREQUENCIES OF COUMARIN (SOLID) IN cm^{-1}

Infrared frequencies present study		Raman frequencies Ref. [1]	Infrared frequencies present study		Raman frequencies Ref. [1]
608	s		1178	w	1173
663	s		1230	s	1228
728	w	726*	1260	s	1259
755	s	764*	1280	s	
829	s		1324	w	1324
890	w		1338	w	
930	s		1372	w	1361
950	w	1030*	1388	w	
1110	s	1098	1398	s	1396
1121	s	1120			1415
1153	w	1152	1435	w	

TABLE 8.1 contd.

Infrared frequencies present study		Raman frequencies Ref. [1]	Infrared frequencies present study		Raman frequencies Ref. [1]
1453	s	1451	1622	s	1623
1471	w		1708	s	1709
1488	w	1485*	1728	w	1729
1563	s	1562	1758	w	
1608	s	1610	1792	w	

* from Reference [2].

TABLE 8.2.

SOLVENT EFFECT ON THE CARBONYL STRETCHING FREQUENCY OF COUMARIN

Solvent	Present study		(Ref. 3)	(Ref. 4)	(Ref.1)	(Ref. 2)
	1708	vw				
CCl_4	1742	s	1742	1738		
	1758	s				
	1710	w				
C_6H_6	1741	s	1736			
	1758	s				
	1705	w				
	1730	s	1721			
CH_3OH	1742	w				
	1760	vw				
	1700	w				
	1728	s	1720			
$CHCl_3$	1740	w		1738		
	1758	w				
	1708	s	1708		1709	1706
(Solid state)	1728	w	1731		1729	1726
	1758	w				
(Vapour)				1776		

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