STUDIES IN MOLECULAR DYNAMICS: NEW CRITERIA FOR EVALUATION OF INTRAMOLECULAR FORCE FIELDS

by

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CERTIFICATE

This is to certify that this thesis is a record of bonafide research carried out by Shri. S. Sasidharan Nair, Research Scholar, during the period 1974-'77 in the Department of Physics, Cochin University under my guidance.

Cochin 682 022
June 22, 1977.

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DECLARATION

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

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PREFACE

The investigations presented in this thesis have been carried out by the author, as a full-time research scholar, during 1974-'77 in the Physics Department of Cochin University.

The present thesis deals with some studies in molecular dynamics, using spectroscopic data. Two new approximation procedures, the "variation method" and the "average bending energy criterion" have been developed for a reliable calculation of molecular force fields and applied to several molecular species belonging to the XY_n type.

Chapter I presents a general introduction to the method of normal coordinate analysis, model force fields, and approximation procedures recently developed in the literature. Methods of calculation of mean amplitudes of vibration, and coriolis constants have also been summarised. The parameter representation is emphasised throughout. Chapter II deals with an application of the variation method to the evaluation of molecular force constants. A formulation of the variation method for the determination of the force constant matrix F has been outlined and adapted to deal with the second order vibrational problem. The method is applied successfully to some hydrides belonging to the bent XY_2 model. Chapter III constitutes a study of the various contributions to the average potential energy of bent XY_2 type molecules due to their zero point vibrations. The variations of the four factors, stretching energy, bending energy, stretch-stretch interaction energy and stretch-bend interaction energy against the parameter characterising the force field has been investigated for some about 23 molecules. From this study a physically meaningful criterion has emerged and is applied to the evaluation of the force field. The parameter value corresponding to the minimum of the average bending energy furnishes an excellent criterion for fixing the force fields with vibrational-frequencies as the only input. The results compare almost exactly with those determined with the use of additional spectroscopic data. In chapters IV, V, VI and VII the "average bending energy criterion" has been successfully made use of for the evaluation of force fields in XY_3(planar), XY_4 (tetrahedral), XY_3 (pyramidal) and XY_6 (octahedral metal-hexafluorides) molecular models.

The original contributions contained in the thesis are the following:

1. A new method based on the variation

technique for the determination of force fields of XY_2 (C_{2v}) type molecules with low mass-ratio.

2. A new criterion for a reliable evaluation of molecular force fields based on the minimum of the average bending energy due to zero point vibrations and its application to several molecules belonging to the XY_n model.

A part of these investigations has been published in the form of the following papers:

1. "Variational Calculation of Molecular Force Fields" - Ind. J. Pure Appl. Phys. 14, 203 (1976).

2. "Parametric Representation of the Average Potential Energy of Zero Point Vibrations" - J. Mol. Spectrosc. 61, 177 (1976).

3. "Average Potential Energy Criterion": Force Fields of Some Planar XY_3 and Tetrahedral XY_4 Molecules - J. Mol. Spectrosc. 65, 142 ~~11, 111 - 111~~ (1977).

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CHAPTER I

INTRODUCTION

A brief review of the method of normal coordinate analysis, model force fields, and approximation procedures recently developed in the literature is presented. Methods of calculation of mean amplitudes of vibration and coriolis constants are also summarised. The parameter representation is emphasised throughout.

Investigations carried out on the infrared and Raman spectra of polyatomic molecules in solid, liquid and gaseous phases have yielded a large wealth of experimental information regarding vibrational frequencies, moments of inertia and internuclear distances. Thermodynamic quantities such as entropy and heat capacity have been calculated from spectral moments of inertia and vibrational frequencies. The vibrational frequencies have been extensively used to fingerprint certain groups in various molecules, but more fundamental is the use of vibrational frequencies in the evaluation of the molecular force field.

Molecular constants such as mean square amplitudes of vibration, shrinkage constants and coriolis coupling coefficients are dependent on the force constants. A force constant is the restoring force per unit displacement (stretching or bending) and is a measure of the strength of chemical binding.

When the force field of a molecule is known, one can calculate the vibrational frequencies of any isotopic substituent. This is an important step especially when the spectrum of the latter cannot be easily obtained. By means of the experimental rules of Badger (1) and Gordy (2) interatomic distances may be calculated from the force constants. Infrared and Raman intensities have been used in conjunction with force constants to calculate the bond dipole moments and polarisabilities and their derivatives (3, 4). The mean square amplitudes of vibration furnish an additional set of parameters for the description of the non-rigid model of the molecule. These quantities may be estimated from electron diffraction data. But the spectroscopic determination of these quantities would be more reliable if the force constants are accurately known. Shrinkage constants calculated from generalised mean square amplitudes can be used for the refinements of bond lengths obtained from electron diffraction. Because of coriolis interaction, degeneracies are split (degenerate interaction) or the band positions are shifted (nondegenerate coupling). The coriolis coupling coefficients estimated from force constants are useful in the study of vibration-rotation interactions, and in the calculation of inertia defect.

Normal coordinate analysis

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

The frequency of a normal vibration is determined by the kinetic and potential energies of the system. The kinetic energy depends on the masses of the individual atoms and their geometrical arrangement within the molecule, while the potential energy arises from interactions between the atoms and is described in terms of a set of force constants. The programme of evaluating force constants and normal coordinates of a molecule is known as normal coordinate analysis. Force constants may be conveniently calculated using Wilson's GF matrix method (6). The essential merit of this method lies in the fact that it leads to a break up of the vibrational secular equation according to the symmetry species of the molecule. To apply the GF matrix method, first, the number of genuine vibrations belonging to each irreducible representation of the point group of the molecule is found by group-theoretical considerations (5, 8). A set of internal coordinates which are changes in bond length, and bond angle is chosen. From the internal coordinates normalised orthogonalised linear combinations called symmetry coordinates are constructed such that they transform according to the characters of the symmetry species to which they belong.

Let R denote the column matrix of internal coordinates r_i and S the column matrix of symmetry coordinates S_i and Q the column matrix of normal coordinates. These are connected by

$$S = UR = LQ \qquad (1.1)$$

where U is an orthogonal matrix and L is called the normal coordinate transformation matrix (7). The potential energy of the molecule is given by the expression

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

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

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

where the tilde denotes the transpose of the column matrix R. The potential energy is unchanged by the transformation to symmetry coordinates. Therefore

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

where F denotes the force constant matrix in symmetry coordinates. It can be seen that

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

The kinetic energy is also expressed in matrix notation as

$$2T = \tilde{\dot{S}}\, G^{-1}\, \dot{S} \qquad (1.6)$$

where G is called the inverse kinetic energy matrix which satisfies the normalisation condition

$$G = L\, \tilde{L} \qquad (1.7)$$

The G matrix elements for a nondegenerate species are given by the relation

$$G_{ij} = \sum_{p} \mu_p\, g_p\, (\vec{s}_{it} \cdot \vec{s}_{jt}) \qquad (1.8)$$

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

$$G_{ij} = \frac{1}{d} \sum_{p} \mu_{p} \, g_{p} \, (\vec{S}_{ia,t} \cdot \vec{S}_{ja,t}) \qquad (1.9)$$

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

$$\vec{S}_{it} = \sum_{k} U_{ik} \, \vec{s}_{kt} \qquad (1.10)$$

U_{ik} being the coefficient of the internal coordinate r_k in the symmetry coordinate S_i. Wilson, Decius and Cross (8) have given expressions for the s_{kt} vectors referring to different types of internal coordinates. Ferigle and Meister (9) have developed methods for writing down these vectors in the case of linear molecules.

Using the lagrangian equations of motions it can be shown that the normal vibration frequencies of the molecule ω_r (cm^{-1}) are given by $L^{-1} \, G \, F \, L = E \Lambda$ or by the roots of the determinantal equation

$$\left| G F - E\Lambda \right| = 0 \qquad (1.11)$$

where E is a unit matrix and Λ is a diagonal matrix with entries $\lambda_r = 4 \pi^2 c^2 \omega_r^2$, c being the velocity of light. This is known as the secular equation of molecular dynamics. If n denotes the number of vibrations belonging to the given species, then the secular equation is of n^{th} degree in λ

The normal coordinates have the property that both the kinetic energy matrix T, and the potential energy matrix, V, are diagonal, thus,

$$2V = \tilde{Q} \Lambda Q \qquad (1.12)$$

$$2T = \tilde{\dot{Q}} E \dot{Q} \qquad (1.13)$$

It can also be shown that

$$\tilde{L} F L = \Lambda \qquad (1.14)$$

Mean Square amplitudes of vibration and Coriolis constants

The average of the square of the instantaneous change in the equilibrium distance between an arbitrary pair of atoms is called the mean square amplitude. The spectroscopic calculation of mean square amplitudes of vibration, which are themselves a set of characteristic constants of the molecule, utilises the data on vibrational frequencies. Cyvin (10, 11) has developed a detailed formalism for the spectroscopic evaluation of mean square amplitudes in terms of the symmetrised mean square amplitude matrix Σ. The mean square amplitudes of vibration referring to internal coordinates are called parallel mean square amplitudes to distinguish them from the generalised mean square amplitudes based on cartesian coordinates. The symmetrised mean square amplitude quantities, Σ_{ij}, are defined by the matrix relation

$$\Sigma = \langle S \tilde{S} \rangle \qquad (1.15)$$

By equation (1.1)

$$\Sigma = L \Delta L \qquad (1.16)$$

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

$$\Delta_r = \frac{h}{8 \pi^2 c \omega_r} \coth \left(\frac{h c \omega_r}{2 k T} \right) \qquad (1.17)$$

Here h is Planck's constant, k the Boltzmann constant, and T the absolute temperature. By making use of the normalisation condition (1.7), it can be shown that

$$\left| \Sigma G^{-1} - E \Delta \right| = 0 \qquad (1.18)$$

An alternative secular equation is

$$\left| \Sigma F - E \Lambda \Delta \right| = 0 \qquad (1.19)$$

Thus Σ_{ij} can be estimated from molecular structural parameters and vibrational frequencies. The symmetrised mean square amplitude Σ_{ij} is a linear combination of the mean square amplitudes $\sigma_{r_\alpha r_\beta}$ in internal coordinates r_α , exactly in the same manner as the F_{ij} are expressed.

According to the rule stated by Jahn (12), two vibrational states can couple through coriolis interaction if the direct product of the symmetry species of the two vibrational states contains a rotational species. Thus, from the character table of the symmetry point group, the allowed types of coriolis interaction can be determined. The method followed in the present thesis is that introduced by Meal and Polo (13) which involves the calculation of the L and C matrices

$$L^{-1} \; C^{\alpha} \; \tilde{L}^{-1} = \zeta^{\alpha} \qquad (1.20)$$

where $\alpha = x,y,z$. The C matrix has elements defined by

$$C^{\alpha}_{ij} = \sum_{p} \mu_p \; (\vec{s}_{ip} \times \vec{s}_{jp}) \cdot \vec{e}_{\alpha} \qquad (1.21)$$

where i and j refer to the symmetry coordinates S_i, and S_j respectively, p to the set of equivalent atoms, μ_p the reciprocal mass of an atom, and $\vec{e}_{\alpha}$ is a unit vector in the α direction.

Model force fields

The inadequacy of frequency data in determining all the $\frac{1}{2} n (n + 1)$ force constants for a symmetry species of order n constitutes the main problem of normal coordinate analysis. The problem in general is indeterminate unless additional data are made use of or some extra assumptions are made which reduce the number of force constants. In the absence of additional data, one can generate an infinite set of force fields in virtue of the relation

$$F = \tilde{L}^{-1} \Lambda \; L^{-1} \qquad (1.22)$$

It follows from (1.7) that

$$L = L_0 \, X \qquad (1.23)$$

where X is an arbitrary orthogonal matrix containing $\frac{1}{2} n (n - 1)$ parameters and L_0 is normalised to G. As a solution to this multiplicity, various approximate force fields have been suggested which imply one or other assumption of a physical or mathematical nature.

One such approximation leads to the central force field of Dennison (14) which postulates only forces along lines joining pairs of atoms. The number of force constants in this model is less than that of the frequencies. However, this assumption is strictly valid only if the molecule is held by ionic interactions, and this is not the case in general.

The simple valence force field (SVFF), first introduced by Bjerrum (15), postulates a strong restoring force in the line of each valence bond whenever the distance between two bonded atoms changes. In addition, there is a resistive force opposing a change of angle between any two bonds.

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

The modern theory of directed valence (16) has been applied by Heath and Linnet (17 - 20) to the formulation of a force,field called the orbital valence force field (OVFF), which eliminates the difficulty of introducing separate angle bending constants for out-of-plane vibrations and makes use of the same constants as those used for in-plane vibrations. OVFF accounts better for the vibration frequencies of certain molecules than does the simple valence force field. This, however, differs from the latter only in the treatment of angular displacements. The OVFF criterion for minimum potential energy is maximum overlap between the bonding orbitals of bonded atoms. SVFF breaks down in the case of molecules containing heavier atoms, and, further, its treatment of bending vibrations is essentially artificial. But OVFF is only an approximation of the GVFF, since the former takes into account only a limited number of force constants. The hybrid bond force field (HBFF), a modification of OVFF based on the correlation of bond strength with bond angle, is successfully applied to ammonia molecule (21).

In the Urey-Bradley force field (UBFF) (22) in addition to the main force constants which represent stretching or bending, repulsion force constants between non-bonded atoms are also introduced. The forces between non-bonded atoms are of the Van der Waals type. The chief advantage of the UBFF is that it contains a smaller number of force constants than the GVFF does, and Shimanouchi (23, 24) has demonstrated the general validity of the UBFF.

Several modifications have been suggested for the conventional UBFF by various workers (25-32). From a comparativ study of the UBFF and the GVFF in some tetrahedral, pyramidal and trigonal planar molecules, Duncan (33) has concluded that, for the Urey-Bradley model to be successful, the non-bonded repulsion force constant must explain both bond-bond and bond-angle interactions at one and the same time. However,this restriction breaks down when the atomic repulsions are not all in one plane, and in these cases the Urey-Bradley model fails to give a true picture.

Parametrisation of F and Σ matrices

In recent years, various types of parameter representations of the force field have been utilised by a number of workers. Török and Pulay (34) have summarised the advantages of the parameter representation first proposed by Taylor (35) and developed by Person and Crawford (7) in fixing the force constants using additional data such as isotopic frequencies, mean square amplitudes of vibration and rotation distortion constants. In the parameter approach the vibrational problem can be set up in terms of a real symmetric matrix W given by

$$W = \tilde{T} F T \tag{1.24}$$

From eq. (1.23), it follows that a mathematically acceptable L matrix may be written as

$$L = T A \tag{1.25}$$

where T is a triangular matrix satisfying the normalisation relation $T \tilde{T} = L \tilde{L}$, and A is an arbitrary orthogonal matrix. The T matrix is taken in the triangular form with the elements $T_{ij} = 0,\ j > i$. The A matrix for a species of order n can be written using $\frac{1}{2} n (n - 1)$ independent parameters e_{ij} (36). Thus,

$$A = \prod A_{ij} \qquad i, j = 1, 2, \ldots\ldots n,\ j > i \tag{1.26}$$

Here A_{ij} is a matrix with the elements

$$A_{ii} = \frac{1}{\sqrt{1 + e_{ij}^{2}}} = A_{jj}$$

$$A_{ij} = \frac{e_{ij}}{\sqrt{1 + e_{ij}^{2}}} = -A_{ji}$$

For n = 2, putting $e_{12} = e$,

$$A = \begin{pmatrix} \dfrac{1}{1+c^2} & \dfrac{c}{1+c^2} \\ \dfrac{-c}{1+c^2} & \dfrac{1}{1+c^2} \end{pmatrix} \qquad (1.27)$$

substituting in eq. (1.22)

$$F_{11} = \frac{1}{1+c^2}\left\{\left[(T_{11}^{-1})^2\lambda_2 + (T_{21}^{-1})^2\lambda_1 \quad c^2\right] + 2\,T_{11}^{-1}\;T_{21}^{-1}\;(\lambda_2 - \lambda_1)\;c + \left[(T_{11}^{-1})^2\lambda_1 + (T_{21}^{-1})^2\lambda_2\right]\right\} \qquad (1.28)$$

$$F_{12} = \frac{1}{1+c^2}\left[T_{21}^{-1}\;T_{22}^{-1}\;\lambda_1\;c^2 + T_{11}^{-1}\;T_{22}^{-1}\;(\lambda_2 - \lambda_1)\;c + T_{21}^{-1}\;T_{22}^{-1}\;\lambda_2\right] \qquad (1.29)$$

$$F_{22} = \frac{1}{1+c^2}\left[(T_{22}^{-1})^2\lambda_1\;c^2 + (T_{22}^{-1})^2\lambda_2\right] \qquad (1.30)$$

Elements of the symmetrised mean square amplitude matrix Σ are obtained from the eqs. (1.16), (1.25) and (1.27) as

$$\Sigma_{11} = \frac{1}{1+e^2}\left[T_{11}^2 \Delta_2 e^2 + T_{11}^2 \Delta_1\right] \quad (1.31)$$

$$\Sigma_{12} = \frac{1}{1+e^2}\left[T_{11} T_{21} \Delta_2 e^2 + T_{11} T_{22} (\Delta_2 - \Delta_1) e + T_{11} T_{21} \Delta_1\right] \quad (1.32)$$

$$\Sigma_{22} = \frac{1}{1+e^2}\left\{\left[(T_{22}^2 \Delta_1 + T_{21}^2 \Delta_2)\right] e^2 + 2 T_{21} T_{22} (\Delta_2 - \Delta_1) e + \left[(T_{21}^2 \Delta_1 + T_{22}^2 \Delta_2)\right]\right\} \quad (1.33)$$

Approximation techniques

Eventhough the exact harmonic force field of the molecule remains undetermined in the absence of additional data, various approximation techniques have been developed for the elucidiation of a physically significant set of force constants using vibrational frequencies, atomic masses and geometrical data as the input. Such criteria would be of considerable help in the study of molecular structure especially when additional inputs such as isotopic frequency shifts, coriolis constants, mean amplitudes and centrifugal distortion constants are not available. A brief account of some of the important attempts made in this direction is given in this section. These methods can be classified into non-iterative and iterative types. A non-iterative method involves the application of some mathematical constraint which immediately leads to a frequency-reproducing F matrix. The iterative methods on the other hand, introduce stepwise coupling or iteration procedures. An excellent survey of approximation methods for the evaluation of force constants has been recently made by Alix et. al. (37).

Iterative methods: stepwise coupling methods

A number of approximation methods are iterative. In this approach starting with an approximate inverse kinetic energy matrix G_0 and force constant matrix F_0, an iterative procedure is employed to obtain the frequency-reproducing force constant matrix F. In the Fadini-Sawodny (38-41) method the choice of the initial set 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 assumed to be given by

$$F_0 = \Lambda_{exp} G_0^{-1} \qquad (1.34)$$

The final true force constant matrix F is determined by the stepwise introduction of the off-diagonal elements G_{ij} of the G matrix. The secular equation for the r^{th} step is then given by

$$\sum_k e_k (G^r F^r)^k = 0 \qquad (1.35)$$

the coefficients e_k are derived from the observed vibrational frequencies. In case the exact solution F^{r-1} is known in terms of a set of approximate potential energy constants, the solution F^r, is

$$F^r = F^{r-1} + \Delta F^r \qquad (1.36)$$

where ΔF^r is a small correction. Developing equation (1.35) in terms of ΔF^r, it is to be seen that

$$\Delta F = R^{-1} J \qquad (1.37)$$

where linearisation is assumed, and R is an $n^2 \times n^2$ matrix of e_k and elements of the $(G^r F^{r-1})$ matrix; J and F are column matrices with n^2 elements.

The Fadini-Sawodny approximation method has been criticised (42) on the ground that in the absence of any restriction on the choice of the coordinate system, any coordinate system can indeed be taken so that the G matrix is diagonal. In such a system a stepwise passage from G_0 to G is meaningless. Further the choice of F_0 is arbitrary, and "the omission of the off-diagonal G elements" at first does not follow from the assumed characteristics of the vibration (43, 8).

Becher and Mattes (44) have developed an iterative technique involving the stepwise introduction of off-diagonal G elements. The iteration is effected by transferring the eigenvectors of an approximate solution of F at the r^{th} step to the exact solution through eq. (1.14).

The approximate F matrix at each step is used to formulate the eigenvector matrix L of the next step. For the r^{th} step, L_r is given by

$$G_r \; F_{r-1} \; L_r = L_r \; \Lambda_r \qquad (1.38)$$

The same eigenvector method has been formulated independently by Johansen (45).

The Chacon-Matzke method (46) is an improvement over the Becher-Mattes approach. Exploiting possible relationships among the F_{ij} elements belonging to various representations, this method enables the evaluation of any number q_s of force constants between n_s and $\frac{1}{2} n_s (n_s + 1)$

Let F^s be a column vector containing the q_s force constants, N^s a matrix having $p_s \, q_s$ elements with its columns arranged in one-one correspondence with those of F^s $\left[p_s = \frac{1}{2} n_s (n_s + 1) \text{ and } q_s < p_s \right]$, and T^s a vector composed of the p_s elements each of which is equal to an observed frequency or zero. The basic equation in the Chacon-Matzke method may be expressed as

$$N^s \; F^s = T^s \qquad (1.39)$$

An approximate F gives the relation

$$N\,F = T \qquad (1.40)$$

where N is a matrix having $\alpha\beta$ elements such that $\alpha = \sum_s P_s$, and β is the total number of force constants to be evaluated.

Let us define a vector M^{ρ} containing the first elements of the matrix $M = Q\,T$, where Q is an orthogonal matrix that satisfies the condition

$$M = Q\,T \qquad (1.41)$$

and

$$Q\,N = K = \begin{pmatrix} K^{\rho} \\ 0^{\rho} \end{pmatrix} \qquad (1.42)$$

Here K^{ρ} is an upper trianfular matrix formed by β^2 elements and 0^{ρ} a null matrix with $(\alpha - \beta)\beta$ elements.

The F matrix is then given by

$$F = (K^{\rho})^{-1}\,M^{\rho} \qquad (1.43)$$

This F matrix is used in the succeeding step of computation and the cycle repeated until the final set reproduces the initial assignment.

Another method based on the stepwise coupling of the G matrix and the transferability of the eigenvector matrices from an approximate to an exact solution of the secular equation has been suggested by Alix and Bernard (47-49). According to them the r^{th} and $(r-1)^{th}$ steps are connected through the commutation relation

$$\left[G_r \cdot F_{r-1},\ G_r \cdot \Delta F_r \right] = 0 \qquad (1.44)$$

This commutation relation together with the Cayley-Hamilton theorem leads to a unique solution of the correction matrix ΔF, thus avoiding the multiplicity of solutions plaguing Fadini's method. Eq.(1.35) used in the Fadini approach is linearised using the above commutation relation. The formulation of the eigenvector matrix L at each step in accordance with the assignment of frequencies is not necessary (50). This method is often known as the matrix polynomial method. From a practical point of view, the method is identical to the logarithmic steps method (51). In problems of large kinematic coupling, application of this polynomial method fails (52).

Non-iterative methods

In the F-trace approach (53-55) the eigenvector matrix L is considered in the parametric form (55)

$$L = V\Gamma^{1/2}X \qquad (1.45)$$

where V is the eigenvector matrix of G, Γ the diagonal matrix containing the eigenvalues of G and X an arbitrary orthogonal matrix containing $\frac{1}{2}n(n-1)$ parameters. The corresponding parametrised F matrix is then

$$F = V\Gamma^{-1/2}\, X\Lambda\tilde{X}\, \Gamma^{-1/2}\, \tilde{V} \qquad (1.46)$$

Billes (53) has suggested that F and G are diagonalised by the same orthogonal matrix V, and the ordering of the eigenvalues of G is such as to select one of the $n!$ solutions of F obtained by permuting the diagonal elements F_{ii}. According to Freeman (55) this orthogonal matrix is determined corresponding to a stationary value of trF. Let the eigenvalues of G be denoted by Γ_i. Using the method of Lagrangian multipliers, the stationary value of trF is reduced to the form

$$\mathrm{tr}F^{s} = \sum_{i} \Gamma_{i}^{-1} \Lambda_{i}^{s} \qquad (1.47)$$

The maximum trF yields a decreasing sequence of Λ_i and increasing sequence of Γ_i values. The reverse ordering corresponds to the solution with minimum trF (56, 43).

The essence of the L-trace approach of Herranz and Castano (57, 58) is that among the different sets of possible L matrices, $L = L_0 X = V \Gamma^{1/2} X$, a characteristic set corresponding to max. trL exists. Applying the constraint that the normal coordinates Q are close to the internal symmetry coordinates S, so that the mixing of different symmetry coordinates in any normal coordinate is small, it can be shown that

$$X = \tilde{V} \qquad (1.48)$$

Therefore

$$L = V \Gamma^{1/2} \tilde{V} \qquad (1.49)$$

$$F = V \Gamma^{-1/2} \tilde{V} \Lambda V \Gamma^{-1/2} \tilde{V} \qquad (1.50)$$

In the version of the method presented by Pulay and Török (59-61) the L matrix is given by $G^{1/2}$.

By a graphical method Strey (62) has investigated the extremal properties of force constants in $n = 2$ cases, varying the angle parameter ϕ systematically over the range of $0 \leq \phi \leq 2\pi$. 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 any other types of molecules the condition f_α minimum represents a satisfactory force field.

Extremal values of off-diagonal force constants have also been exploited for approximating the molecular force field (63–67). 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.

Torkington (68–70) proposed the approximation

$$(G\,F)_{ij} = 0 \quad , j > i \qquad (1.51)$$

Müller et. al (71–75) have shown that this is equivalent to the condition

$$L_{ij} = 0 \qquad j > i \qquad (1.52)$$

This implies that the L matrix is triangular. The elements of the triangular matrix L are given by

$$G_{ij} = \sum_{k=1}^{n} L_{ik} \cdot L_{jk} \quad , \; j > i \qquad (1.53)$$

In the L matrix approximation developed by Müller the L matrix is approximated by a lower triangular matrix. This approach yields reasonable results for force constants in situations where the vibrations are characteristic (71-75). However, the mean amplitudes of vibration calculated by this method are more reliable than the force constants because these are not very sensitive to small changes in the latter. Müller et.al. (71-74) have also shown the equivalence between the extremal properties of F and L. According to them min F_{22} corresponds to $L_{12} = 0$ for $n = 2$ cases. The method has been successfully applied to $n = 3$ cases (75), and widely investigated in second order problems (71-75), (76-81). 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. However, the method does not work well for species containing two stretching or two bending vibrations. For strongly coupled vibrations, several empirical improvements have been reported (82, 83).

For the n^{th} order problem, the L matrix approximation has been applied using Wilson's method of separation of high and low frequencies (84). In this approach the n^{th} order problem is reduced to the $(n - 1)^{th}$ order by factoring out the highest frequency vibration and solving the new secular determinant using the L matrix approximation method.

In the extended L matrix approximation method (for $n = 2$ cases) Muller et.al. (85) 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 (86).

According to the approximation method formulated by Reddington and Aljibury (87), the constraints are made directly on the restoring forces acting on the 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 R_k is assumed to be parallel to the corresponding internal-coordinate. It is also assumed that the restoring force exerted by the molecule for each internal coordinate 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

$$-\frac{\partial E}{\partial \phi_{ij}} = \sum_{1}^{n} \frac{\partial E}{\partial R_k} \frac{\partial R_k}{\partial \phi_{ij}} = 0 \qquad (1.54)$$

$$i, j = 1 \ldots\ldots\ldots n \qquad j 7 i$$

connecting the molecular energy E to ½ n (n − 1) arbitrary parameters ϕ_{ij}. $\frac{\partial E}{\partial R_k}$ is calculated through the virial theorem using the geometrical parameters of the molecule. The method is found to be suitable for obtaining reliable set of force constants for species with no redundant $\overset{a}{\wedge}$ symmetry coordinate.

Dewames and Wolfram (88) have applied the Green's function technique to the general vibrational problem of perturbed molecules. Starting with an unperturbed molecule, the vibrational frequencies are given by

$$(F - M\omega^2)\ X = 0 \qquad (1.55)$$

where X_i^j, i = 1 to 3, j denotes the atom, are the cartesian coordinates of the atoms of the unperturbed molecule. M is a diagonal matrix of diagonal 3 x 3 blocks whose elements are the masses of the various atoms in the molecule, ω is the angular frequency and F the force constant matrix. However, it is convenient to work in the mass-transformed representation in which an interaction matrix D is defined through the relation

$$D = M^{-1/2}\ F\ M^{-1/2} \qquad (1.56)$$

For a related molecule

$$(F' - M'\omega^2)\ X' = 0 \qquad (1.57)$$

By factoring out the dynamical matrix for the unperturbed molecule one arrives at the secular determinant for the vibrational frequencies of the perturbed molecule in the form

$$\left| G(\omega^2)\,(\Delta M\ M^{-1}\,\omega^2 - \Delta D) + E \right| = 0 \qquad (1.58)$$

where $G(\omega^2) = (\omega^2 - D)^{-1}$ is the Green's function for the unperturbed molecule, ΔD the mass transformed F matrix, E is the identity matrix.

If the mixing parameters for a molecule are determined from the isotopic frequencies, then the exact force constants can be generated through

$$D_{ij} = \sum_{n} X_{in}\, X_{jn}\, \omega_n^2 \qquad (1.59)$$

Here in this method the force constant is generated from frequencies directly without invoking any assumption regarding potential.

In a recent paper Santhakumari, Babu Joseph and Krishna Pillai (89) have defined a bond asymmetry parameter η_b for a bond in terms of cartesian force constants. It is found that the η_b value depends on the interbond angle or the percentage p character. Using the graph between η_b and interbond angle, they have calculated the force fields of several molecules. This method has been extended to various XY_n models such as planar XY_3, pyramidal XY_3, and tetrahedral XY_4 (90). For planar XY_3 and tetrahedral XY_4 systems, η_b assumes a characteristic constant value depending on whether the molecule is a hydride or nonhydride. This approach is not strictly an approximation in the same sense as the other noniterative methods, but may better be regarded as a semi-empirical method based on certain observed correlations.

Force constants may be obtained by the method of "relative Raman intensities", "high-low frequency separation method" or the "point mass model". Using relative Raman intensities in the framework of the bond polarisability theory, the force constants of XY_4 (T_d) molecules have been evaluated (91-94).

The high-low frequency separation method (8) as well as the point mass model (95, 96) lead to a reduction in the order of the secular equation.

The iterative as well as non-iterative methods reviewed in this chapter are based on certain assumptions which may not be strictly valid from a physical point of view. Most approximations are tailored to suit particular classes of molecules. For instance, the Muller approximation yields satisfactory force fields in $n = 2$ cases with small kinematic coupling. The success of iterative methods depends crucially on the choice of the initial set. In the absence of additional experimental data it is always necessary to resort to approximations. The successful approximations may be deemed to convey some physics which is otherwise not obvious in normal coordinate treatments based on first principles. Motivated by these considerations two approximation procedures, the variation method and the average bending energy criterion, have been developed and applied to large number of molecular species, the results of which are reported in the following chapters of the present thesis.

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CHAPTER II

VARIATIONAL CALCULATION OF MOLECULAR FORCE FIELDS

A variational method of calculation of molecular force fields is developed and applied to the second order vibrational problem of several molecules belonging to the XY_3 (C_{3v}) model. The method has been applied to both hydrides as well as nonhydrides, but excellent results are obtained only for molecules with a low mass ratio m_y/m_x.

Introduction

The parameter representation (1, 2) provides a unified picture of the various approximate force fields (3-6). Since a variational eigenvector can be generated by means of a set of parameters it is natural to try to connect the parameter representation of force constants and the variation method. Eventhough the variation technique occupies a prominent position among quantum mechanical methods of computation of eigenvalues, it has not yet been exploited in force constant calculation. Accordingly in this chapter the application of the variation method to the evaluation of molecular force field has been investigated.

Variation Method

Let F represent the symmetrised force constant matrix of order n corresponding to a certain irreducible vibrational species of a molecule. Since F is Hermitian, its eigenvalues ϕ_i are real and eigenvectors orthogonal. These eigenvectors can be normalised and span an n-dimensional normed linear space. For finite n, this space is necessarily complete (7). If f and g are vectors in this space, their scalar product is defined as the matrix product.

$$(f, g) = \tilde{f} g \qquad (2.1)$$

Consider an arbitrary vector X in this space which can be expressed as a linear combination of the orthonormalised eigenvectors X_{F_i} of the F matrix. Thus, as we are interested in normalised vectors,

$$X = \sum_{i=1}^{n} e_i \; X_{F_i} \qquad (2.2)$$

such that $\sum_{i=1} e_i^2 = 1$, e_i being assumed to be real in physically interesting cases. Now consider the product

$$X \, F \, X = \sum_{i,j} e_i \, e_j \, \tilde{X}_{F_i} \, F \, X_{F_j}$$

$$= \quad {}_{i} \; e_i^2 \quad {}_{i} \qquad (2.3)$$

where ϕ_i is the eigenvalue corresponding to the eigenvector X_{F_i}. If ϕ_0 denotes the lowest eigenvalue of F, then the variational theorem asserts:

$$\phi_0 \leq \tilde{X} \, F \, X \qquad (2.4)$$

However, this inequality is devoid of any computational significance, because unlike any quantum mechanical Hamiltonian with specified interaction potentials, the matrix F itself is unknown.

It has been shown (2) that the molecular vibrational problem can be set up using a real symmetric matrix W given by eq. (1.24). If F' is an arbitrary force field that reproduces the frequencies Λ, a matrix W' is defined analogous to W as

$$W' = \tilde{T} F' T \qquad (2.5)$$

Suppose this is diagonalised by an orthogonal matrix A'. If $F' \neq F$ (the true force field), then, generally, $A \tilde{A}' \neq \tilde{A}' A \neq E$, where A is the matrix that diagonalises W and E is the identity matrix. Since W' has, by construction, the same spectrum of eigenvalues as W itself,

$$F' = \tilde{P}' \Lambda P' \qquad (2.6)$$

where $P' = \tilde{A}' T^{-1}$.

If P represents the transformation matrix generating the exact F-matrix, then

$$\tilde{P}^{-1} F P^{-1} = \tilde{P}'^{-1} F' P'^{-1} \qquad (2.7)$$

which implies

$$F = \tilde{K}' F' K' \qquad (2.8)$$

where

$$K' = T A' \tilde{A} T^{-1} \qquad (2.9)$$

It may be noted that if $F' = F$ then $K' = E$. Eq.(2.8) shows that the exact F matrix is related to the arbitrary frequency-reproducing F' matrix through a similarity transformation.

Let us now define a vector Y' in the n dimensional hyperspace as

$$Y' = K'^{-1} X' \qquad (2.10)$$

with norm given by

$$\tilde{Y}' Y' = \tilde{X}' \tilde{K}'^{-1} K'^{-1} X'$$

$$= \tilde{X}' V X' \qquad (2.11)$$

where $V = \tilde{K}'^{-1} K'^{-1}$, $V = E$ for $F' = F$, the true force field. Then by eq. (2.4)

$$\phi_0 \leq \tilde{Y}' F Y' \Big/ \tilde{Y}' Y'$$

or using eq. (2.8)

$$\phi_0 \leq \tilde{X}' F' X' \Big/ \tilde{X}' V X' \qquad (2.12)$$

The variational problem then is to minimise the function

$$\phi_0 = \tilde{X}_0' F' X_0' \Big/ \tilde{X}_0' V X_0' \qquad (2.13)$$

with respect to all the parameters generating X_0', V, and F'.

For the 2 x 2 vibrational problem let us denote the generating parameters of X', V and F' by α, β and θ, respectively. For the true force field $\beta = 0$. Rewriting eq. (2.13)

$$\phi_0 = \tilde{X}_0'(\alpha) F'(\theta) X_0'(\alpha) \Big/ \tilde{X}_0'(\alpha) V(\beta) X_0'(\alpha)$$

~~$X_0'(\;)$~~ (2.14)

Applying the necessary conditions for a minimum

$$\frac{\partial \phi_0}{\partial \alpha} = 0, \quad \frac{\partial \phi_0}{\partial \beta} = 0, \quad \frac{\partial \phi_0}{\partial \theta} = 0 \qquad (2.15)$$

together with the condition $\beta = 0$ for the true force field, it follows that α is the diagonalising parameter for F which is determined by the F elements themselves. Again, at the variational minimum $\tilde{X}_e'(\alpha)\, V(\beta)\, X_e'(\alpha) = 1$. Accordingly a search for the minimum of the smaller eigenvalue ϕ_e of F' as a function of a single parameter θ is made.

Distinction between variational and extremal force fields

The force field obtained by the variational principle is to be distinguished from any of the extremal force fields, as can easily be verified in the second order case. The variational force field can be easily distinguished from that resulting from the F_{22} minimum assumption suggested by Strey (8) for nonhydrides. The smaller eigenvalue ϕ_e in the second order case is

$$\phi_o = \tilde{X}_e \, F \, X_e \tag{2.16}$$

where X_e is the corresponding eigenvector. The minimal criterion is

$$\frac{d\phi_e}{d\theta} = 0 \tag{2.17}$$

Minimising with respect to the parameter θ,

$$\tilde{X}_e \frac{dF}{d\theta} X_e + \frac{d\tilde{X}_e}{d\theta} F X_o + \tilde{X}_e F \frac{dX_e}{d\theta} = 0 \tag{2.18}$$

Let the eigenvector

$$X_e = \begin{pmatrix} X_{e1} \\ X_{e2} \end{pmatrix} \qquad (2.19)$$

The minimal criterion given by eq.(2.17) now reads

$$X_{e1}\left(X_{e1}\frac{d F_{11}}{d \theta} + X_{e2}\frac{d F_{12}}{d \theta} \right) + X_{e2}\left(X_{e1}\frac{d F_{12}}{d \theta} + X_{e2}\frac{d F_{22}}{d \theta} \right)$$

$$= -2 \left[X_{e1}\left(F_{11}\frac{d X_{e1}}{d \theta} + F_{12}\frac{d X_{e2}}{d \theta} \right) + X_{e2}\left(F_{12}\frac{d X_{e1}}{d \theta} + F_{22}\frac{d X_{e2}}{d \theta} \right) \right] \qquad (2.20)$$

From this it is evident that the criteria $\frac{d \phi_e}{d \theta} = 0$ and $\frac{d F_{22}}{d \theta} = 0$ are generally independent of each other.

Application to XY_2 (C_{2v}) type molecules

The XY_2 molecular model is illustrated in Fig. (2.0). The above method has been applied to the second order vibrational problem of molecules belonging to the XY_2 (C_{2v}) model. The

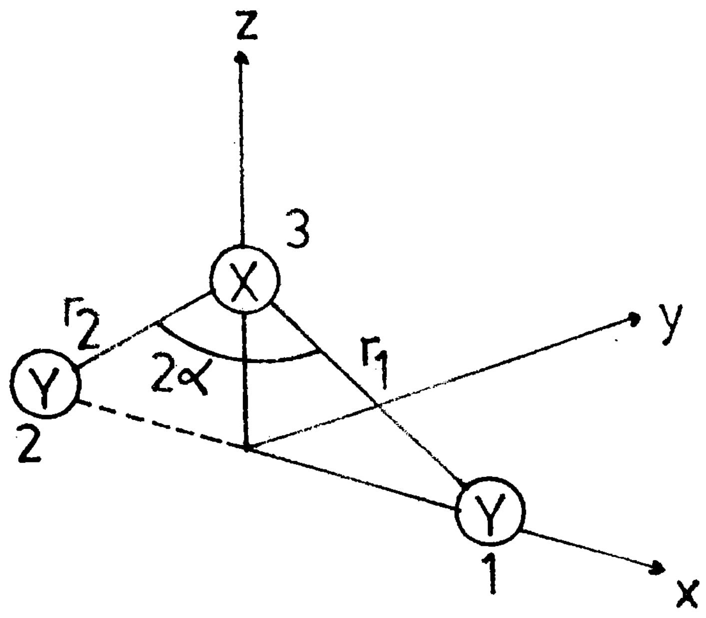


Fig.(2.0) XY_2 Molecular Model
(Symmetry C_{2v})

vibrations of a bent XY_2 type molecule can be classified into $2 A_1 + B_2$ species. The following set of symmetry coordinates has been made use of in this investigation (9).

$$S_1 \; (A_1) \; = \; 2^{-1/2} \; (\Delta r_1 + \Delta r_2)$$

$$S_2 \; (A_1) \; = \; r \, \Delta\alpha$$

$$S \; (B_1) \; = \; 2^{-1/2} \; (\Delta r_1 - \Delta r_2)$$

where Δr_1 and Δr_2 are the changes in bond lengths and $\Delta\alpha$ the change in bond angle YXY. r denotes the equilibrium X - Y distance. The G_{ij} are calculated through the relations (9)

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

$$G_{12} = -2^{1/2} \mu_x \sin 2\alpha \quad \text{and}$$

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

where 2α is the equilibrium YXY angle and μ_x and μ_y are the reciprocal masses of atoms X and Y respectively. T_{ij} and T_{ij}^{-1} are given by the relations

$$T_{11} = \sqrt{G_{11}}$$

$$T_{21} = \frac{-G_{12}}{T_{11}} \quad \text{and}$$

$$T_{22} = \sqrt{G_{22} - T_{21}^{2}}$$

and

$$T_{11}^{-1} = \frac{1}{T_{11}}$$

$$T_{21}^{-1} = \frac{-T_{21}}{T_{11}\,T_{22}} \qquad \text{and}$$

$$T_{22}^{-1} = \frac{1}{T_{22}}$$

These values together with the harmonic frequencies are given in Table 2.1.

Results and discussion

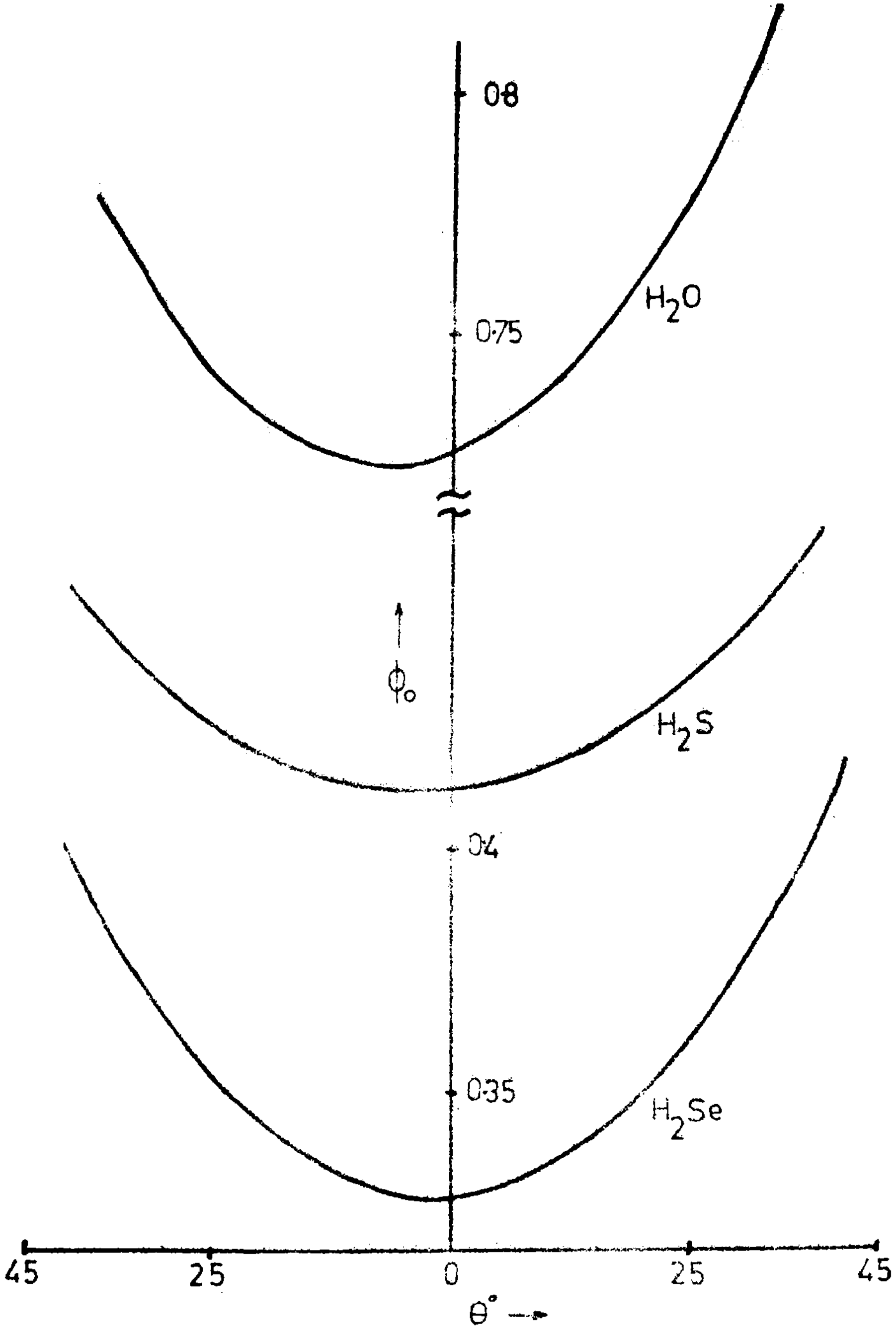
The intramolecular force fields of H_2O, H_2S, H_2Se, SO_2, NO_2 and ClO_2 have been studied by the variational method. The geometric and harmonic frequency data required in this programme of investigation are taken from the literature (10–16). Though $(\phi_e)_{min}$ can in principle be determined by direct calculation, the graphical method (Fig. 2.1) has been adopted mainly because it furnishes a display of the variation of ϕ_e with Θ. However, only in the cases of H_2O, H_2S, H_2Se and their isotopes, force fields in excellent agreement with previously reported values could be evaluated. The force constants obtained in these cases are reported in Table 2.2. with the corresponding $(\phi_e)_{min}$ values.

A plot of Θ_{min} which represents the value of Θ at which ϕ_e is a minimum versus the mass ratio $\rho = m_y / m_x$ has also been made (Fig. 2.2). For bent XY_2 type molecules, this is a smooth curve indicating that as ρ increases, Θ_{min} shifts away from zero. Referring to standard force fields, it can be concluded that the more remote Θ_{min} is from zero, the less likely will the corresponding force field be the exact force field. Thus only for very small ρ values, the variational force field is close to the exact force field. The variational force fields have been employed to predict the vibrational frequencies of the isotopic forms D_2O, D_2S and D_2Se also.

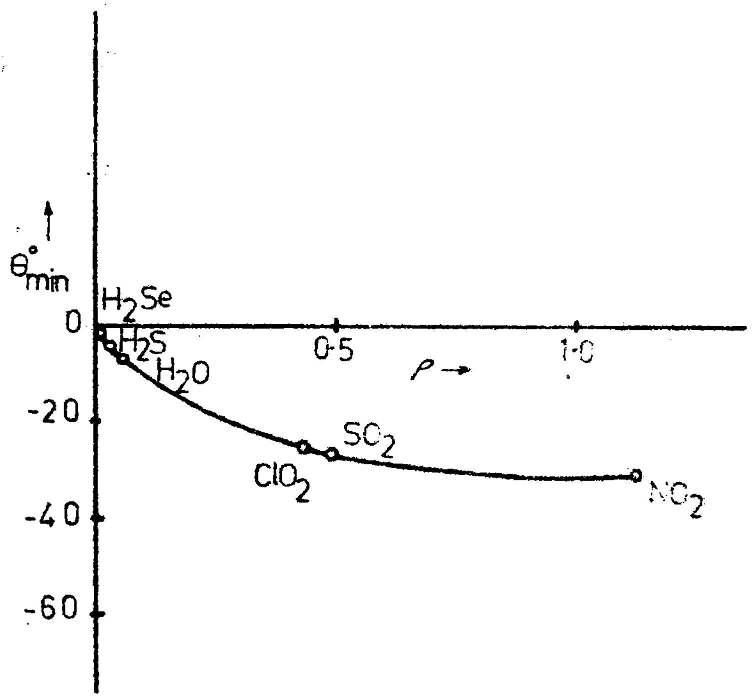
Extension of the variational principle to higher order vibrational problems requires the minimisation of ϕ_e with respect to $\frac{n(n-1)}{2}$ parameters. Naturally, the graphical method cannot be used in this domain.

Fig. (2.1). Variation of ϕ_e with θ for H_2 Se, H_2 S and H_2 O.

Fig. (2.2). Dependence of θ_{min} on ρ for bent XY_2 type molecules.


0·8
0·75
0·4
0·35
ϕ_0
H_2O
H_2S
H_2Se
45
25
0
25
45
θ° →

Fig·2·1·


θ°_{min}
0
-20
-40
-60
0·5
1·0
ρ →
H_2Se
H_2S
H_2O
ClO_2
SO_2
NO_2

Fig·2·2·

Table 2.1

Harmonic frequencies and structural data of the XY_2 type molecules

Molecule	G_{11}	G_{12}	G_{22}	T_{11}^{-1}	T_{12}^{-1}	T_{22}^{-1}	Interbond angle (in degrees)	ω_1 (cm^{-1})	ω_2 (cm^{-1})	Ref.
H_2O	1.0391	-0.0860	2.1410	0.9810	0.0563	0.6850	104.525	3832.17	1648.47	10
H_2S	1.0220	-0.0440	2.0490	0.9891	0.0301	0.6990	92.20	2721.92	1214.51	11
H_2Se	1.0050	-0.0180	2.0100	0.9980	0.0130	0.7054	90.56	2438.66	1057.60	12
NO_2	0.0843	-0.0730	0.3672	3.4449	1.5600	1.8120	134.07	1357.80	756.80	13
ClO_2	0.0776	-0.0553	0.2060	3.5890	1.0410	2.2854	117.60 ± 1	962.80	455.40	14, 16
SO_2	0.0784	-0.0384	0.2180	3.5710	1.0994	2.2413	119.32	1167.60	526.27	15

Table 2.2

Θ_{min} values, variational F elements and isotopic frequencies of bent XY_2 type molecules

Molecule	Θ_{min}	Variational F elements (md /Å)	Previous result (md /Å)	Ref.	Isotope	Frequency (cm^{-1}) Calculated	Frequency (cm^{-1}) Experimental	Ref.
H_2O	- 6°17'	F_{11} 8.3350	8.342 ± 0.012	18	D_2O	ω_1 2756.0	2764.0	10
		F_{12} 0.5795	0.283 ± 0.27			ω_2 1208.0	1206.0	
		F_{22} 0.7895	0.769 ± 0.018					
H_2S	- 3°26'	F_{11} 4.2699	4.264 ± 0.007	17	D_2S	ω_1 1955.0	1947.0	11
		F_{12} 0.1630	0.210 ± 0.054			ω_2 870.0	874.0	
		F_{22} 0.4308	0.435 ± 0.006					
H_2Se	- 1°43'	F_{11} 3.4896	3.487 ± 0.001	17	D_2Se	ω_1 1740.0	1734.0	12
		F_{12} 0.0661	0.033 ± 0.031			ω_2 752.0	753.0	
		F_{22} 0.3292	0.331 ± 0.001					
SO_2	-25°10'							
NO_2	-30°07'							
ClO_2	-24°42'							

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CHAPTER III

PARAMETER REPRESENTATION OF AVERAGE POTENTIAL ENERGY OF ZERO POINT VIBRATIONS: APPLICATION TO XY_2 (C_{2v})TYPE MOLECULES

The variation of contributions to the average vibrational potential energy with a parameter characterising the force field has been mapped for some twenty three bent symmetrical XY_2 systems. A simple and physically significant criterion for the calculation of extremely reliable harmonic force fields is found to emerge from this study. Minimisation of the main average bending energy contribution $f_\alpha \sigma_\alpha$ yields excellent force fields for nonhydrides in agreement with standard force fields fixed with the help of additional data. For hydrides also this criterion leads to generally satisfactory force fields.

Introduction

In this chapter the variation of the different contributions to the average potential energy $\langle V \rangle$ of some bent XY_2 molecules due to zero point vibrations with the parameter generating the force field has been investigated. This study is motivated by the fact that some useful landmark different from that leading to the minimisation of the lowest eigenvalue of the F matrix discussed in the preceding chapter may exist from the point of view of energy contributions arising from internal coordinates to the average vibrational potential energy.

Average vibrational potential energy

In terms of internal valence coordinates r_i, the potential function may be written in the harmonic approximation as

$$2\,V = \sum_{i,j} f_{ij}\, r_i\, r_j \qquad (3.1)$$

where f_{ij} is the corresponding force constant. Taking averages in the sense defined by Cyvin (1)

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

$$= \sum_{i,j} f_{ij}\, \sigma_{ij} \qquad (3.2)$$

where the σ_{ij} are vibrational mean square amplitudes defined as $\sigma_{ij} = \langle r_i \; r_j \rangle$. At any finite temperature, vibrational excitation occurs with a Boltzmann distribution, and the above mentioned averaging process implies a thermal averaging in addition to the quantum mechanical averaging. In order to avoid the higher vibrational states and the consequent variation of $\langle V \rangle$ with temperature, ground states undergoing zero point vibrations are made the subject of study. In terms of internal symmetry coordinates one may express eq. (3.2) as

$$\langle 2\,V \rangle = \sum_{i,j} F_{ij} \; \Sigma_{ij} \qquad (3.3)$$

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

Application to XY_2 type molecules

The symmetry coordinates are given in Chapter II. For the bent symmetric XY_2 type molecular model, shown in Fig. (2.0), the potential energy is written as

$$\begin{aligned} 2\,V = f_r \left[(\Delta r_1)^2 + (\Delta r_2)^2 \right] &+ r^2 f_\alpha (\Delta\alpha)^2 \\ &+ 2\,f_{rr} \,(\Delta r_1 \,\Delta r_2) + 2\,r\,f_{r\alpha} \\ &(\Delta r_1 + \Delta r_2) \qquad (3.4) \end{aligned}$$

where Δr_1 and Δr_2 are stretch increments and $\Delta\alpha$ is the change in bond angle and r denotes the equilibrium X - Y distance. Averaging as in eq. (3.2)

$$\langle 2 V \rangle = 2 f_r \sigma_r + f_\alpha \sigma_\alpha + 2 f_{rr} \sigma_{rr} + 4 f_{r\alpha} \sigma_{r\alpha} \qquad (3.5)$$

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

Using the symmetry coordinates introduced in Chapter II we have

$$f_r = \frac{F_{11} + F_{33}}{2}$$

$$f_{rr} = \frac{F_{11} - F_{33}}{2} \qquad (3.6)$$

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

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

and

$$\sigma_r = \frac{\Sigma_{11} + \Sigma_{33}}{2}$$

$$\sigma_{rr} = \frac{\Sigma_{11} - \Sigma_{33}}{2}$$

$$\sigma_{r\alpha} = \frac{\Sigma_{12}}{\sqrt{2}} \qquad (3.7)$$

$$\sigma_\alpha = \Sigma_{22}$$

In the case of an XY_2 type molecule, F_{ij} and Σ_{ij} for the A_1 species can be written in terms of a single parameter in the following form (2, 3)

$$F_{ij} = \frac{(p_{ij}\, c^2 + q_{ij}\, c + r_{ij})}{1 + c^2} \qquad (3.8)$$

and

$$\Sigma_{ij} = \frac{(l_{ij}\, c^2 + m_{ij}\, c + n_{ij})}{1 + c^2} \qquad (3.9)$$

where the coefficients p_{ij}, q_{ij}, r_{ij}, l_{ij}, m_{ij} and n_{ij} can be obtained from the geometry, atomic masses, and fundamental frequencies (harmonic, wherever available) of the molecule. These are given in Table 3.1. Also,

$$F_{33} = \frac{\lambda_3}{G_{33}}$$

and

$$\Sigma_{33} = G_{33}\, \Delta_3 \qquad (3.10)$$

Using eqs. (3.6) to (3.10), variation of each of the terms in eq. (3.5) has been mapped by systematically changing the value of the parameter c. Earlier studies (3, 4) have shown that F_{ij} and Σ_{ij} elements exhibit extremal behaviour, when expressed as functions of a parameter. However, the simultaneous role of F_{ij} and Σ_{ij} in determining the average vibrational potential energy contributions has not been studied so far.

Results and discussion

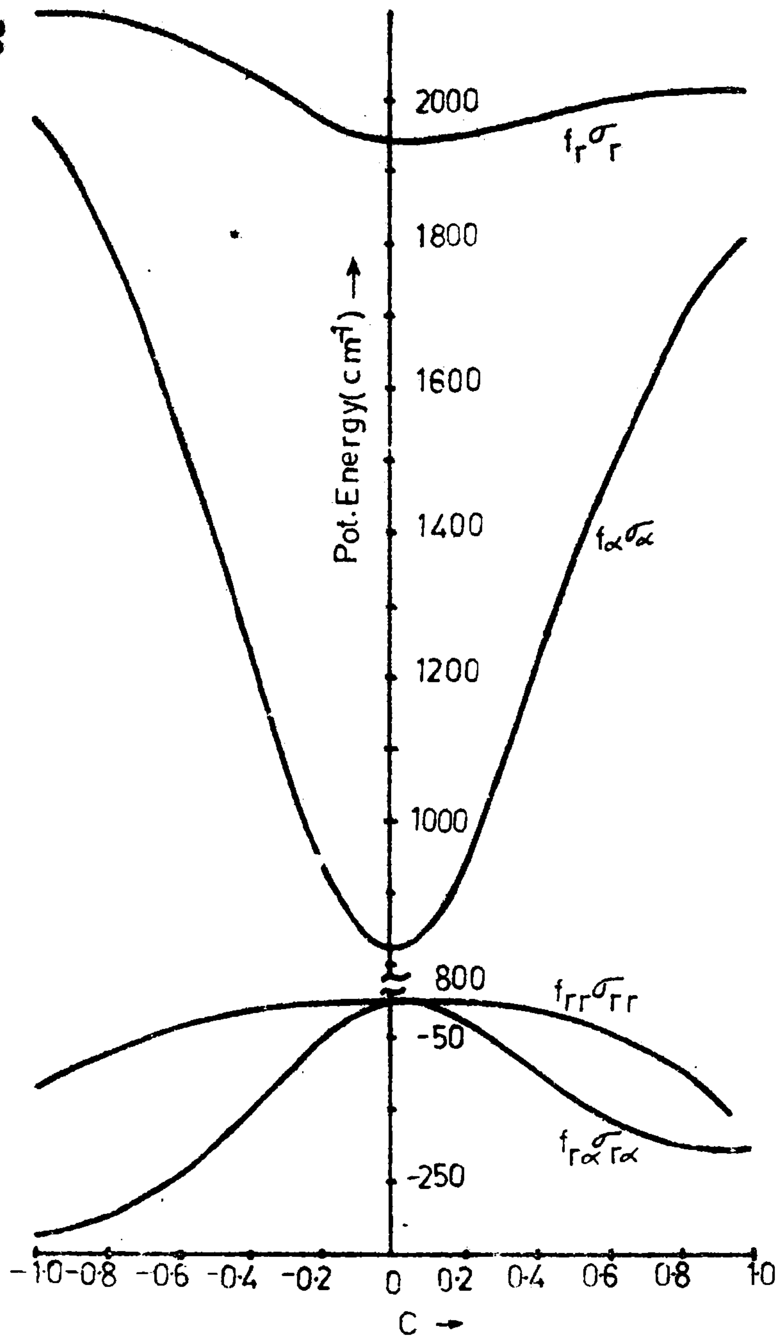
Török (5) has shown that for a given assignment of frequencies the range of the parameter e must be restricted to − 1 to + 1. Consequently the variation of the average potential energy terms studied in eq. (3.5) has been restricted to this range. It is noted that the various contributions show extremal behaviour inside this range. Plots of the $f_{ij}\sigma_{ij}$ quantities versus e are shown in Figs. (3.1) to (3.10). In the case of hydrides, the average stretching energy as well as the bending energy exhibits a minimum within the range $-1 \leq e \leq +1$, while the stretch-stretch interaction energy $f_{rr}\sigma_{rr}$ has a maximum near the origin. For all the nonhydride species studied, we find that there exists a minimum for the average bending energy $f_{\alpha}\sigma_{\alpha}$ in the vicinity of the origin. The value of the parameter e corresponding to this minimum of the bending energy term is found to yield a force field, which agrees excellently well with that fixed with the aid of additional experimental data. This criterion is called the average bending energy criterion. Table 3.2 gives the force constants calculated by this method. The calculations were done on a digital computer. For nonhydrides, these force constants are in excellent agreement with standard force constants, while for hydrides the bending energy minimum condition gives a force field which agrees satisfactorily with the standard values. However, for hydrides as well, other criteria such as $f_r \sigma_r$ = maximum, and $f_{rr} \sigma_{rr}$ = maximum lead to results far different from exact ones. In table 3.3 are given the parameter values at minimum or maximum for each of the four terms in the average potential energy expression (3.5)

Conclusion

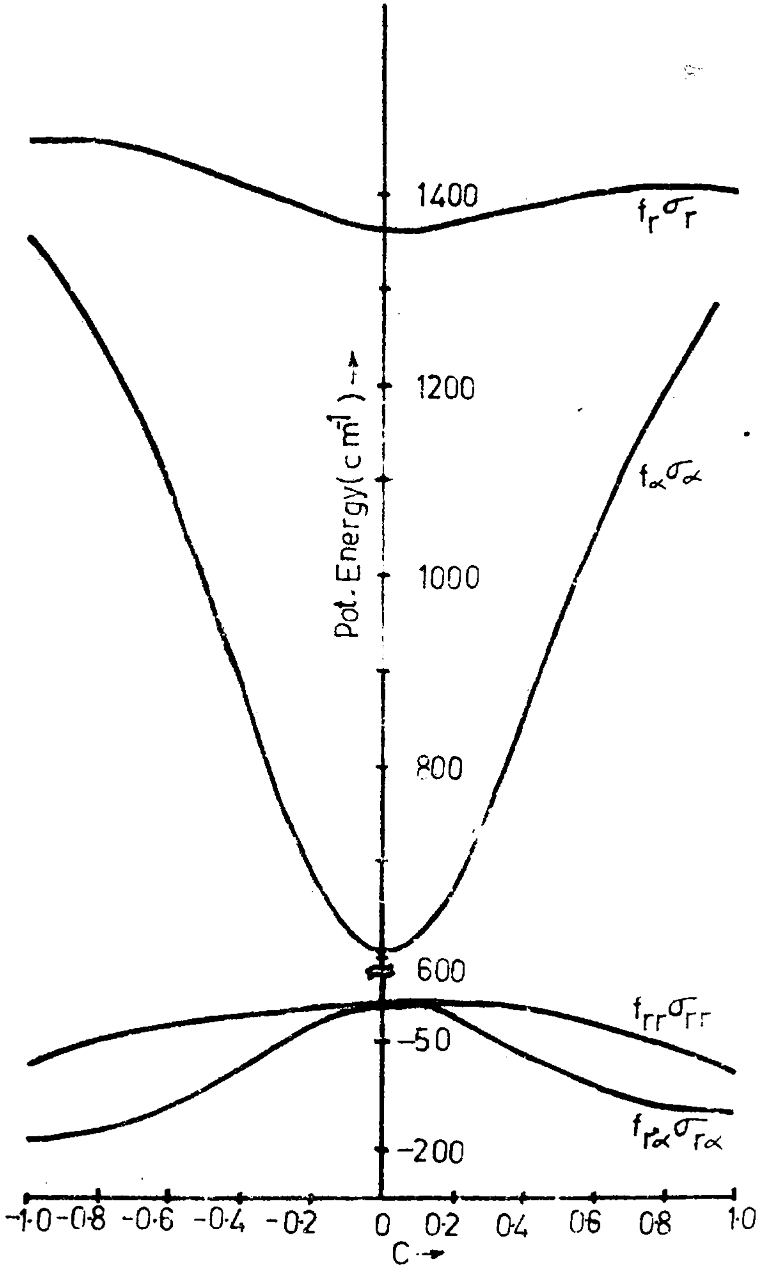
In this chapter the variation of the various contributions to the average potential energy due to zero point vibrations has been studied with the aid of a parameter characterising the force field, for 23 molecular species belonging to the bent symmetric XY_2 model. As a result of this investigation a unique criterion seems to emerge from the extremal behaviour of average energy contributions. This enables us to fix the F elements of the second order vibrational species A_1. The minimum of the main bending contribution to the average potential energy ($f_\alpha \sigma_\alpha$) gives results in very good agreement with standard force fields fixed by invoking additional data. The fact that for non-hydrides like NO_2 , SeO_2, SO_2, etc. and for hydrides like H_2O, H_2S, and H_2Se, etc., the average energy force fields are in excellent agreement with standard force fields indicates that this criterion is preferable to various other approximations currently in vogue. The present approach deals with the extremal behaviour of average potential energy contributions and stands distinct from the method of extremal force constants (3). It may be noted that the average bending energy criterion employed in this present work has not been proposed a priori but has emerged as a result of investigation of a large number of systems. An interesting observation in this context is that the results obtained for isotopic species are very nearly equal Figs.(3.11) to (3.12). In the succeeding chapters the method of average bending energy of zero point vibrations is extended to a large number of molecules belonging to the XY_3 (D_{3h}), XY_3 (C_{3v}), XY_4 (T_d) and XY_6 (O_h) models.

Figs. (3.1) - (3.10). Plots of average potential energy terms for various bent XY_2 type molecules in the range $-1 \leq c \leq +1$.

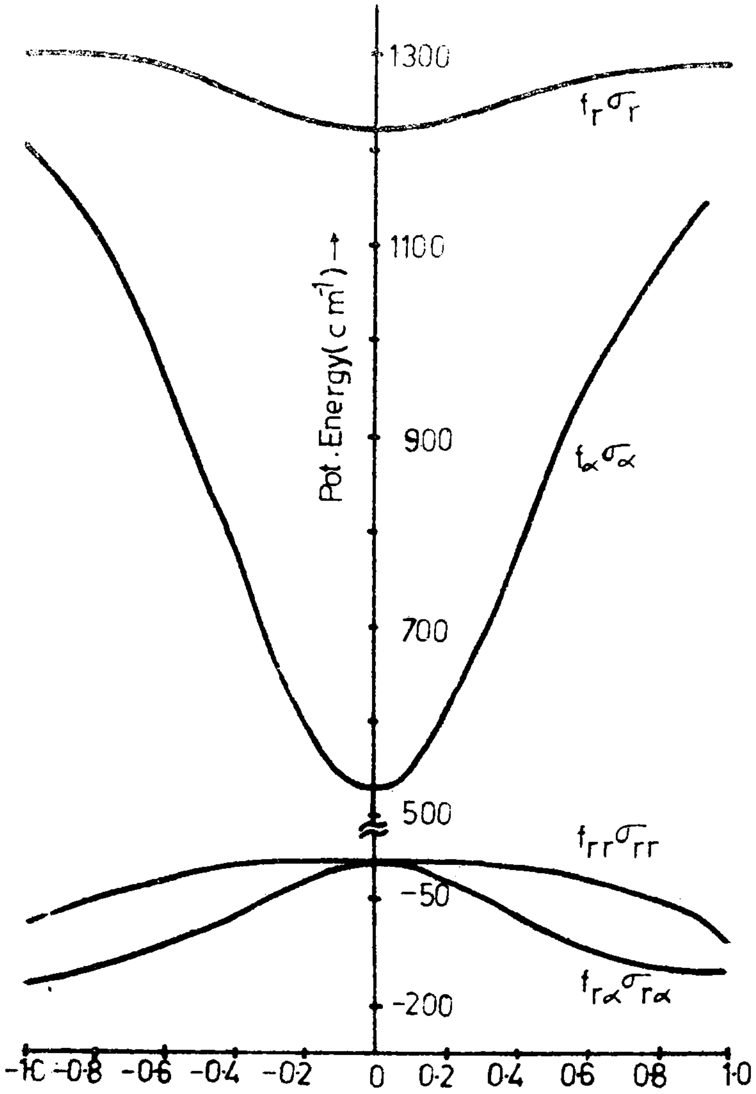
Figs. (3.11) and (3.12). Variation of $f_\alpha \sigma_\alpha$ for isotopic substituents of H_2O and SO_2.



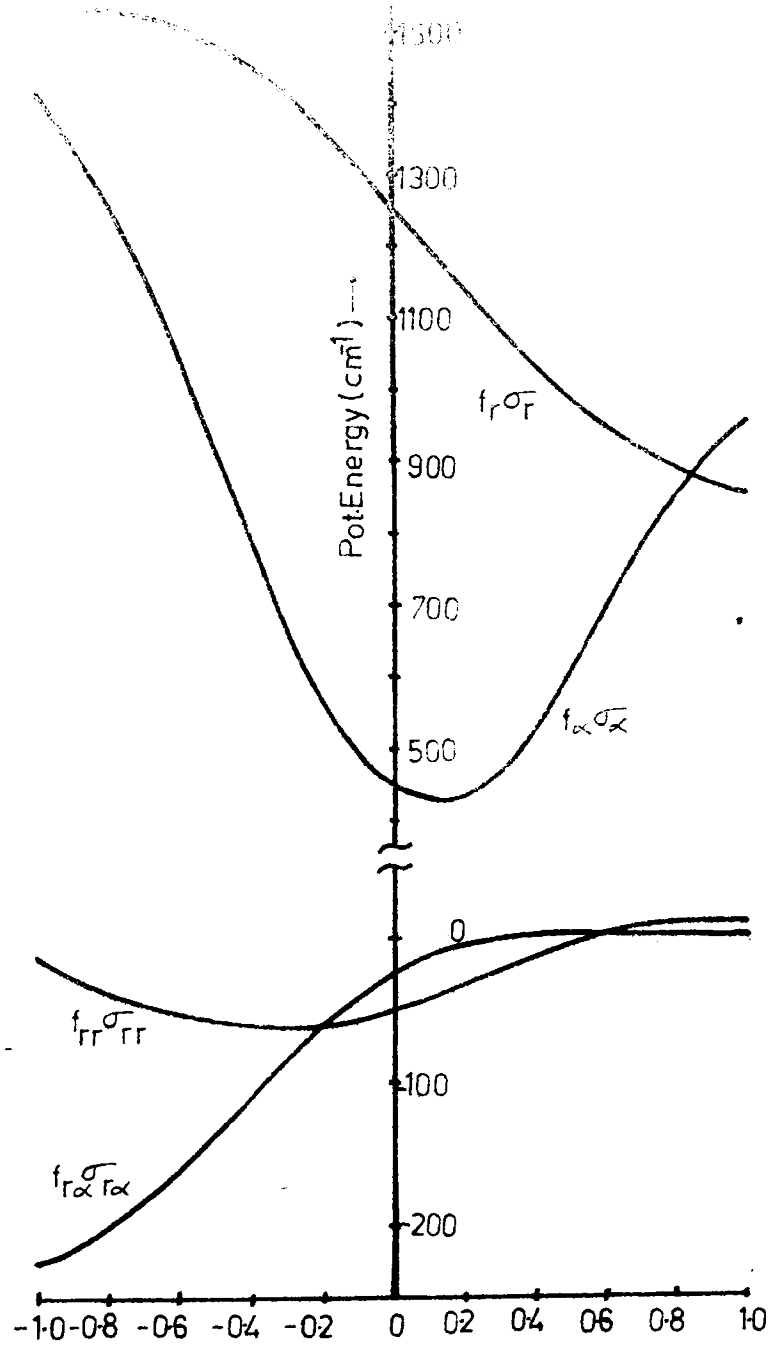
Fig·3·1· H_2O



Fig·3·2· H_2S



Fig·33· H_2Se



Fig· 3·4· NO_2

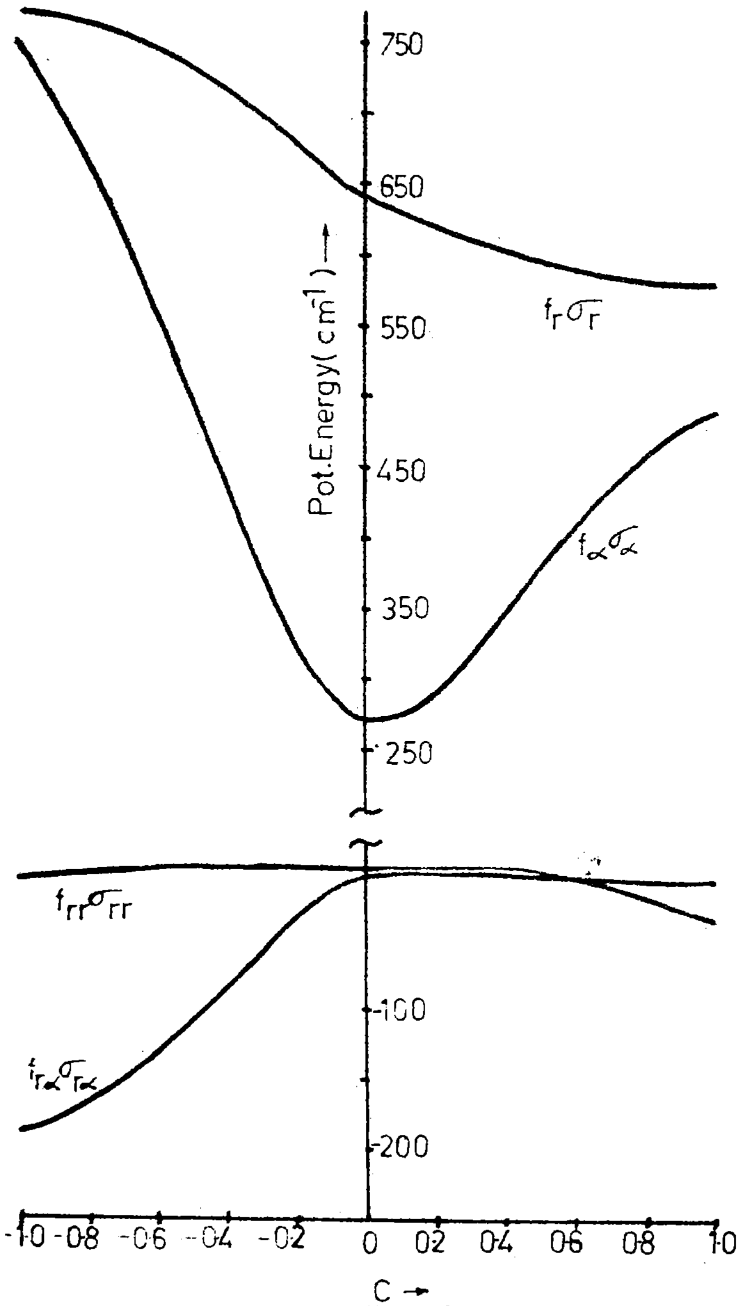


Fig. 3.5. SO$_2$

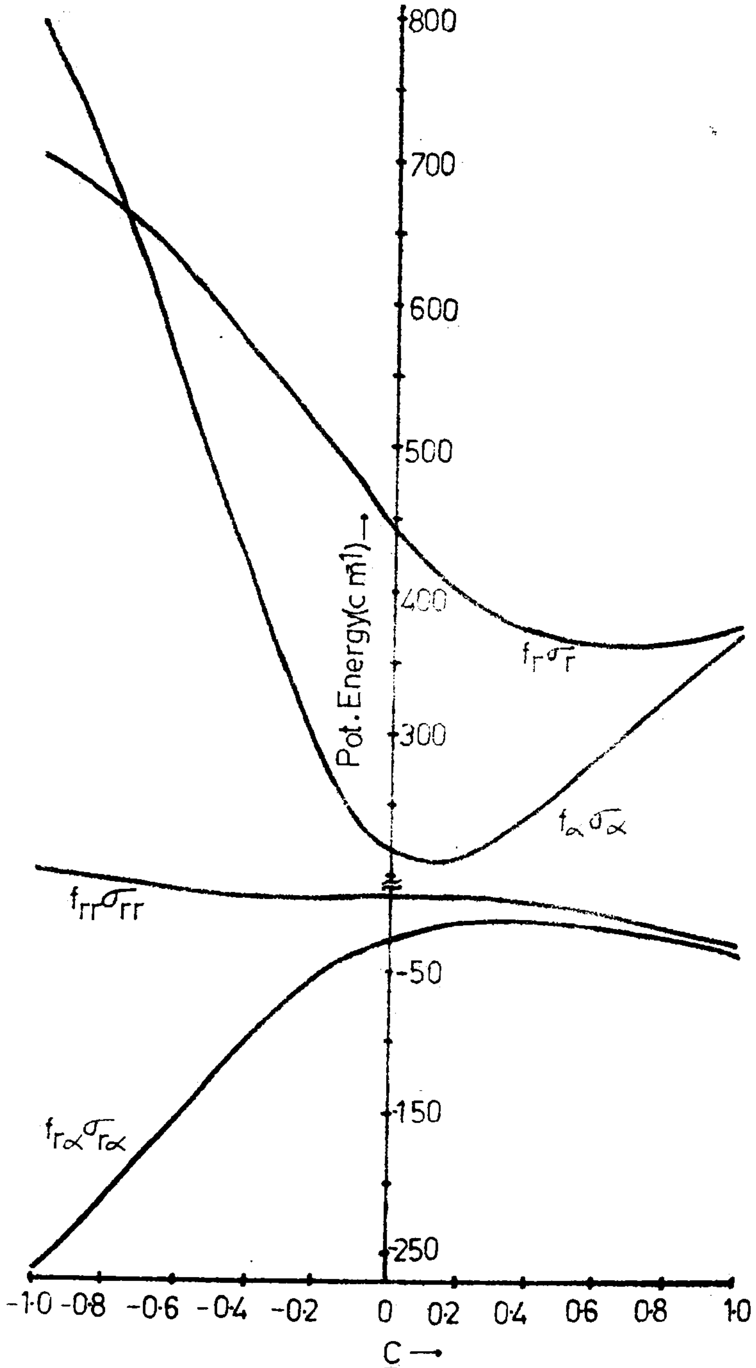
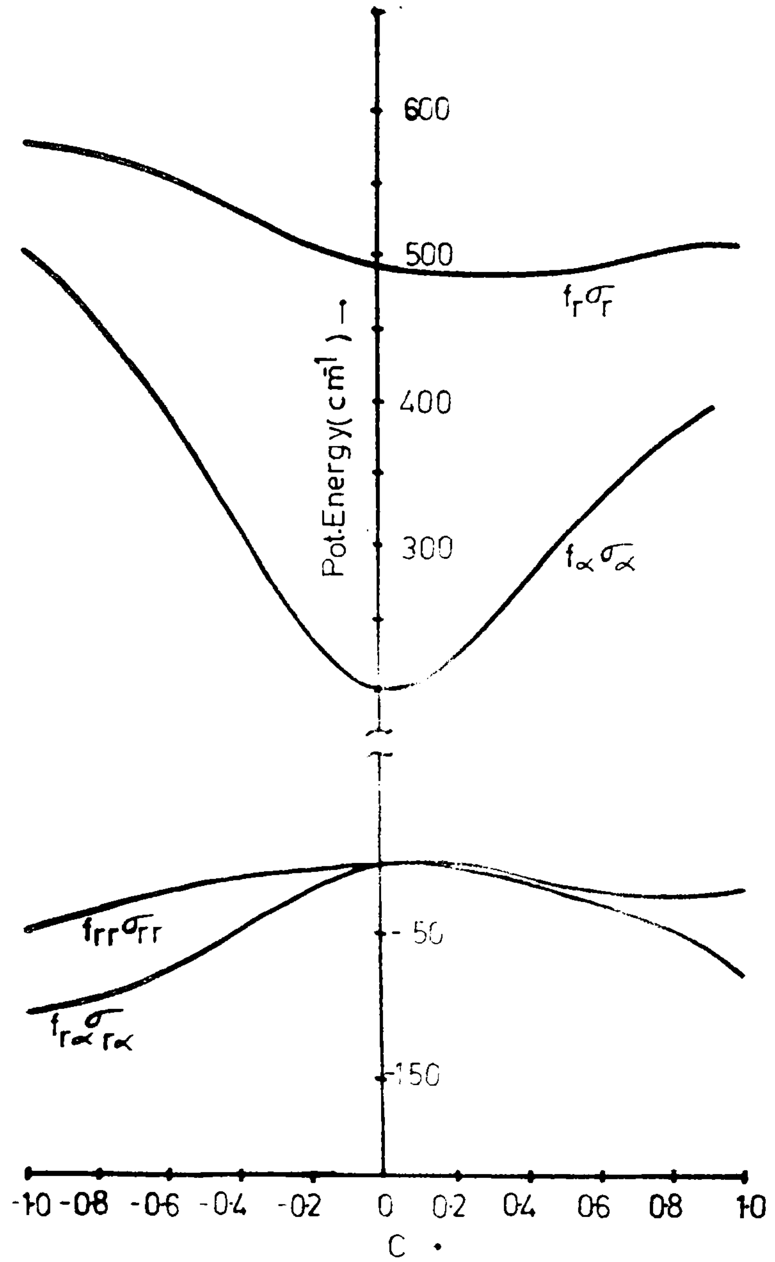
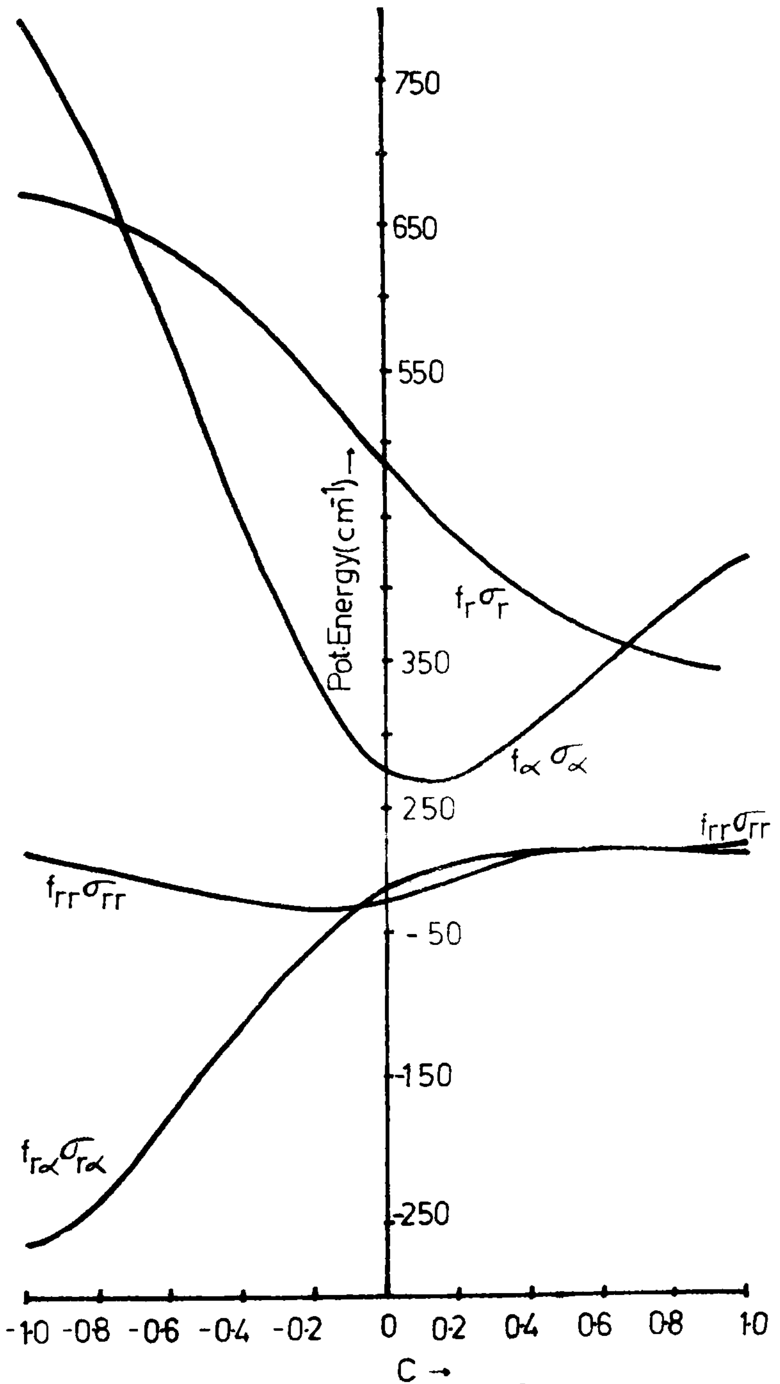


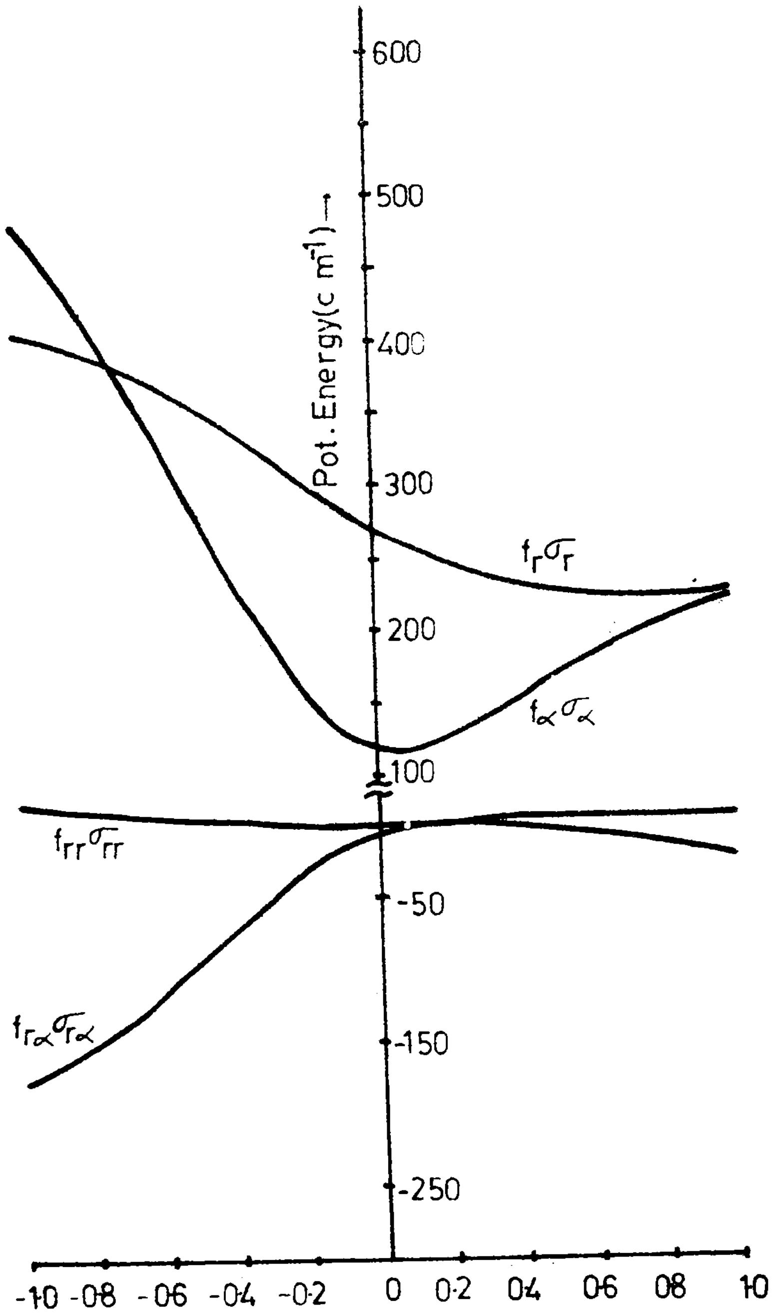
Fig. 3.6. Cl$_2$O



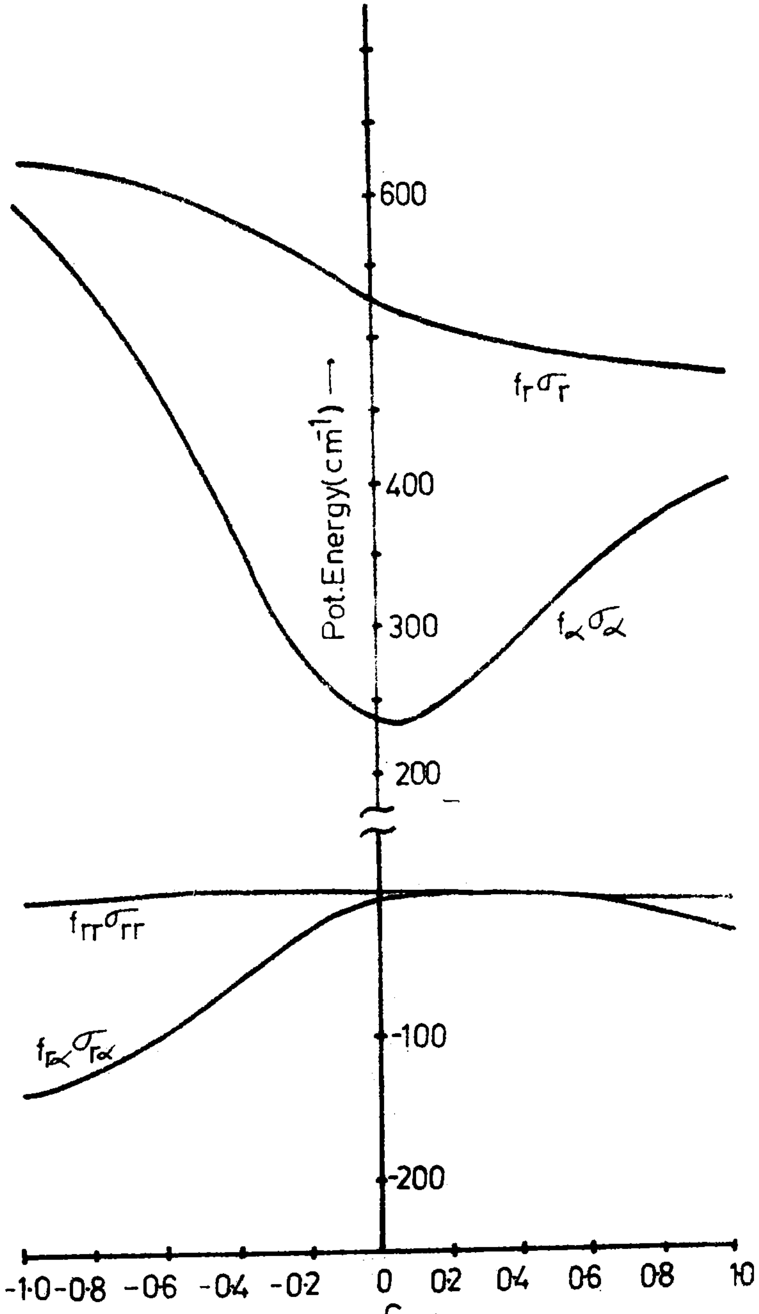
Fig·3·7 SeO_2



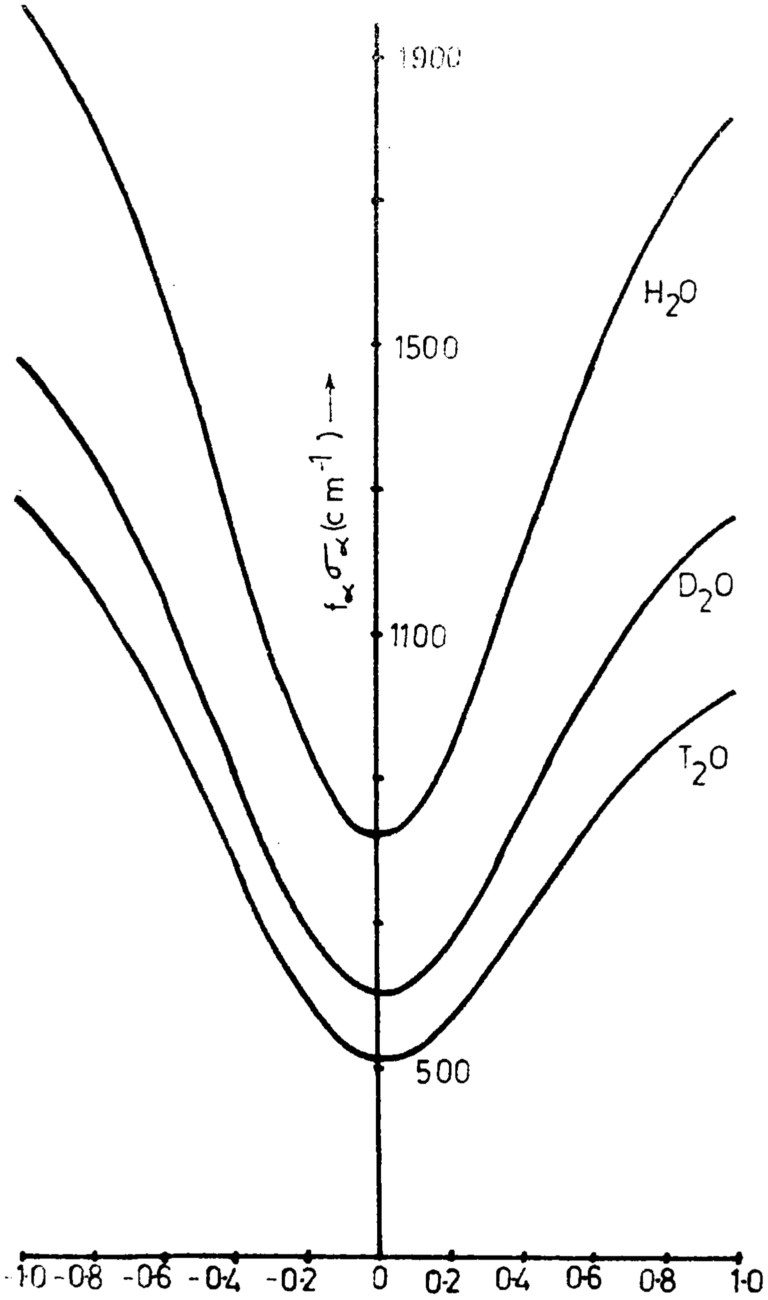
Fig·3·8·F_2O



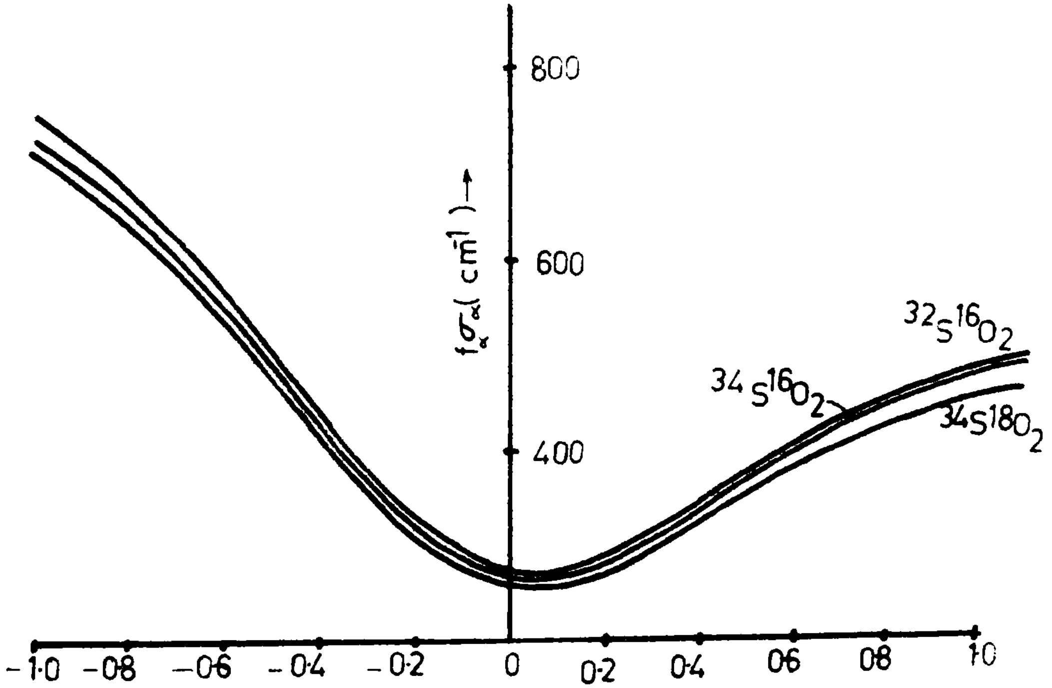
Fig·3·9· Cl_2O



Fig·3·10· ClO_2



Fig·3·11·



Fig·3·12·

Table 5.1

Frequencies and structural data of some XY_2 (C_{2v}) type molecules

Molecule	G_{11}	G_{12}	G_{22}	G_{33}	T_{11}^{-2}	T_{12}^{-1}	T_{22}^{-1}	ω_1 (cm^{-1})	ω_2 (cm^{-1})	ω_3 (cm^{-1})	Reference
H_2O	1.0391	-0.0856	2.1409	1.0704	0.9610	0.0564	0.6846	3832.17	1648.47	3942.53	16
D_2O	0.5433	-0.0856	1.1494	0.5747	1.3566	0.1478	0.9383	2763.8	1206.39	2888.78	16
T_2O	0.3784	-0.0856	0.8194	0.4097	1.6256	0.2529	1.1180	2303	1014	2439.26	16
H_2S	1.0221	-0.0446	2.0489	1.0245	0.9891	0.0301	0.6989	2721.92	1214.51	2733.36	17
D_2S	0.5265	-0.0446	1.0578	0.5289	1.3782	0.0815	0.9740	1947	874	1965.57	17
T_2S	0.3616	-0.0441	0.7280	0.3640	1.6629	0.1434	1.1763	1623	724	1629.18	17
H_2Se	1.0046	-0.0179	2.0098	1.0049	0.9976	0.0126	0.7054	2438.66	1057.6	2453.77	20
D_2Se	0.5090	-0.0179	1.0186	0.5093	1.4016	0.0349	0.9911	1734	753	1764.61	20
T_2Se	0.3441	-0.0179	0.6886	0.3443	1.7047	0.0628	1.2058	1425	619	1436.09	20
$^{14}NO_2$	0.0843	-0.0726	0.3672	0.1836	3.4449	1.5600	1.8115	1357.8	756.8	1665.5	18
$^{15}NO_2$	0.0827	-0.0677	0.3511	0.1755	3.4752	1.5046	1.8391	1343.55	746.94	1628.57	7, 1
$^{32}S^{16}O_2$	0.0784	-0.0384	0.2179	0.1090	3.5710	1.0994	2.2413	1167.6	526.27	1380.91	19
$^{32}S^{18}O_2$	0.0775	-0.0363	0.2127	0.1064	3.5916	1.0586	2.2604	1143.96	513.37	1343.8	1

(continued ...)

Table 3.1 (contd.)

Molecule	G_{11}	G_{12}	G_{22}	G_{33}	F^{-1}_{11}	F^{-1}_{12}	F^{-1}_{22}	ω_1 (cm^{-1})	ω_2 (cm^{-1})	ω_3 (cm^{-1})	Reference
$^{34}S^{16}O_2$	0.0715	-0.0386	0.2043	0.1022	3.7393	1.2590	2.3344	1099.82	496.5	1316.91	1
$^{34}S^{18}O_2$	0.0706	-0.0363	0.1988	0.0994	3.7641	1.2119	2.3560	1092.11	492.17	1299.12	1
$^{35}Cl\ O_2$	0.0776	-0.0354	0.2076	0.1038	3.5889	1.0407	2.2854	962.8	455.4	1128.2	9
$^{37}Cl\ O_2$	0.0770	-0.0389	0.2042	0.1021	3.6033	1.0119	2.2987	957.67	451.89	1115.84	9
$Se\ O_2$	0.0734	-0.0177	0.1539	0.0769	3.6910	0.6248	2.5857	900.0	400.0	967.0	13
$F_2\ O$	0.0998	-0.0857	0.2609	0.1304	3.1648	1.9835	2.3107	929.82	460.7	826.0	14
$^{35}Cl_2O$	0.0689	-0.0826	0.2266	0.1133	3.8096	3.3583	2.8006	688.0	320.0	969.0	14
$^{37}Cl_2O$	0.0674	-0.0826	0.2235	0.1117	3.8531	3.5099	2.8614	679.9	313.35	962.37	14
$^{35}Cl_2S$	0.0558	-0.0433	0.1315	0.0657	4.3098	2.5870	3.2165	514.0	208.0	534.0	14
$^{37}Cl_2S$	0.0525	-0.0433	0.1284	0.0642	4.3730	2.7221	3.2873	507.95	202.96	528.77	14

Table 3.2

Force fields of bent symmetric XY_2 molecules determined by the $f_\alpha \sigma_\alpha$ minimum condition ((in md/Å)

Molecule	f_r		f_{rr}	
	Present work	Previous result	Present work	Previous result
$^{14}N\ O_2$	10.873	10.927 ± 0.065	1.972	2.058 ± 0.065
$^{15}N\ O_2$	10.829		1.927	
$^{32}S^{16}O_2$	10.241	10.006 ± 0.003 10.02	−0.0698	0.0236 ± 0.0025 0.03
$^{34}S^{16}O_2$	9.936		−0.068	
$^{32}S^{18}O_2$	9.957		−0.046	
$^{34}S^{18}O_2$	9.948		−0.055	
$Se\ O_2$	6.822	6.91 ± 0.1	−0.340	
$F_2\ O$	4.088	3.941 ± 0.1	1.006	0.859 ± 0.1
$^{35}Cl\ O_2$	7.111	7. 018	−0.115	−0.1699

(Contd . .)

Table 3.2 (contd.)

Molecule	f_r		f_{rr}	
	Present work	Previous result	Present work	Previous result
$^{37}Cl\ O_2$	7.091	7.16	-0.106	-0.1699
$^{35}Cl_2O$	4.497	4.485 4.422	-0.586	-0.399 -0.462
$^{37}Cl_2O$	4.501		-0.382	
$^{35}Cl_2S$	2.704	2.580 2.836	0.148	 0.254
$^{37}Cl_2S$	2.717		0.151	
H_2O	8.439	8.454 ± 0.001 8.449 ± 0.006	-0.116	-0.101 ± 0.001 -0.107 ± 0.006
D_2O	8.415	8.454 ± 0.005 8.472 ± 0.028	-0.145	-0.101 ± 0.005 -0.085 ± 0.028
T_2O	8.404		-0.152	
H_2S	4.284	4.280 ± 0.005	-0.015	-0.016 ± 0.005
D_2S	4.269	4.280 ± 0.005	-0.028	-0.017 ± 0.005

(contd..)

Table 3.2 (contd)

Molecule	f_r		f_{rr}	
	Present work	Previous Result	Present work	Previous result
T_2S	4.294		−0.002	
H_2Se	3.509	3.509 ± 0.000	−0.021	−0.0215 ± 0.000
D_2Se	3.541	3.544 ± 0.001	−0.061	−0.058 ± 0.001
T_2Se	3.502		−0.027	

Table 3.2 (contd)

Force fields of bent symmetric XY_2 molecules determined by the $f_\alpha \sigma_\alpha$ minimum condition (in md/Å)

Molecule	f_α		$f_{r\alpha}$		References
	Present work	Previous result	Present work	Previous result	
$^{14}N\ O_2$	1.132	1.125 ± 0.003	0.362	0.390 ± 0.020	8
$^{15}N\ O_2$	1.136		0.329		
$^{32}S^{16}O_2$	0.828	0.7953 ± 0.000 0.793	0.107	0.189 ± 0.005 0.20	6 7
$^{34}S^{16}O_2$	0.801		0.089		
$^{32}S^{18}O_2$	0.799		0.130		
$^{34}S^{18}O_2$	0.780		0.116		
$Se\ O_2$	0.632		0.031	0.015 ± 0.01	13
$F_2\ O$	0.688	0.72 ± 0.01	0.221	0.149 ± 0.04	10
$^{35}Cl\ O_2$	0.644	0.651	0.085	0.006	9

(contd . .)

Table 3.2 (contd)

Molecule	f_α		$f_{r\alpha}$		Reference
	Present work	Previous result	Present work	Previous result	
$^{37}Cl\ O_2$	0.641	0.651	0.077	0.006	9
$^{35}Cl_2O$	0.494	0.416 0.40	0.239	0.349 0.332	15 12
$^{37}Cl_2O$	0.495		0.247		
$^{35}Cl_2S$	0.270	0 .294 0. 067	0.065	 0.0764	13 14
$^{37}Cl_2S$	0.269		0.067		
$H_2\ O$	0.751	0.759 ± 0.002 0.769 ± 0.018	0.010	0.231 ± 0.01 0.200 ± 0.19	11 2
$D_2\ O$	0.756	0.760 ± 0.004 0.764 ± 0.01	0.019	0.235 ± 0.03 0.192 ± 0.17	11 2
$T_2\ O$	0.758		0.057		
$H_2\ S$	0.425	0.435 ± 0.006	0.013	0.148 ± 0.03	11
$D_2\ S$	0.427	0.434 ± 0.006	0.008	0.144 ± 0.03	11

(contd . .)

Table 3.2 (contd)

Molecule	f_α		$f_{r\alpha}$		Reference
	Present work	Previous result	Present work	Previous result	
T_2S	0.428		0.020		
H_2Se	0.328	0.331 ± 0.001	0.004	0.025 ± 0.02	11
D_2Se	0.328	0.331 ± 0.001	0.008	0.054 ± 0.02	11
T_2Se	0.328		-0.002		

Table 3.3

Parameter values corresponding to the extrema of average potential energy terms

Quantity Extremised / Molecule	$f_\alpha \sigma_\alpha$	$f_r \sigma_r$	$f_{rr} \sigma_{rr}$		$f_{r\alpha} \sigma_{r\alpha}$	
	c value at minimum	c value at minimum	c value(s) at minimum	c value(s) at maximum	c value at minimum	c value at maximum
H_2O	0.01	0.09	1.0	0.00	1.0	0.03
D_2O	0.02	0.2	1.0	0.03	0.9	0.06
T_2O	0.02	0.3	1.0	0.05	0.9	0.08
H_2S	0.00	0.06	1.0	−0.01	1.0	0.02
D_2S	0.01	0.1	1.0	−0.01	0.9	0.03
T_2S	0.01	0.2	1.0	−0.05	0.9	0.05
H_2Se	0.00	0.02	1.0	0.00	1.0	0.01
D_2Se	0.00	0.04	1.0	−0.01	1.0	0.02
T_2Se	0.01	0.06	1.0	−0.01	1.0	0.02
$^{14}NO_2$	0.10	1.0	−0.3	1.0	1.0	0.6
$^{15}NO_2$	0.10	1.0	−0.3	1.0	1.0	0.7

(contd . .)

Table 3.3 (contd)

Quantity Extremised / Molecule	$f_\alpha \sigma_\alpha$	$f_r \sigma_r$	$f_{rr} \sigma_{rr}$		$f_{r\alpha} \sigma_{r\alpha}$	
	e value at minimum	e value at minimum	e value(s) at minimum	e value(s) at maximum	e value at minimum	e value at maximum
$^{32}S^{16}O_2$	0.05	1.0	-0.2	-0.6,0.2	0.7	0.2
$^{34}S^{16}O_2$	0.05	1.0	-0.2	-0.5,0.2	0.7	0.2
$^{32}S^{18}O_2$	0.05	1.0	-0.2	-0.6,0.2	0.7	0.2
$^{34}S^{18}O_2$	0.05	1.0	-0.2	-0.6,0.3	0.7	0.2
$^{35}Cl\ O_2$	0.05	1.0	-0.2	-0.5,0.2	0.8	0.2
$^{37}Cl\ O_2$	0.05	1.0	-0.2	-0.5,0.2	0.8	0.2
$^{35}Cl_2O$	0.11	0.7	-0.4,1.0	0.2	1.0	0.5
$^{37}Cl_2O$	0.11	0.6	-0.4,1.0	0.2	1.0	0.5
$^{35}Cl_2S$	0.07	0.9	-0.1,1.0	0.3	0.9	0.4
$^{37}Cl_2S$	0.07	0.9	- 0.1,1.0	0.3	0.9	0.4
$F_2\ O$	0.10	1.0	-0.2	0.9	0.9	0.5
$Se\ O_2$	0.03	0.2	1.0	0.0	0.8	0.2

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CHAPTER IV

AVERAGE BENDING ENERGY CRITERION: FORCE FIELDS OF SOME PLANAR XY_3 TYPE MOLECULES

The minimization of the average potential energy contribution from bending deformation due to zero point vibrations is shown to be an excellent criterion for fixing the harmonic force fields of planar XY_3 type molecules.

Introduction

In the preceding chapter the average potential energy contributions arising from different internal valence coordinates of a molecule undergoing zero point vibrations have been studied, and it has been noted that for a large number of XY_2 (C_{2v}) molecules, the minimum of the zero point average bending energy term $f_\alpha \sigma_\alpha$ corresponds more or less exactly to the actual force field. In the present chapter an attempt is made to extend the criterion of minimum average bending energy to nonhydride molecules belonging to the planar XY_3 model.

Planar XY_3 model

Shown in Fig. (4.0) is the XY_3 molecular model of D_{3h} symmetry (1). Under the harmonic approximation, the potential energy function of the general valence type for this type of molecule may be written as

$$\begin{aligned} 2V = {} & f_r(\Delta r_1^2 + \Delta r_2^2 + \Delta r_3^2) \\ & + r^2 f_\alpha (\Delta\alpha_1^2 + \Delta\alpha_2^2 + \Delta\alpha_3^2) \\ & + r^2 f_\gamma \gamma^2 + 2 f_{rr} (\Delta r_1 \Delta r_2 \\ & + \Delta r_2 \Delta r_3 + \Delta r_3 \Delta r_1) + 2 r f_{r\alpha} \\ & \Delta r_1 (\Delta\alpha_2 + \Delta\alpha_3) + \Delta r_2 (\Delta\alpha_1 + \Delta\alpha_3) \\ & + \Delta r_3 (\Delta\alpha_1 + \Delta\alpha_2) \quad + 2 r f_{r\alpha}' \\ & (\Delta r_1 \Delta\alpha_1 + \Delta r_2 \Delta\alpha_2 + \Delta r_3 \Delta\alpha_3) \end{aligned}$$

$$+ 2r^2 f_{\alpha\alpha} (\Delta\alpha_1 \Delta\alpha_2 + \Delta\alpha_2 \Delta\alpha_3$$

$$+ \Delta\alpha_3 \Delta\alpha_1) \qquad (4.1)$$

where the Δr_i are changes in bond length, $\Delta\alpha_i$ changes in inter-bond angles and γ, the out-of-plane bending angle and r, the equilibrium bond length. Taking averages, we have

$$\langle 2V \rangle = 3 f_r \sigma_r + 3 f_\alpha \sigma_\alpha$$

$$+ 6 f_{rr} \sigma_{rr} + 6 f_{\alpha\alpha} \sigma_{\alpha\alpha}$$

$$+ 12 f_{r\alpha} \sigma_{r\alpha} + 6 f'_{r\alpha} \sigma'_{r\alpha}$$

$$+ f_{\gamma} \gamma \qquad (4.2)$$

where the $\sigma\, r_i\, r_j$ denote mean square amplitudes evaluated at absolute zero.

The vibrations of a planar XY_3 type molecule may be classified into $A_1' + A_2'' + 2E'$ species. The symmetry coordinates adopted in this calculation are (2)

$$S_1 (A_1') = 3^{-1/2} (\Delta r_1 + \Delta r_2 + \Delta r_3)$$

$$S_2 (A_2'') = s_1 + s_2 + s_3 - 3 s_4$$

$$S_{3a} (E') = 6^{-1/2}\, r (2\Delta r_1 - \Delta r_2 - \Delta r_3)$$

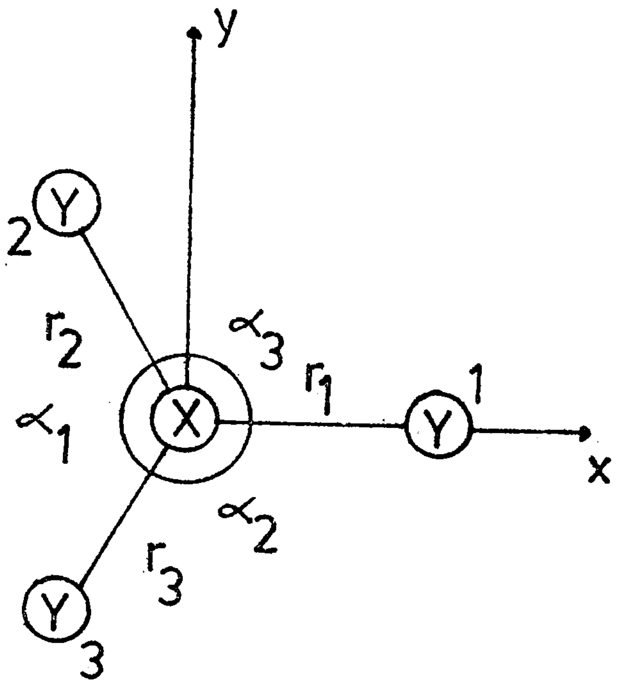


Fig. (4.0) Planar Symmetrical XY_3 Molecular Model. (Symmetry D_{3h}).

$$S_{4a}(E') = 6^{-1/2}(2\Delta\alpha_1 - \Delta\alpha_2 - \Delta\alpha_3)$$

$$S_{3b}(E') = 2^{-1/2}(\Delta r_2 - \Delta r_3)$$

$$S_{4b}(E') = 2^{-1/2}\, r\,(\Delta\alpha_2 - \Delta\alpha_3)$$

The A_2'' coordinate representing out-of-plane bending is given in terms of cartesian displacements.

The G elements for the E' species are given by (2)

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

$$G_{34} = \frac{3}{2}\, 3^{1/2}\mu_x \quad \text{and}$$

$$G_{44} = 3\left(\frac{3}{2}\mu_x + \mu_y\right)$$

Expressing the potential energy in symmetry coordinates eq. (4.2) is rewritten in the form

$$\langle 2V\rangle = F_{11}\Sigma_{11} + F_{22}\Sigma_{22} + 2(F_{33}\Sigma_{33} + 2F_{34}\Sigma_{34} + F_{44}\Sigma_{44}) \qquad (4.3)$$

where

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

$$\begin{aligned} F_{22} &= f_{\gamma} \\ F_{33} &= f_{r} - f_{rr} \\ F_{34} &= f_{r\alpha} - f_{r\alpha}' \\ F_{44} &= f_{\alpha} - f_{\alpha\alpha} \end{aligned} \tag{4.4a}$$

and

$$\begin{aligned} \Sigma_{11} &= \sigma_{r} + 2\ \sigma_{rr} \\ \Sigma_{22} &= \sigma_{\gamma} \\ \Sigma_{33} &= \sigma_{r} - \sigma_{rr} \\ \Sigma_{34} &= \sigma_{r\alpha} - \sigma_{r\alpha}' \\ \Sigma_{44} &= \sigma_{\alpha} - \sigma_{\alpha\alpha} \end{aligned} \tag{4.4b}$$

The factor 2 outside the brackets in eq. (4.3) arises from the double degeneracy of the E' species vibrations. In the following considerations the out-of-plane contribution $f_{\gamma}\sigma_{\gamma}$ is dropped, since, it belongs to an independent first order species, and the term 'bending energy' refers only to in-plane bending. Thus the pure bending energy contributions in eq. (4.2) are the terms in $f_{\alpha}\sigma_{\alpha}$ and $f_{\alpha\alpha}\sigma_{\alpha\alpha}$. Hence the average zero point bending energy of the molecule may be written as

$$\langle 2\ V_{\alpha} \rangle = 3\ (\ f_{\alpha}\sigma_{\alpha} + 2\ f_{\alpha\alpha}\sigma_{\alpha\alpha}\ ) \tag{4.5}$$

Now consider the last term in eq. (4.3). From eqs. (4.4), we have

$$
\begin{aligned}
F_{44}\,\Sigma_{44} &= f_{\alpha}\sigma_{\alpha} + f_{\alpha\alpha}\sigma_{\alpha\alpha} - f_{\alpha}\sigma_{\alpha\alpha} \\
&\quad - f_{\alpha\alpha}\sigma_{\alpha} \qquad (4.6)
\end{aligned}
$$

However, the redundant coordinate belonging to the A_1' species may be written as

$$
\begin{aligned}
S_0 &= 3^{-1/2}\, r\,(\Delta\alpha_1 + \Delta\alpha_2 + \Delta\alpha_3) \\
&= 0 \qquad (4.7)
\end{aligned}
$$

and this gives

$$\Sigma_{00} = \sigma_{\alpha} + 2\,\sigma_{\alpha\alpha} = 0 \qquad (4.8)$$

Using eq. (4.8) in eq. (4.6) we obtain

$$
\begin{aligned}
2\,F_{44}\,\Sigma_{44} &= 3\,(\,f_{\alpha}\sigma_{\alpha} + 2\,f_{\alpha\alpha}\sigma_{\alpha\alpha}\,) \\
&= \langle 2\,V_{\alpha} \rangle \qquad (4.9)
\end{aligned}
$$

The average bending energy in terms of symmetry coordinates is, therefore given, by the expression $F_{44}\,\Sigma_{44}$.

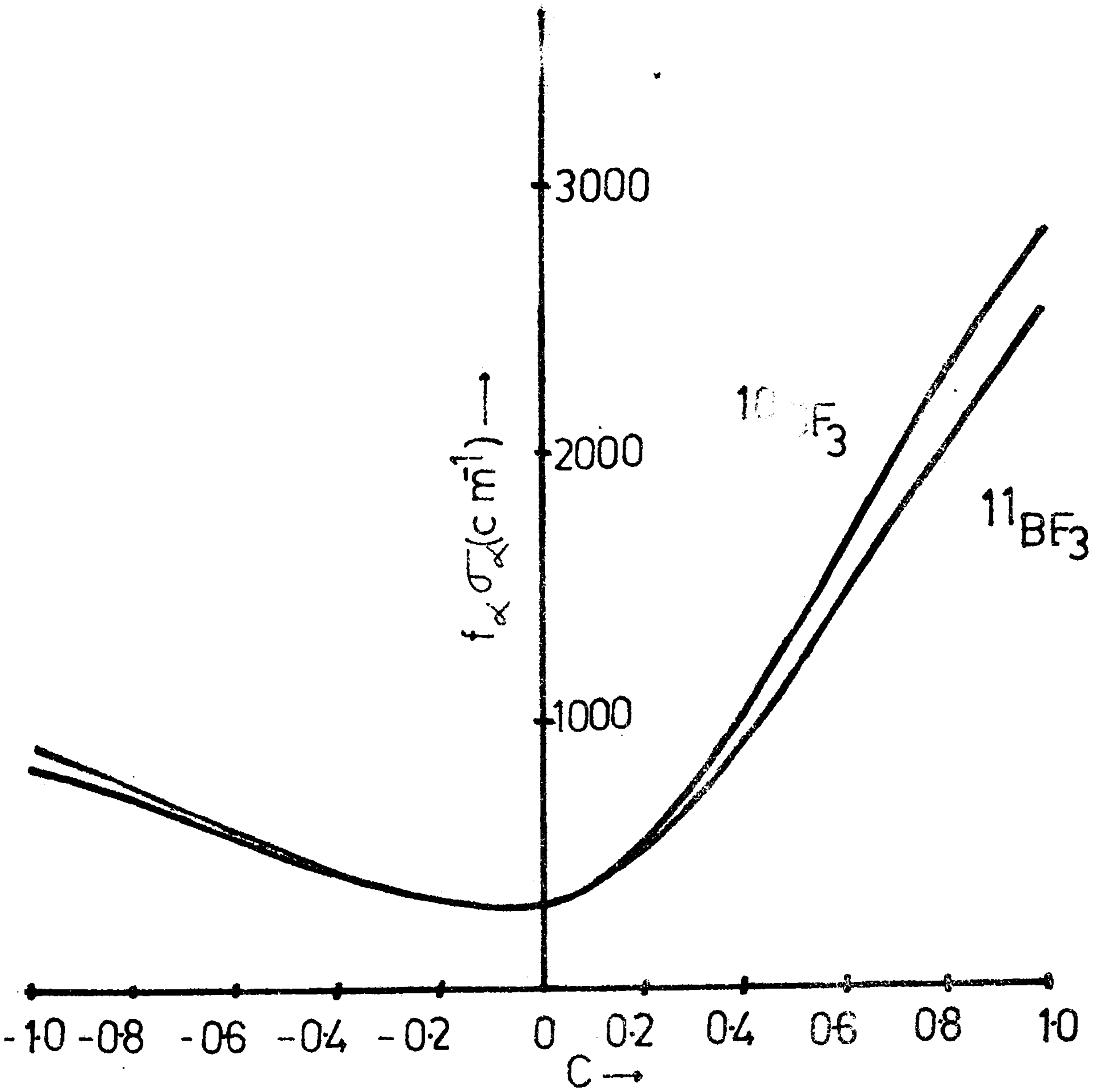
F_{ij} and Σ_{ij} for the E' species are parametrised and the parameter value corresponding to the minimum of the bending energy is noted. The force constants are recalculated using this value of the parameter.

Structural data and frequencies (harmonic, wherever available) for the XY_3 (D_{3h}) molecules investigated in this chapter are listed in Table 4.1.

Discussion

In molecules belonging to the XY_2 (C_{2v}), XY_3 (D_{3h}) types, it is found that the normal vibrations occur in such a way that the average zero point potential energy contribution from the bending deformation is quite close to its minimum possible value. The minimisation of the average bending energy of zero point vibrations with respect to the parameter characterising the mixing of symmetry coordinates, turns out to be a good criterion for the evaluation of harmonic force constants of molecules of the planar XY_3 type also. The results obtained in this way compare very well with standard force constants fixed with the help of additional data. These results are reported in Table 4.2. Figs. (4.1) to (4.5) give the variation of $F_{44}\ \Sigma_{44}$ with parameter c in the range $-1 \leq c \leq +1$ for the molecules under study. The isotopic invariance of force constants in ${}^{10}B\ F_3 - {}^{11}B\ F_3$, ${}^{10}B\ Br_3 - {}^{11}B\ Br_3$, ${}^{10}B\ Cl_3 - {}^{11}B\ Cl_3$ and ${}^{10}B\ I_3 - {}^{11}B\ I_3$ groups is particularly noted.

Figs. (4.1) - (4.5). Variation of average bending energy for $B F_3$, $B Br_3$, $B Cl_3$, $B I_3$, $S O_3$ and their isotopic substituents.


3000
2000
1000
$f_\alpha \sigma_\alpha^{-}(c\,m^{-1})$ →
$^{10}BF_3$
$^{11}BF_3$
-1·0
-0·8
-0·6
-0·4
-0·2
0
0·2
0·4
0·6
0·8
1·0
C →

Fig·4·1·

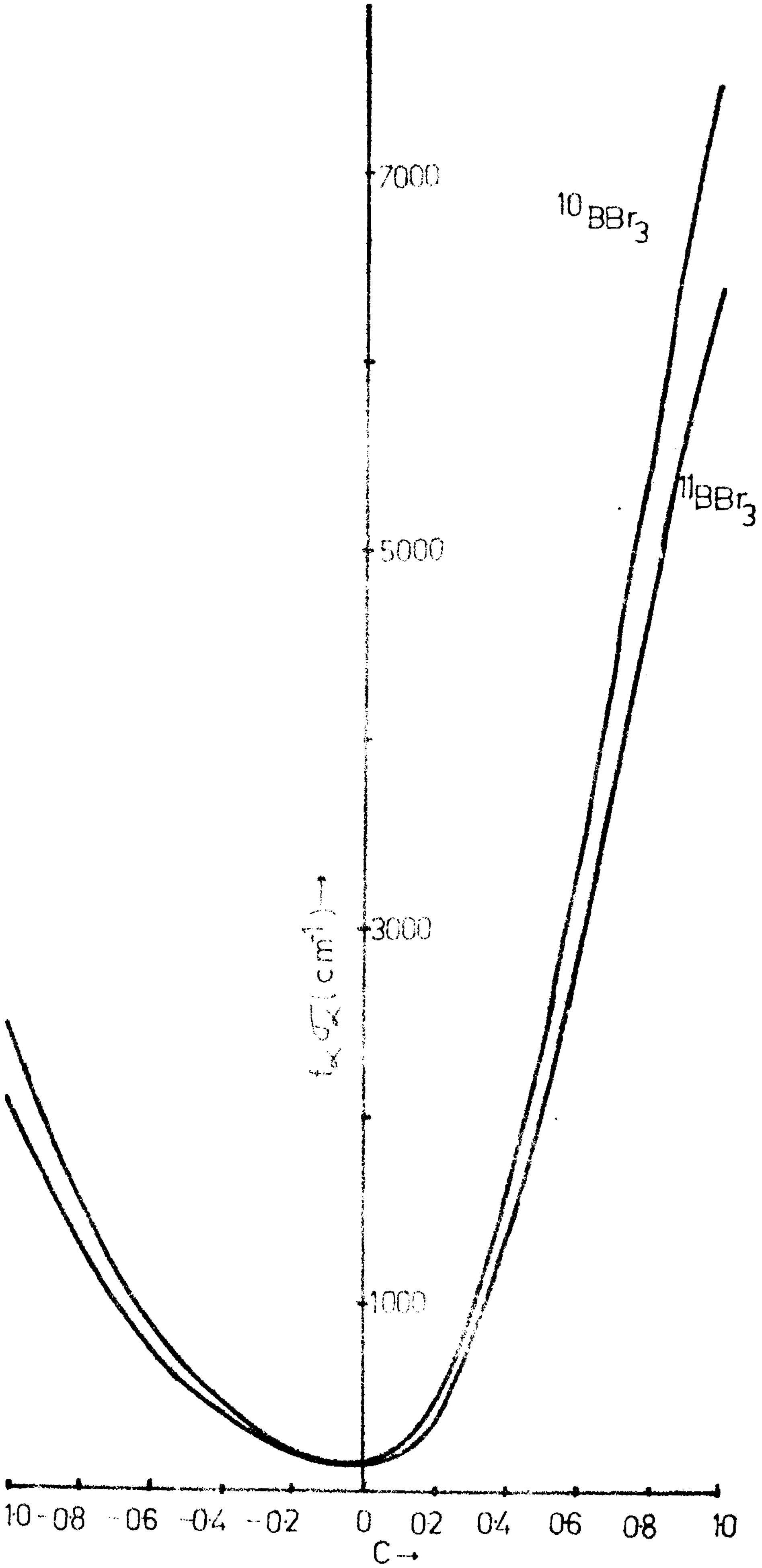
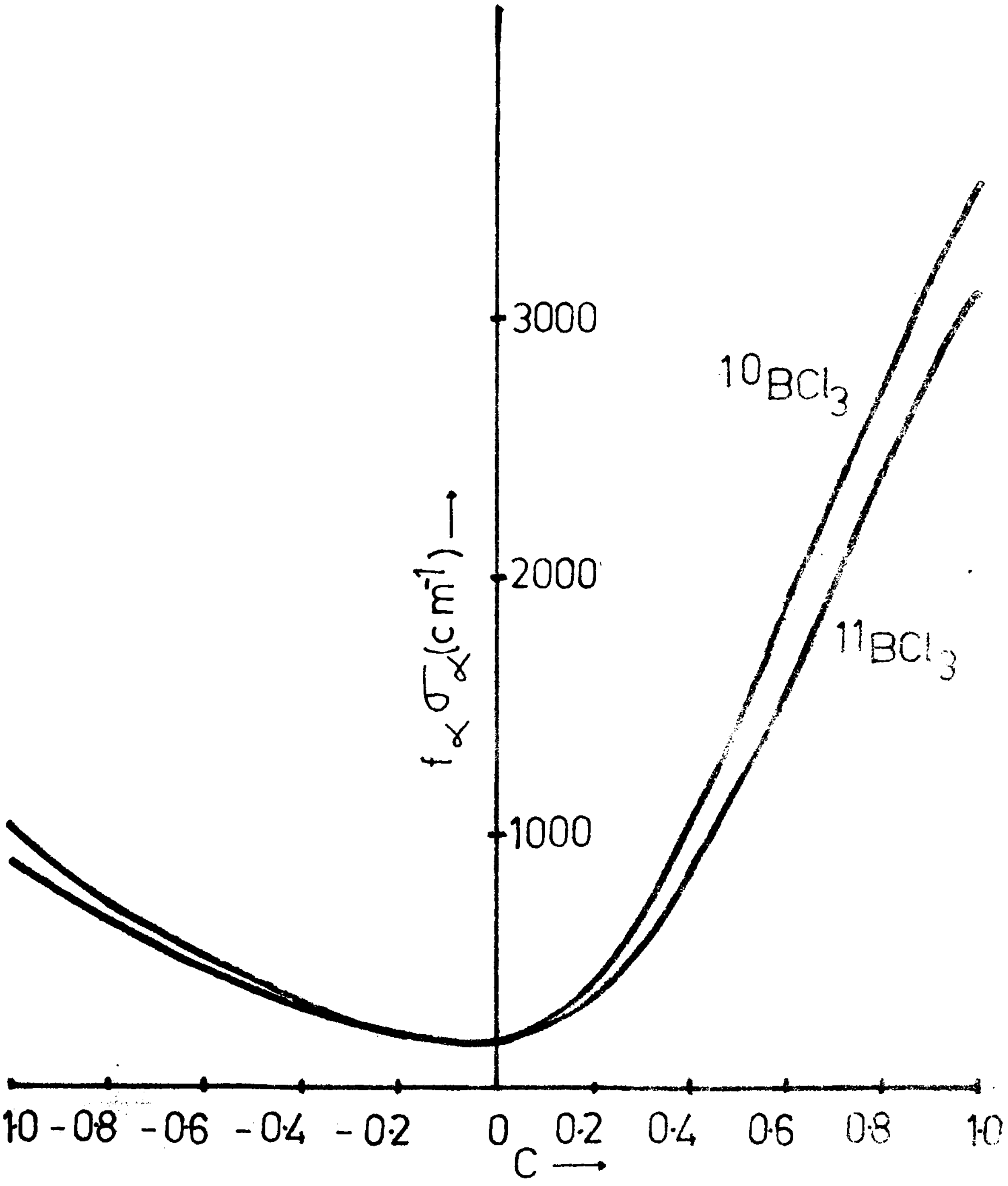

7000
5000
3000
1000
$^{10}BBr_3$
$^{11}BBr_3$
$t_\alpha \sigma_\alpha$ (cm^{-1}) →
1·0
-0·8
-0·6
-0·4
-0·2
0
0·2
0·4
0·6
0·8
1·0
C →

Fig.4.2.



3000
2000
1000
$f_\alpha \sigma_\alpha (cm^{-1})$ →
$^{10}BCl_3$
$^{11}BCl_3$
1·0
-0·8
-0·6
-0·4
-0·2
0
0·2
0·4
0·6
0·8
1·0
C →

Fig·4·3·

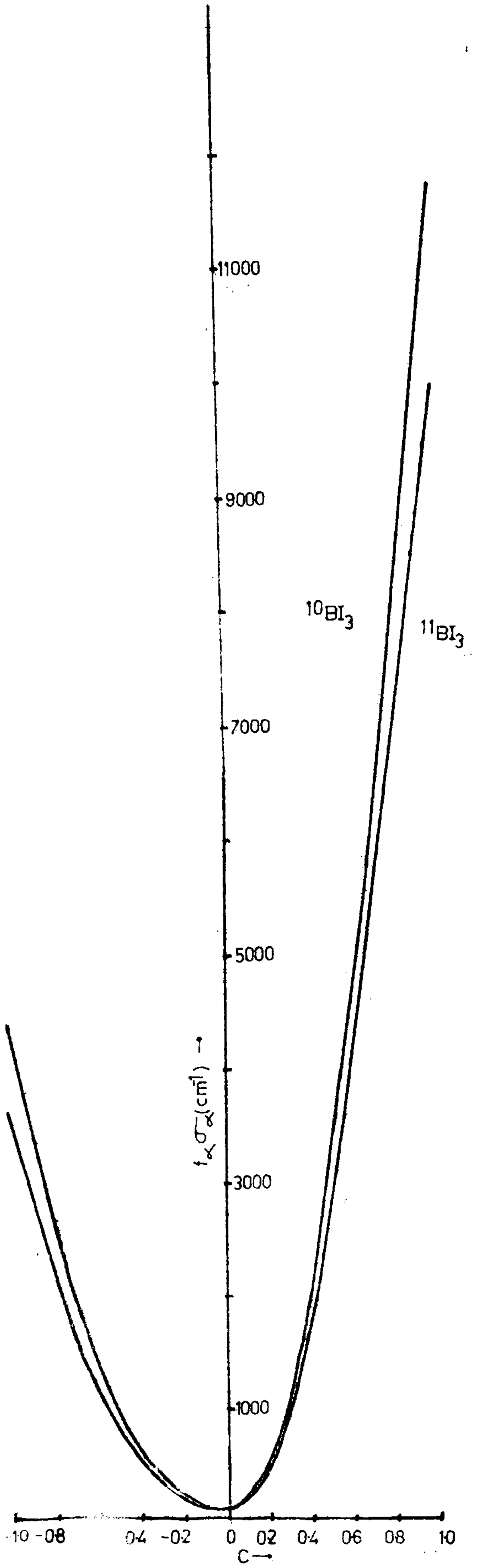
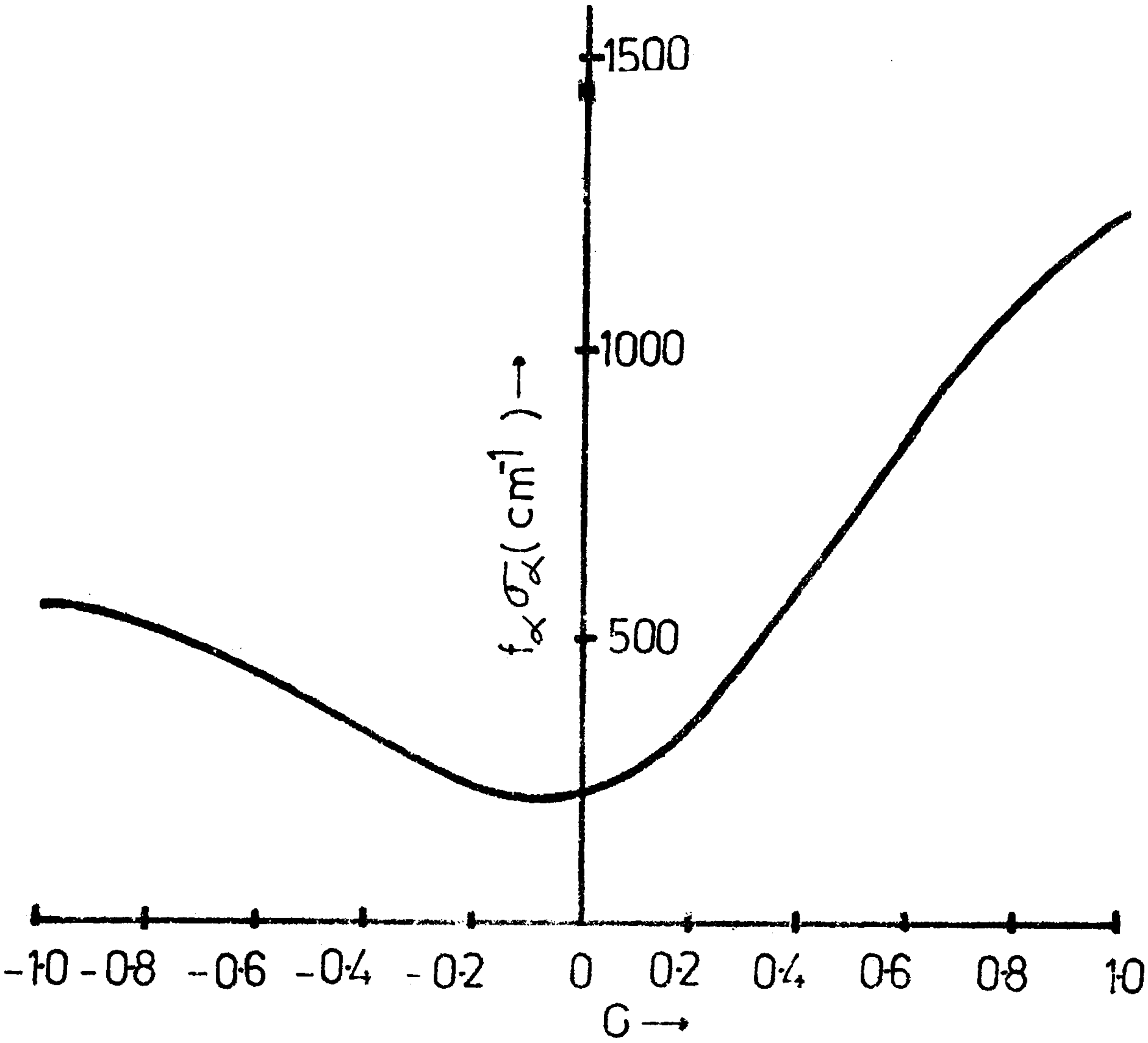

11000
9000
7000
5000
3000
1000
$f_{\alpha}\sigma_{\alpha}(cm^{-1})$ →
$^{10}BI_3$
$^{11}BI_3$
-1.0 -0.8
0.4 -0.2
0 0.2 0.4 0.6 0.8 1.0
C →

Fig.44.


1500
1000
500
$f_\alpha \sigma_\alpha (cm^{-1}) \rightarrow$
-1·0
-0·8
-0·6
-0·4
-0·2
0
0·2
0·4
0·6
0·8
1·0
G →

Fig·4·5· SO_3

Table 4.1

Frequencies and structural data for the E' species vibrations in planar XY_3 type molecules

Molecule	G_{33}	G_{34}	G_{44}	τ_{33}^{-1}	τ_{34}^{-1}	τ_{44}^{-1}	ω_1 (cm^{-1})	ω_2 (cm^{-1})	Reference
$^{10}B\ F_3$	0.2024	0.2595	0.6075	2.2226	-2.4455	1.9078	1497	482	2, 7, 5, 6
$^{11}B\ F_3$	0.1889	0.2360	0.5666	2.3010	-2.3966	1.9181	1446	480	2, 7, 12,8,9,11
$^{10}B\ Cl_3$	0.1780	0.2595	0.5340	2.3701	-3.6922	2.5531	995	244	2, 7
$^{11}B\ Cl_3$	0.1645	0.2360	0.4935	2.4659	-3.6479	2.5421	956	243	2, 7
$^{10}B\ Br_3$	0.1623	0.2594	0.4870	2.4820	-5.9495	3.7219	856	150	2, 7
$^{11}B\ Br_3$	0.1488	0.2360	0.4463	2.5927	-5.9150	3.7287	820	150	2, 7
$^{10}B\ I_3$	0.1577	0.2595	0.4731	2.5182	-7.6638	4.6575	737	100	2, 7
$^{11}B\ I_3$	0.1441	0.2360	0.4324	2.6341	-7.6352	4.6631	704	100	2, 7
$S\ O_3$	0.1093	0.0810	0.3279	3.0249	-1.4330	1.9325	1333	440	10

Table 4.2

Force constants of some planar XY_3 type molecules (in md/Å)

Molecule	e minimum of $F_{44}\Sigma_{44}$	Force field						Reference
		Present work			Previous Result			
		F_{33}	F_{34}	F_{44}	F_{33}	F_{34}	F_{44}	
$^{10}B\ F_3$	-0.07	6.451	-0.316	0.519	6.683 ± 0.05	-0.37 ± 0.02	0.5095 ± 0.002	3, 4
$^{11}B\ F_3$	-0.07	6.462	-0.312	0.519				
$^{10}B\ Cl_3$	-0.05	3.287	-0.177	0.234	3.47 ± 0.13	-0.25 ± 0.04	0.247 ± 0.004	3, 4
$^{11}B\ Cl_3$	-0.05	3.294	-0.177	0.233				
$^{10}B\ Br_3$	-0.03	2.769	-0.186	0.189	2.79 ± 0.23	-0.195 ± 0.07	0.191 ± 0.007	3, 4
$^{11}B\ Br_3$	-0.03	2.785	-0.189	0.189				
$^{10}B\ I_3$	-0.02	2.140	-0.141	0.131	2.25	-0.17	0.13	3, 4
$^{11}B\ I_3$	-0.02	2.145	-0.144	0.131				
$S\ O_3$	-0.04	9.480	-0.102	0.432	10.605 ± 0.312	-0.359 ± 0.218	0.616 ± 0.015	3, 4

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CHAPTER V

AVERAGE BENDING ENERGY CRITERION: FORCE FIELDS OF TETRAHEDRAL XY_4 TYPE MOLECULES

The average bending energy criterion is applied to the evaluation of force fields of some 53 molecules belonging to the tetrahedral XY_4 molecular model. It is seen that the force constants thus obtained compare very well with established values.

Tetrahedral XY_4 molecule

Fig. (5.0) shows the XY_4 molecular model. The normal vibrations of a tetrahedral XY_4 molecule can be classified into types $A_1 + E + 2\,F_2$. The second order species F_2 consists of triply degenerate stretching and bending vibrational modes. The following set of symmetry coordinates (1) has been employed in the present investigation.

$$S_1\,(A_1) = \frac{1}{2}\,(\Delta r_1 + \Delta r_2 + \Delta r_3 + \Delta r_4)$$

$$S_{2a}\,(E) = 12^{-1/2}\,r(\,2\Delta\alpha_{23} - \Delta\alpha_{12} - \Delta\alpha_{13} + 2\Delta\alpha_{14} - \Delta\alpha_{34} - \Delta\alpha_{24})$$

$$S_{2b}\,(E) = \frac{1}{2}\,r\,(\Delta\alpha_{13} - \Delta\alpha_{12} + \Delta\alpha_{24} - \Delta\alpha_{34})$$

$$S_{3a}\,(F_2) = \frac{1}{2}\,(\Delta r_1 - \Delta r_2 + \Delta r_3 - \Delta r_4)$$

$$S_{4a}\,(F_2) = 2^{1/2}\,r\,(\Delta\alpha_{24} - \Delta\alpha_{13})$$

$$S_{3b}\,(F_2) = \frac{1}{2}\,(\Delta r_1 + \Delta r_2 - \Delta r_3 - \Delta r_4)$$

$$S_{4b}\,(F_2) = 2^{-1/2}\,r\,(\Delta\alpha_{34} - \Delta\alpha_{12})$$

$$S_{3c}\,(F_2) = \frac{1}{2}\,(-\Delta r_1 + \Delta r_2 + \Delta r_3 - \Delta r_4)$$

$$S_{4c}\,(F_2) = 2^{-1/2}\,r\,(\Delta\alpha_{14} - \Delta\alpha_{23})$$

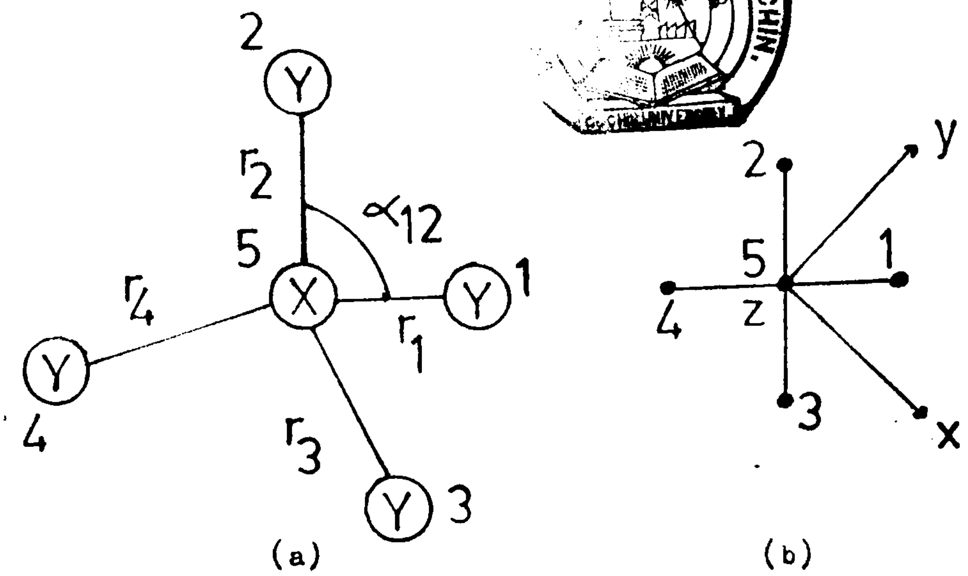


Fig. (5.0) Tetrahedral XY_4 Model (Symmetry T_d) In Fig. (5.0a) the atoms numbered 1 and 4 are situated below the xy plane and 2 and 3 above it. The six angle bendings α_{ij} are exemplified by α_{12}.

$$S(A_1) = 6^{-1/2}\, r\,(\Delta\alpha_{12} + \Delta\alpha_{13} + \Delta\alpha_{23} + \Delta\alpha_{34} + \Delta\alpha_{24} + \Delta\alpha_{14}) = 0$$

where the Δr_i are increments in XY stretching and the $\Delta\alpha_{ij}$ denote changes in the YXY angle. The G matrix elements are given by the relations(1)

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

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

$$G_{44} = 2\left(\frac{8}{3}\mu_x + \mu_y\right)$$

The general valence potential function for this type of molecule is written as

$$\begin{aligned}2V = {} & f_r(\Delta r_1^2 + \Delta r_2^2 + \Delta r_3^2 + \Delta r_4^2) \\ & + r^2 f_\alpha(\Delta\alpha_{12}^2 + \Delta\alpha_{13}^2 + \Delta\alpha_{23}^2 + \\ & \Delta\alpha_{34}^2 + \Delta\alpha_{24}^2 + \Delta\alpha_{14}^2) + 2 f_{rr} \\ & (\Delta r_1\,\Delta r_3 + \Delta r_3\,\Delta r_4 + \Delta r_4\,\Delta r_1 + \\ & \Delta r_1\,\Delta r_2 + \Delta r_3\,\Delta r_2 + \Delta r_4\,\Delta r_2) + \\ & 2r f_{r\alpha}\Big[\Delta r_1(\Delta\alpha_{13} + \Delta\alpha_{14} + \Delta\alpha_{12}) \\ & + \Delta r_3(\Delta\alpha_{31} + \Delta\alpha_{34} + \Delta\alpha_{32}) \\ & + \Delta r_4(\Delta\alpha_{43} + \Delta\alpha_{41} + \Delta\alpha_{42})\end{aligned}$$

$$+ \Delta r_2 (\Delta\alpha_{21} + \Delta\alpha_{23} + \Delta\alpha_{24}) \Big]$$

$$+ 2 r f'_{r\alpha} (\Delta r_1 \Delta\alpha_{34} + \Delta r_3 \Delta\alpha_{41}$$

$$+ \Delta r_4 \Delta\alpha_{31}) + 2 r^2 f_{\alpha\alpha} \Big[(\Delta\alpha_{12} + \Delta\alpha_{34})$$

$$(\Delta\alpha_{13} + \Delta\alpha_{14} + \Delta\alpha_{23} + \Delta\alpha_{24})$$

$$+ (\Delta\alpha_{13} + \Delta\alpha_{24}) (\Delta\alpha_{23} + \Delta\alpha_{14}) \Big]$$

$$+ 2 r^2 f_{\alpha\alpha'} \Big[\Delta\alpha_{12} \Delta\alpha_{34} + \Delta\alpha_{13} \Delta\alpha_{24}$$

$$+ \Delta\alpha_{14} \Delta\alpha_{23} \Big] \qquad (5.1)$$

where r, Δr_i and $\Delta\alpha_{ij}$ have the usual meanings. Taking averages we have

$$\langle 2 V \rangle = 4 f_r \sigma_r + 6 f_\alpha \sigma_\alpha$$

$$+ 12 f_{rr} \sigma_{rr} + 24 f_{\alpha\alpha} \sigma_{\alpha\alpha}$$

$$+ 18 f_{r\alpha} \sigma_{r\alpha} + 6 f_{r\alpha}' \sigma_{r\alpha}'$$

$$+ 6 f_{\alpha\alpha'} \sigma_{\alpha\alpha}' \qquad (5.2)$$

In terms of the symmetry coordinates the average potential energy becomes

$$2 V = F_{11} \Sigma_{11} + 2 F_{22} \Sigma_{22} +$$

$$3 (F_{33} \Sigma_{33} + 2 F_{34} \Sigma_{34} + F_{44} \Sigma_{44})$$

$$(5.3)$$

where the factors 2 and 3 account for the double and triple degeneracies, respectively. Now from the symmetry coordinates,

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

$$\Sigma_{22} = \sigma_{\alpha} - 2 \sigma_{\alpha\alpha} + \sigma_{\alpha\alpha'}$$

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

$$\Sigma_{44} = \sigma_{\alpha} - \sigma_{\alpha\alpha'} \qquad (5.4)$$

The pure bending energy contribution can be expressed in symmetry coordinates as $2 F_{22} \Sigma_{22} + 3 F_{44} \Sigma_{44}$. Substituting from (5.4) this becomes

$$\begin{aligned} 2 F_{22} \Sigma_{22} + 3 F_{44} \Sigma_{44} = {} & 5 f_{\alpha} \sigma_{\alpha} - f_{\alpha} \sigma_{\alpha\alpha'} \\ & - f_{\alpha\alpha'} \sigma_{\alpha} + 5 f_{\alpha\alpha'} \sigma_{\alpha\alpha'} + 8 f_{\alpha\alpha} \sigma_{\alpha\alpha} \\ & - 4 f_{\alpha} \sigma_{\alpha\alpha} - 4 f_{\alpha\alpha} \sigma_{\alpha} - 4 f_{\alpha\alpha} \sigma_{\alpha\alpha'} - \\ & 4 f_{\alpha\alpha'} \sigma_{\alpha\alpha} \end{aligned} \qquad (5.5)$$

Since the redundant coordinate $S(A_1)$ gives a vanishing mean-square amplitude, we get the constraint

$$\sigma_{\alpha} + 4 \sigma_{\alpha\alpha} + \sigma_{\alpha\alpha'} = 0 \qquad (5.6)$$

Using eq. (5.6) in eq. (5.5) the average zero point bending energy is given by

$$\langle 2 V_{\alpha} \rangle = 6 \left(f_{\alpha} \sigma_{\alpha} + 4 f_{\alpha\alpha} \sigma_{\alpha\alpha} + f_{\alpha\alpha'} \sigma_{\alpha\alpha'} \right) \qquad (5.7)$$

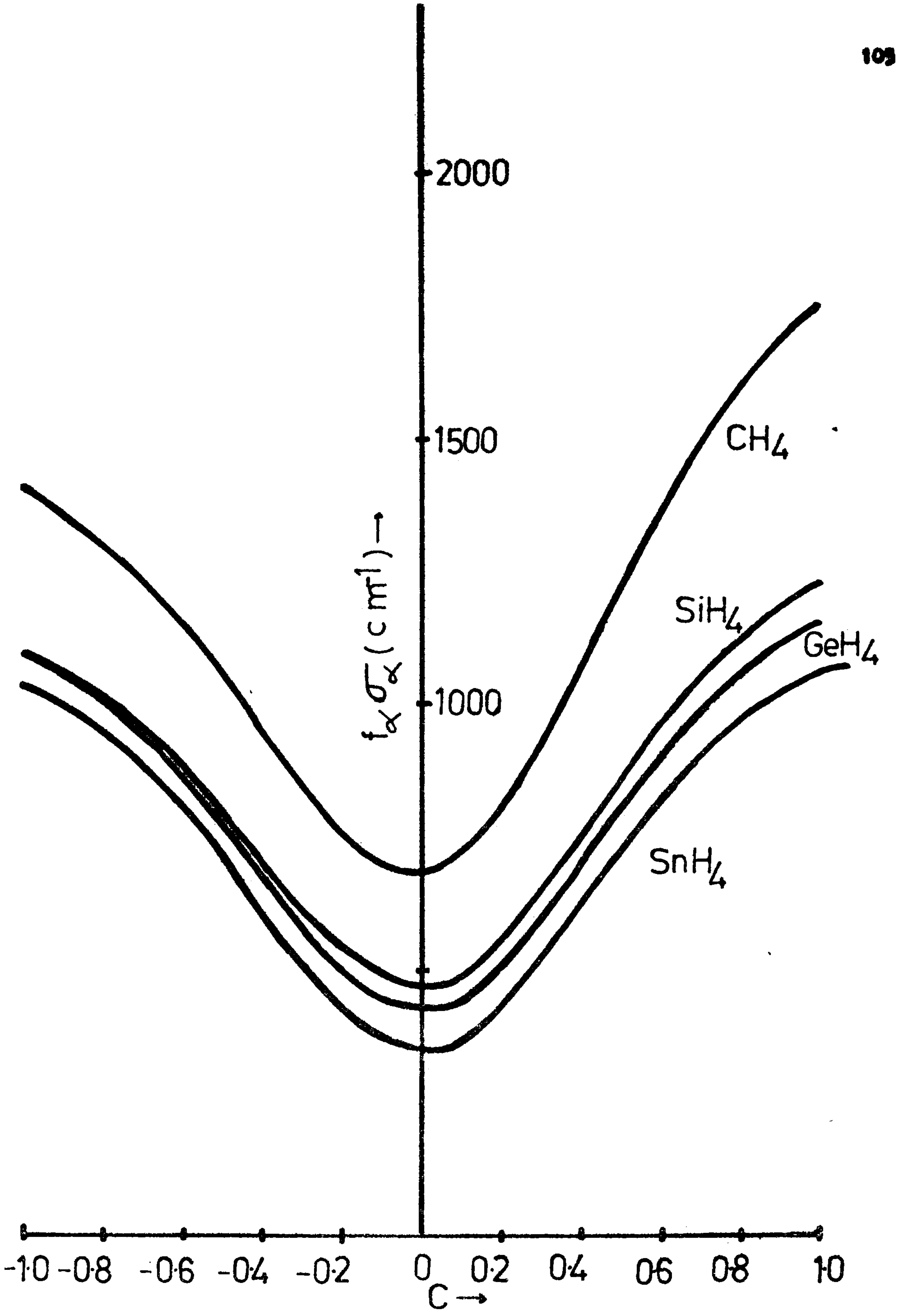
Since E is an independent species and the term $F_{22}\Sigma_{22}$ is a fixed one, the variation of $\langle 2 V_{\alpha} \rangle$ can be studied by varying the term $F_{44}\Sigma_{44}$ alone as a function of the parameter for the F_2 species and the minimum of the average bending energy is obtained. Vibrational frequencies (harmonic, wherever available of the molecules studied in this chapter are presented in Table 5.1.

Results and discussion

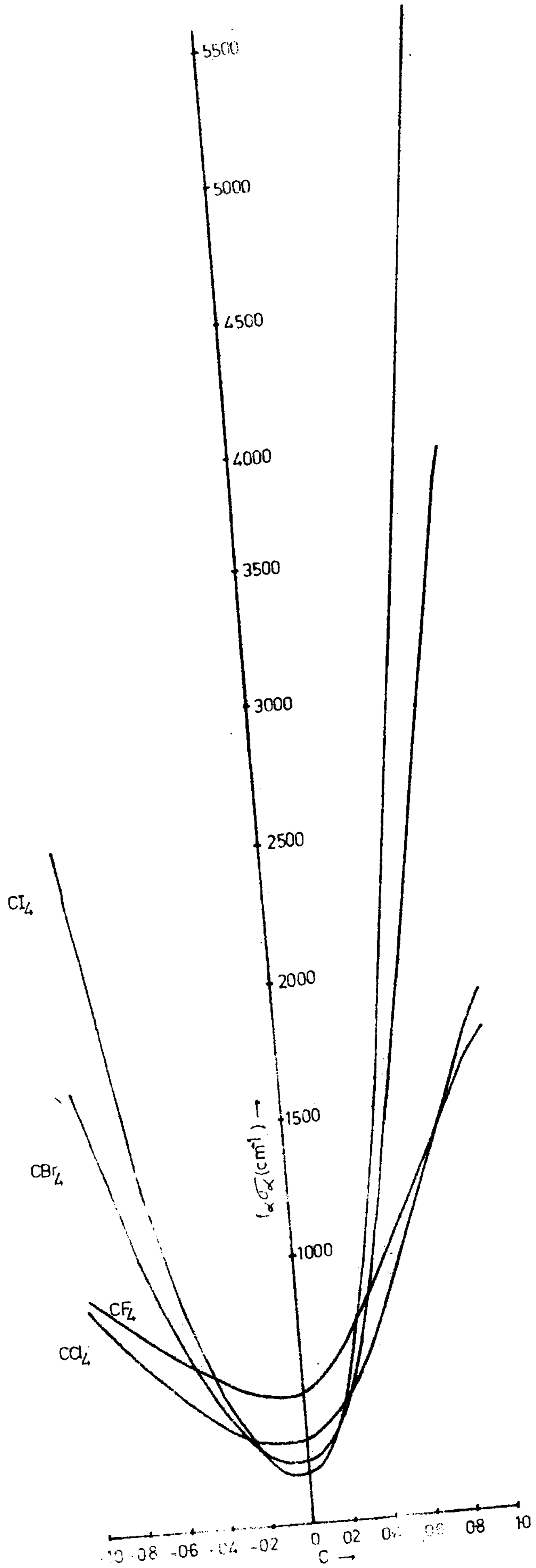
The force constants of a very large class of XY_4 type molecules are calculated by minimising the average bending energy function $F_{44}\Sigma_{44}$ (Figs. 5.1 to 5.10), and the resulting values are tabulated in Table 5.2. The present results compare excellently with the standard values reported in the literature marked by 'E' in this tabulation. It is seen that the normal vibrations occur in such a way that the average zero point potential energy contribution from the bending deformation is quite close to its minimum possible value. The force fields of the molecules marked by an asterik are compared with those reported on the assumption of valence forces, i.e., $F_{34} = 0$, and in the rest of the cases with Urey-Bradley or orbital valence force fields. In the XY_4 model also the isotopic invariance of the force fields is very conspicuous. The variation of the average bending energy for CF_4 and CH_4 groups of molecules is shown in Figs. (5.11) to (5.12).

Figs. (5.1) - (5.10). Plots of average bending energy for several tetrahedral XY_4 type molecular species studied in this chapter.

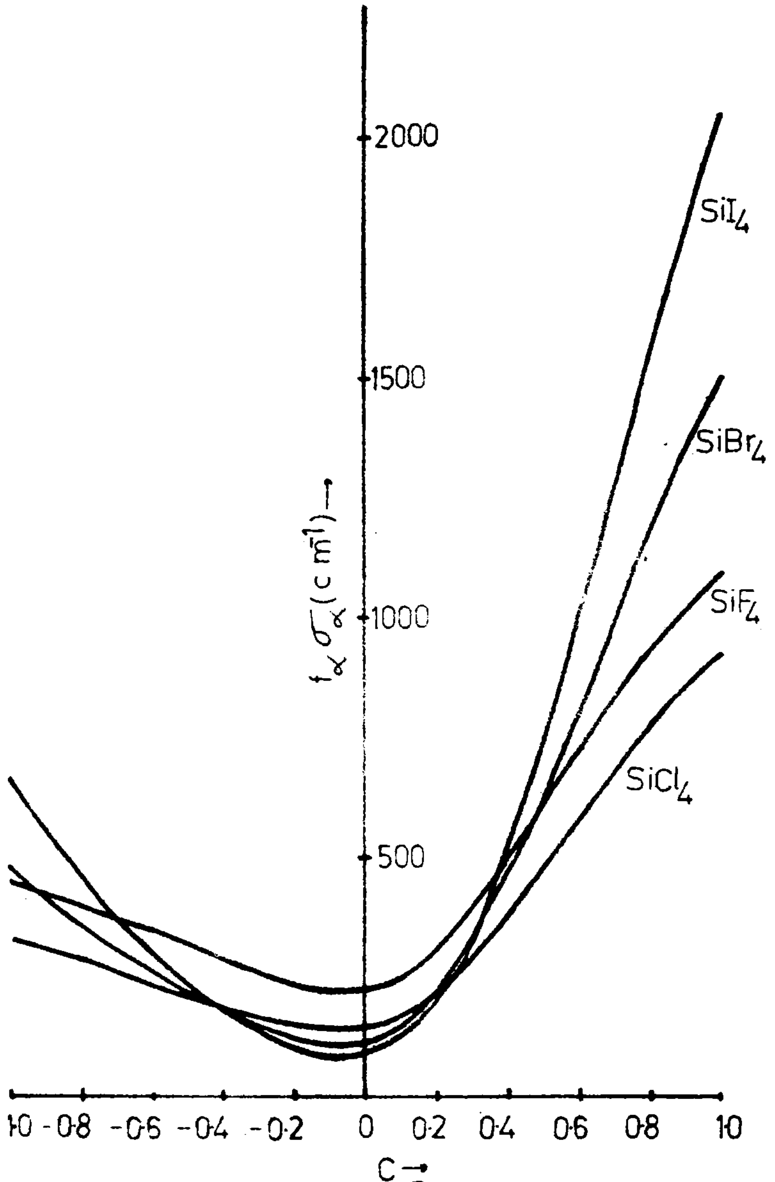
Figs. (5.11) and (5.12). Relationship between average bending energy and parameter for isotopic substituents of CH_4 and CF_4.


2000
1500
1000
$f_\gamma \sigma_\gamma (cm^{-1}) \rightarrow$
CH$_4$
SiH$_4$
GeH$_4$
SnH$_4$
-1·0
-0·8
-0·6
-0·4
-0·2
0
0·2
0·4
0·6
0·8
1·0
C →

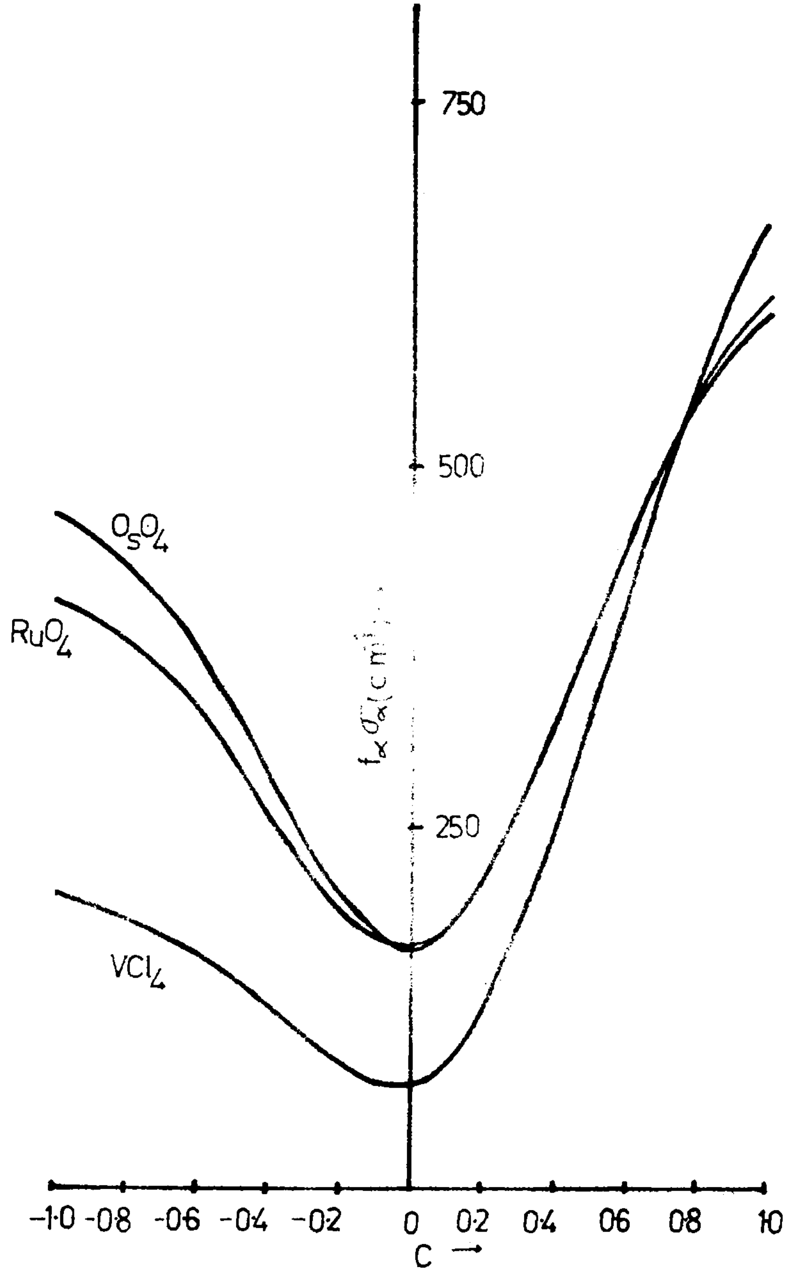
Fig·5·1·


5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
$f_\alpha \sigma_\alpha (cm^{-1})$ →
CI_4
CBr_4
CF_4
CCl_4
-10
-08
-06
-04
-02
0
02
04
06
08
10
C →

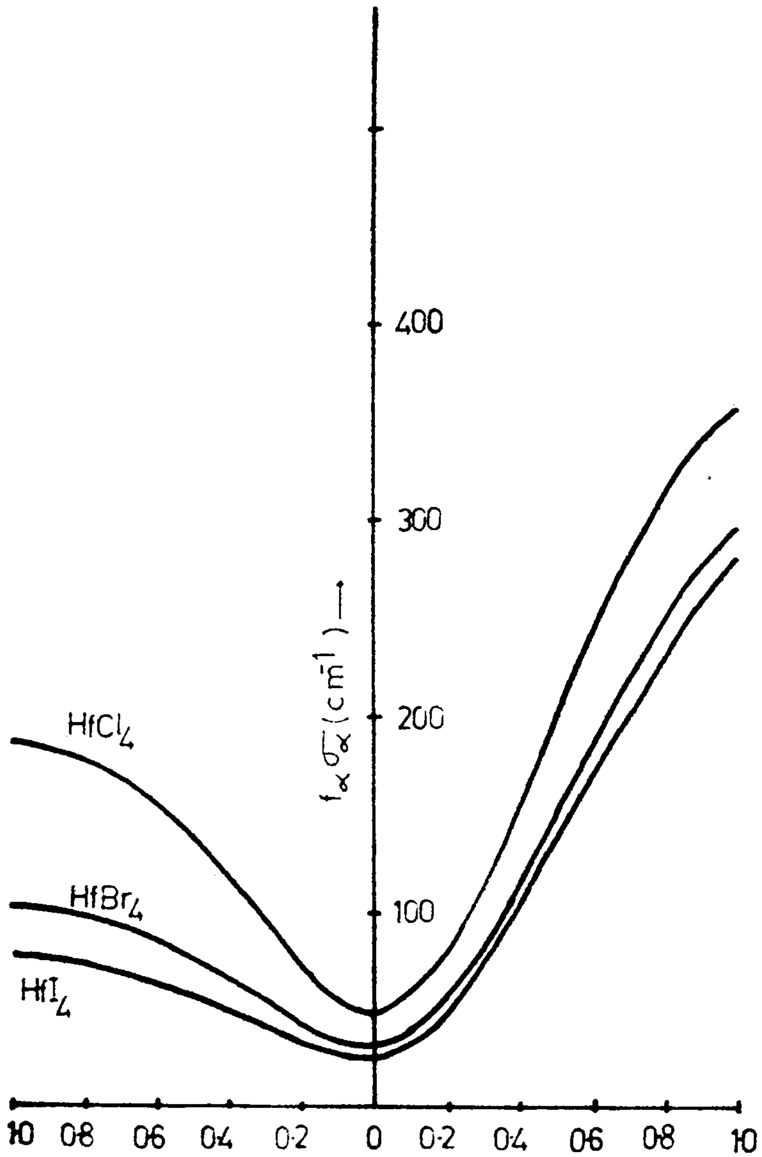
Fig·5·2·


$f_\alpha \sigma_\alpha$ (c m^{-1}) →
2000
1500
1000
500
SiI$_4$
SiBr$_4$
SiF$_4$
SiCl$_4$
1·0 -0·8 -0·6 -0·4 -0·2 0 0·2 0·4 0·6 0·8 1·0
C →

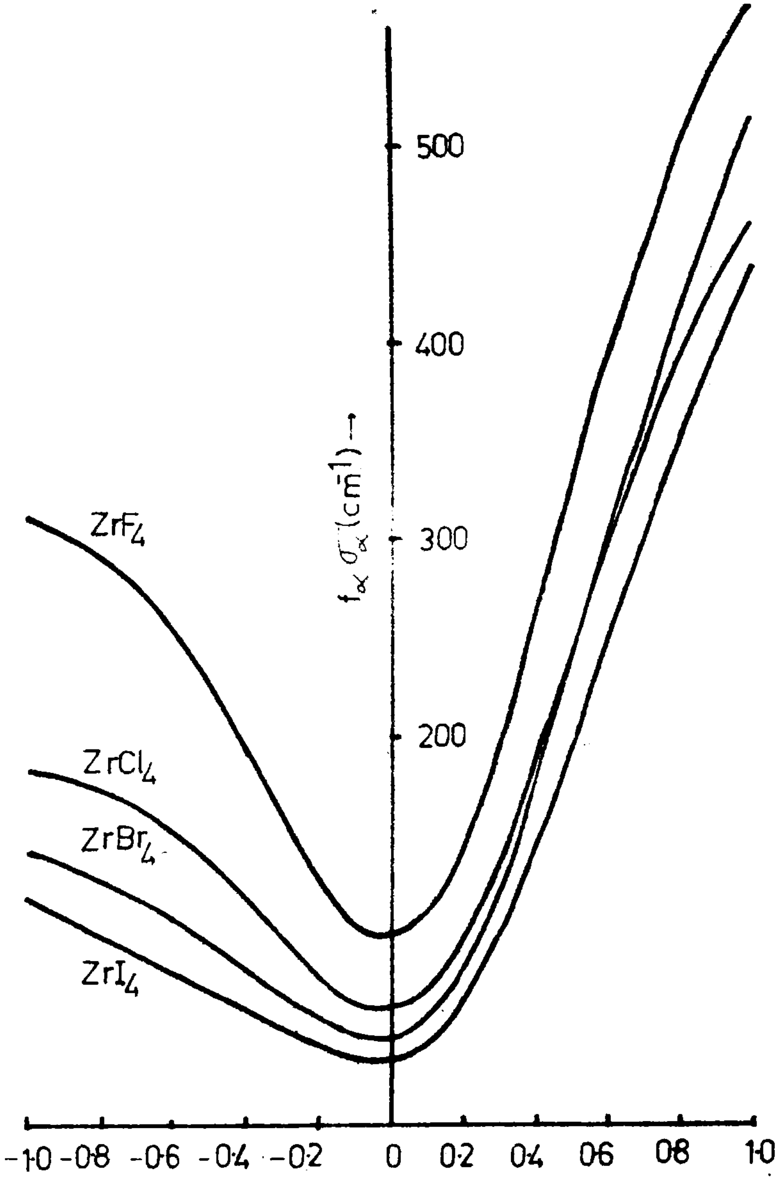
Fig·5·3·


$f_\alpha \sigma_\alpha$ (c m^{-1}) →
750
500
250
O$_s$O$_4$
RuO$_4$
VCl$_4$
-1·0 -0·8 -0·6 -0·4 -0·2 0 0·2 0·4 0·6 0·8 1·0
C →

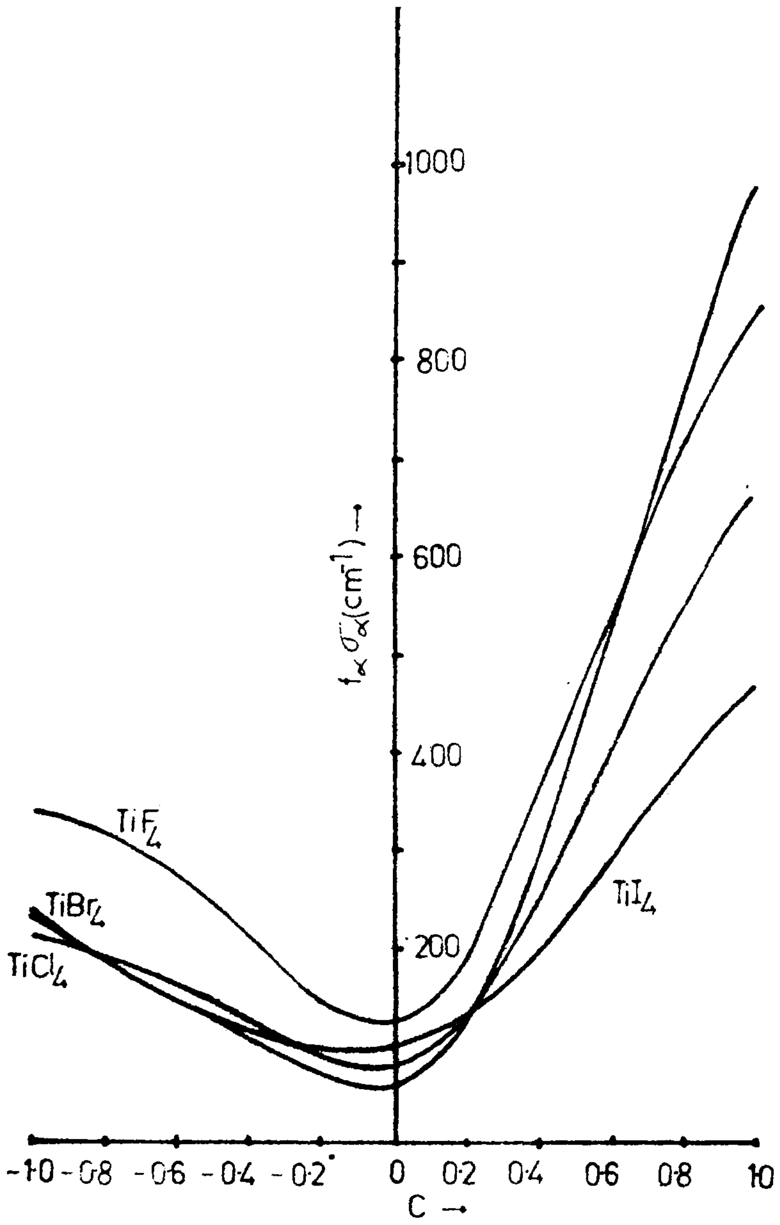
Fig·5·4·


HfCl4
HfBr4
HfI4
fα σα (cm⁻¹) →
100
200
300
400
1·0
0·8
0·6
0·4
0·2
0
0·2
0·4
0·6
0·8
1·0
C →

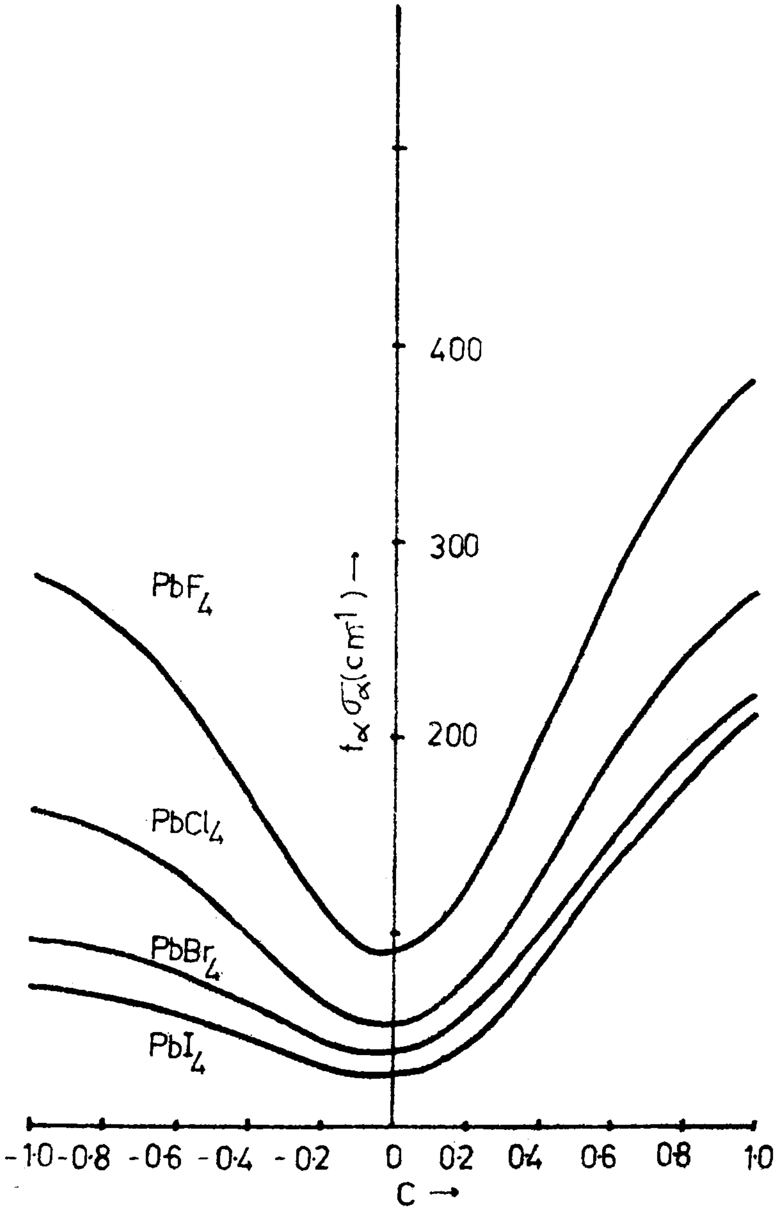
Fig·5·5·


ZrF4
ZrCl4
ZrBr4
ZrI4
fα σα (cm⁻¹) →
200
300
400
500
-1·0
-0·8
-0·6
-0·4
-0·2
0
0·2
0·4
0·6
0·8
1·0
C →

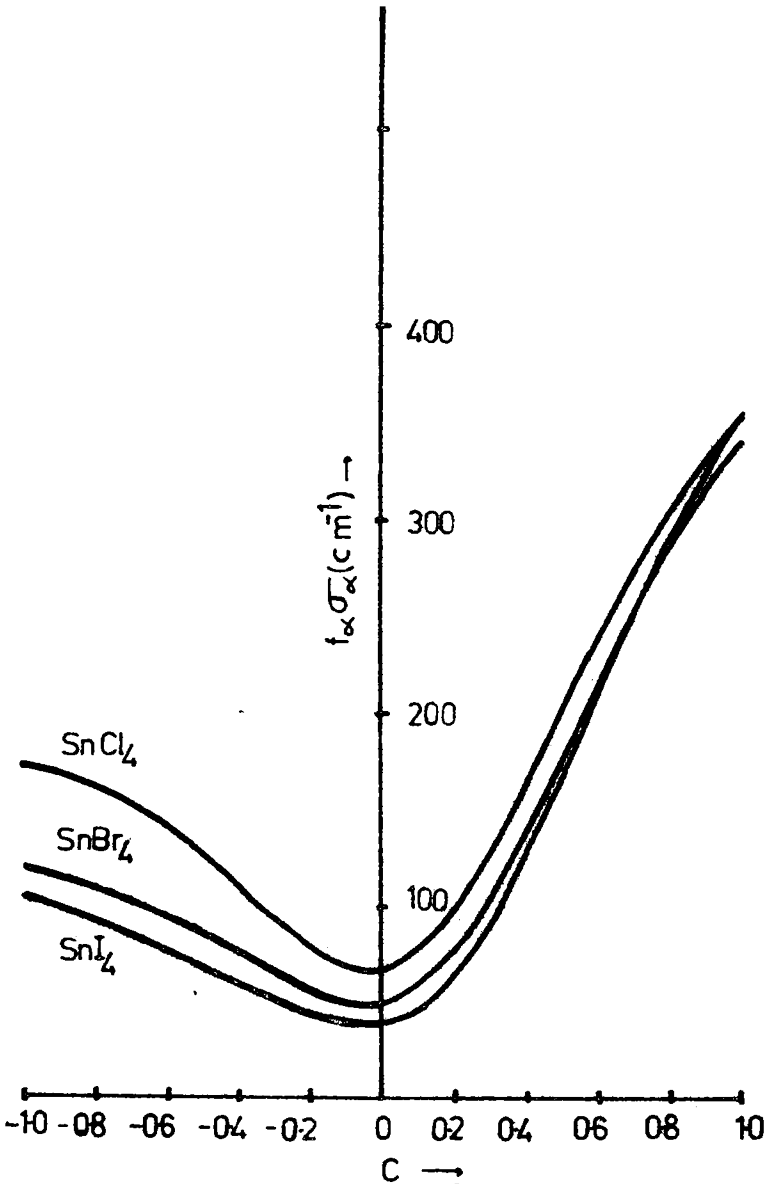
Fig·5·6·


1000
800
600
400
200
$t_\alpha \sigma_\alpha (cm^{-1}) \rightarrow$
TiF_4
$TiBr_4$
$TiCl_4$
TiI_4
-1·0 -0·8 -0·6 -0·4 -0·2 0 0·2 0·4 0·6 0·8 1·0
C →

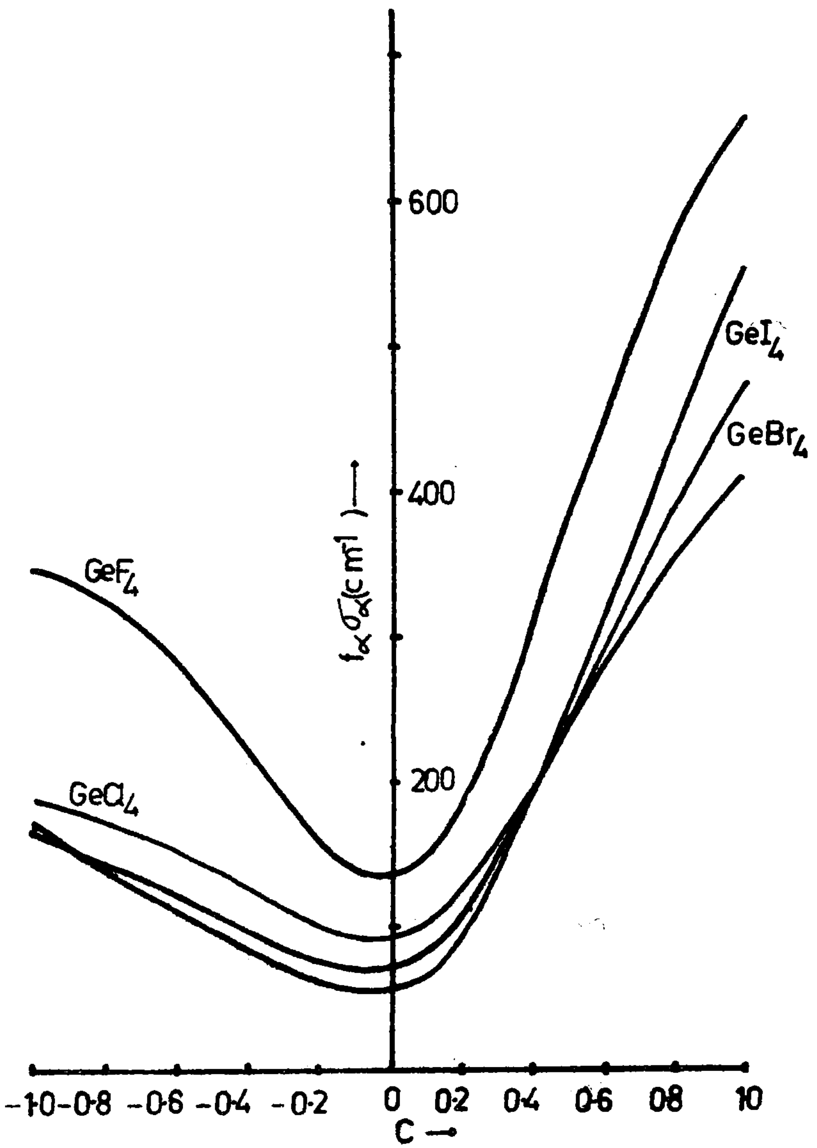
Fig·5·7·


400
300
200
$t_\alpha \sigma_\alpha (cm^{-1}) \rightarrow$
PbF_4
$PbCl_4$
$PbBr_4$
PbI_4
-1·0 -0·8 -0·6 -0·4 -0·2 0 0·2 0·4 0·6 0·8 1·0
C →

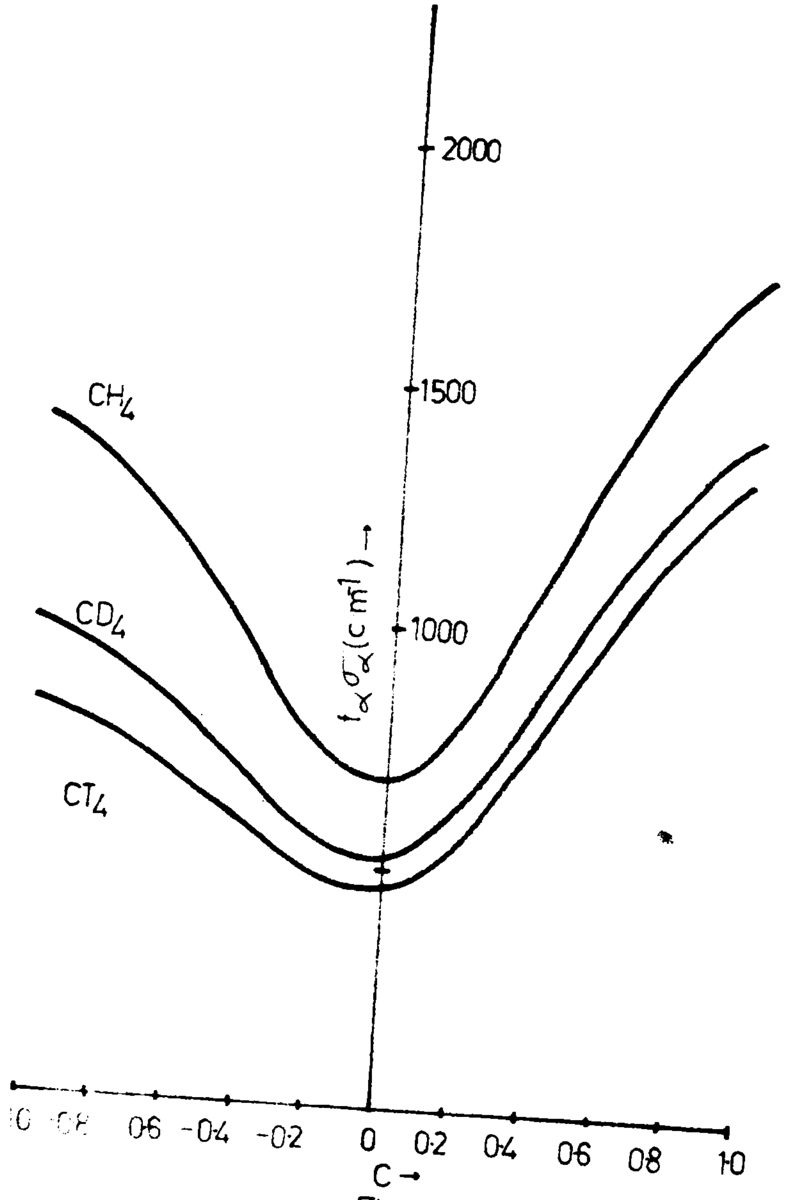
Fig·5·8·



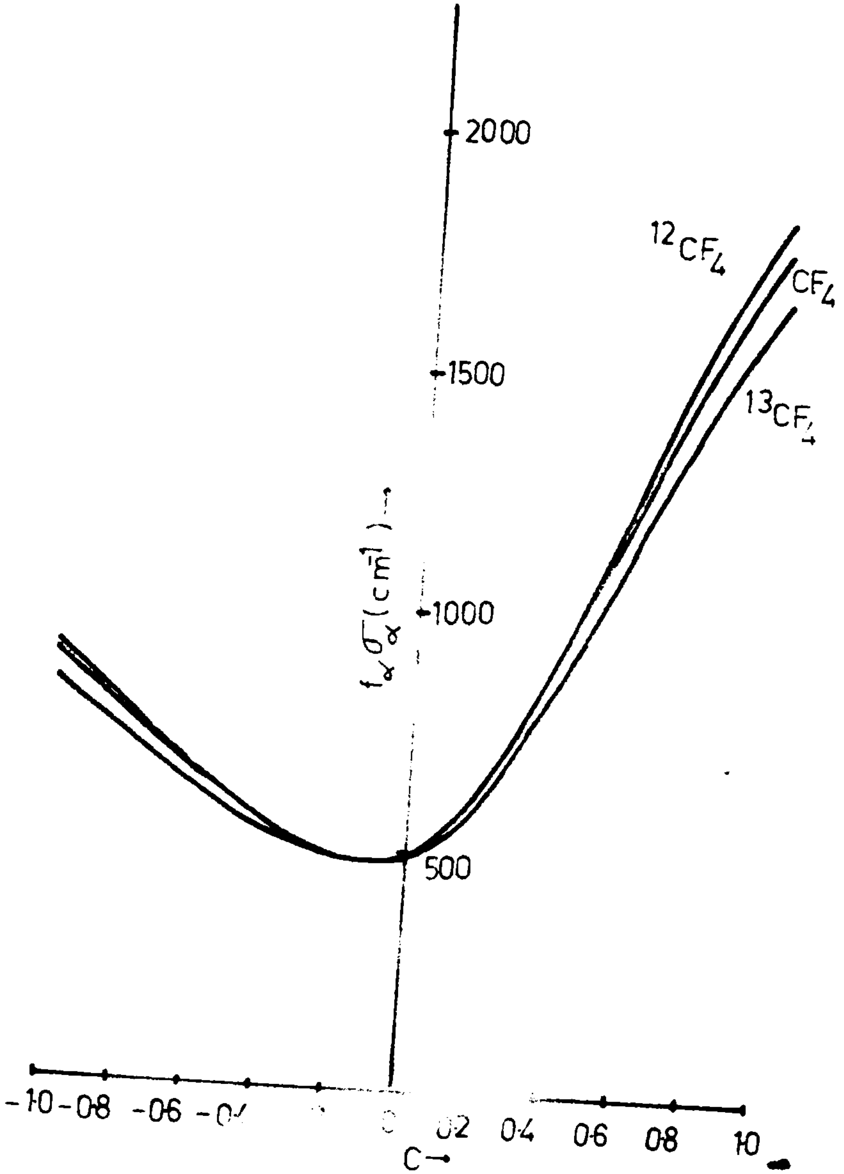
Fig·5·9·



Fig·5·10·



Fig·5·11·



Fig·5·12·

Table 5.1

Frequencies and structural data for the F_2 species of XY_4 (T_d) molecules

Molecule	G_{33}	G_{34}	G_{44}	T^{-1}_{33}	T^{-1}_{34}	T^{-1}_{44}	ω_1 (cm^{-1})	ω_2 (cm^{-1})	Reference
$C\ H_4$	1.1031	0.2220	2.4285	0.9521	- 0.1304	0.6477	3158.0	1357.0	11
$C\ D_4$	0.6075	0.2220	1.4371	1.2830	- 0.3139	0.9588	2336.7	1026.3	11
$C\ T_4$	0.4426	0.2220	1.1072	1.5032	- 0.5027	1.0021	1994.1	879.7	11
$Si\ H_4$	1.0396	0.0949	2.1740	0.9808	- 0.0621	0.6796	2312.0	940.0	11
$Si\ D_4$	0.5440	0.0949	1.1829	1.3557	- 0.1615	0.3257	1672.5	689.8	11
$Si\ T_4$	0.3790	0.0949	0.8530	1.6243	- 0.2751	1.0982	1397.0	581.2	11
$Ge\ H_4$	1.0105	0.0367	2.0577	0.9948	- 0.0254	0.6974	2195.0	846.0	11
$Ge\ D_4$	0.5149	0.0367	1.0665	1.3936	- 0.0692	0.9695	1565.1	609.1	11
$Ge\ T_4$	0.3499	0.0367	0.7366	1.6905	- 0.1226	1.1682	1289.1	506.0	11
$Sn\ H_4$	1.0053	0.0225	2.0291	0.9983	- 0.0157	0.7021	1965.0	697.0	11
$Sn\ D_4$	0.5077	0.0225	1.0379	1.4034	- 0.0435	0.9820	1396.8	498.6	11
$Sn\ T_4$	0.3428	0.0225	0.7081	1.7080	- 0.0780	1.1896	1147.1	411.8	11

(contd... 2)

Table 5.1 (contd.)

Molecule	G_{33}	G_{34}	G_{44}	F^{-1}_{33}	F^{-1}_{34}	F^{-1}_{44}	ω_1 (cm^{-1})	ω_2 (cm^{-1})	Reference
CF_4	0.1637	0.2220	0.5495	2.4720	- 2.7240	2.0077	1285.7	635.6	11
$^{13}CF_4$	0.1552	0.2051	0.5154	2.5386	- 2.6735	2.0229	1272.5	628.8	11
$^{12}CF_4$	0.1637	0.2222	0.5497	2.4713	- 2.7246	2.0076	1311.8	631.3	11
CCl_4	0.1592	0.2220	0.5005	2.6800	- 4.1682	2.6136	791.0	314.1	11
CBr_4	0.1235	0.2220	0.4690	2.8452	- 6.7928	3.7792	665.7	181.8	11
CI_4	0.1189	0.2220	0.4598	2.9001	- 8.7805	4.7040	555.2	123.0	11
SiF_4	0.1001	0.0949	0.2951	3.1607	- 2.0942	2.2081	1031.0	391.0	11
$^{28}SiF_4$	0.1003	0.0953	0.2959	3.1577	- 2.0975	2.2070	1031.0	389.5	11
$^{30}SiF_4$	0.0971	0.0890	0.2852	3.2089	- 2.0598	2.2267	1014.0	386.6	11
$SiCl_4$	0.0757	0.0949	0.2465	3.6352	- 3.5175	2.8040	610.0	221.0	11
$SiBr_4$	0.0599	0.0949	0.2149	4.0831	- 6.2252	3.9332	487.0	137.0	11
SiI_4	0.0553	0.0949	0.2056	4.2506	- 8.2916	4.8341	405.0	94.0	12
VCl_4	0.0544	0.0523	0.1611	4.2881	- 2.8928	3.0052	475.0	128.0	11
OsO_4	0.0695	0.0140	0.1530	3.7929	- 0.5204	2.5807	959.7	328.0	11

(contd ...)

Table 5.1 (contd.)

Molecule	G_{33}	G_{34}	G_{44}	F^{-1}_{33}	F^{-1}_{34}	F^{-1}_{44}	ω_1 (cm^{-1})	ω_2 (cm^{-1})	Reference
$Ru\ O_4$	0.0757	0.0264	0.1778	3.6348	- 0.8490	2.4356	913.0	330.0	11
$Hf\ Cl_4$	0.0357	0.0149	0.0863	5.2941	- 1.4801	3.5346	378.0	93.0	11
$Hf\ Br_4$	0.0199	0.0149	0.0549	7.0739	- 3.5747	4.7815	240.0	60.0	11
$Hf\ I_4$	0.0154	0.0149	0.0456	8.0715	- 5.5190	5.6705	185.0	46.0	11
$Zr\ F_4$	0.0672	0.0292	0.1637	3.8562	- 1.1186	2.5732	668.0	190.0	12
$Zr\ Cl_4$	0.0428	0.0292	0.1149	4.8325	- 2.2155	3.2456	423.0	114.0	11
$Zr\ Br_4$	0.0271	0.0292	0.0855	6.0711	- 4.7254	4.3855	309.0	78.0	11
$Zr\ I_4$	0.0225	0.0292	0.0742	6.6671	- 6.8259	5.2530	211.0	55.0	11
$Ti\ Cl_4$	0.0560	0.0557	0.1678	4.2241	- 2.9621	2.9820	485.0	140.0	11
$Ti\ Br_4$	0.0403	0.0557	0.1364	4.9783	- 5.6535	4.0975	383.0	90.5	11
$Ti\ I_4$	0.0357	0.0557	0.1271	5.2914	- 7.7620	4.9797	225.0	100.0	12
$Pb\ F_4$	0.0591	0.0129	0.1310	4.1146	- 0.6086	2.7929	570.0	180.0	11
$Pb\ Cl_4$	0.0346	0.0129	0.0822	5.3726	- 1.3356	3.5950	341.0	99.0	11

(contd ...)

Table 5.1 (contd)

Molecule	G_{33}	G_{34}	G_{44}	F^{1}_{33}	F^{-1}_{34}	F^{-1}_{44}	ω_1 (cm^{-1})	ω_2 (cm^{-1})	Reference
Pb Br_4	0.0189	0.0129	0.0508	7.2645	- 3.3131	4.8779	231.0	73.0	11
Pb I_4	0.0143	0.0129	0.0415	8.3579	- 5.1968	5.7802	168.0	48.0	11
Sn Cl_4	0.0394	0.0225	0.1014	5.0352	- 1.9142	3.3604	403.0	129.0	11
Sn Br_4	0.0237	0.0225	0.0699	6.4892	- 4.2868	4.5311	279.0	88.0	11
Sn I_4	0.0191	0.0225	0.0607	7.2331	- 6.3481	5.4006	216.0	63.0	11
Ge F_4	0.0710	0.0367	0.1787	3.7529	- 1.2946	2.5021	800.0	260.0	11
Ge Cl_4	0.0466	0.0367	0.1299	4.6336	- 2.4828	3.1479	451.0	171.0	11
Ge Br_4	0.0309	0.0367	0.0985	5.6905	- 5.0815	4.2718	327.0	112.0	11
Ge I_4	0.0262	0.0367	0.0892	6.1723	- 7.1969	5.1422	264.0	80.0	11

Table 5.2

Force fields of F_2 species of XY_4 (T_d) type molecules (in md/Å)

Molecule	c minimum value of F_{44} Σ_{44}	Force fields						Reference
		Present work			Previous result			
		F_{33}	F_{34}	F_{44}	F_{33}	F_{34}	F_{44}	
$C\,F_4$	− 0.10	6.718	− 0.972	0.983				
$^{12}C\,F_4$	− 0.10	6.906	− 0.944	0.977	6.907 ± 0.459	−0.938 ± 0.112	0.971 ±0.046E	2, 3
$^{13}C\,F_4$	− 0.10	6.849	− 0.932	0.982				
$C\,Cl_4$	− 0.04	3.387	− 0.552	0.400	3.35 ± 0.75	−0.32 ± 0.21	0.38 ±0.05 E	2, 3
$Si\,F_4$	− 0.07	6.142	− 0.168	0.452				
$^{28}Si\,F_4$	− 0.07	6.128	− 0.165	0.448	6.406 ± 0.371	−0.291 ± 0.154	0.438 ±0.012E	2, 3
$^{30}Si\,F_4$	−0.07	6.117	− 0.154	0.449				
$Si\,Cl_4$	− 0.08	2.865	− 0.141	0.256	2.96 ± 0.09	−0.145 ± 0.005	0.256 ±0.005E	2, 3
$Si\,Br_4$	− 0.06	2.577	− 0.159	0.178	1.64 2.92	0.00 0.00	0.24* 0.127*	6 10
$Si\,I_4$	− 0.04	1.853	− 0.140	0.125	1.16	0.00	0.18*	6

(contd ...)

Table 5.2 (contd.)

Molecule	e minimum value of $F_{44}\Sigma_{44}$	Force fields Present work F_{33}	 F_{34}	 F_{44}	 Previous result F_{33}	 F_{34}	 F_{44}	Reference
OsO_4	- 0.01	7.804	- 0.038	0.422	8.11 ± 0.08	-0.10 ± 0.10	0.47 ± 0.01	4
RuO_4	-0. 02	6.480	- 0.057	0.382	6.49 ± 0.05	-0.07 ± 0.05	0.381 ± 0.002E	2, 3
VCl_4	- 0.04	2.401	- 0.022	0.089	2.09 ± 0.16	0.15 ± 0.06	0.12 ± 0.02 E	2, 3
$TiCl_4$	- 0.04	2.445	- 0.04	0.104	2.56 ± 0.47	-0.06 ± 0.22	0.12 ± 0.02 E	2, 3
$TiBr_4$	- 0.04	2.11	- 0.047	0.082	2.133 2.05	-0.045 0.00	0.195 0.09*	5 6
TiI_4	- 0.08	1.038	- 0.183	0.150	0.587	-0.151	-0.138	5
$SnCl_4$	- 0.03	2.411	- 0.02	0.112	2.68 ± 0.08	-0.22 ± 0.10	0.118 ± 0.01 E	2, 3
$SnBr_4$	- 0.04	1.922	- 0.041	0.095	1.85 2.28	0.00 0.00	0.10* 0.064*	6 10
SnI_4	- 0.05	1.417	- 0.033	0.070	1.33 1.351	0.00 -0.026	0.07* 0.075	6 8
GeF_4	- 0.03	5.275	- 0.035	0.251	5.807 ± 0.237	-0.283 ± 0.43	0.274 ± 0.014E	2, 3
$GeCl_4$	- 0.05	2.557	- 0.062	0.173	2.73 ± 0.13	-0.13 ± 0.08	0.170 ± 0.003E	2, 3

(Contd ...)

Table 5.2 (contd)

Molecule	e minimum value of $F_{44}\Sigma_{44}$	Force fields						Reference
		Present work			Previous result			
		F_{33}	F_{34}	F_{44}	$\bar{F}_{33}$	$\bar{F}_{34}$	$\bar{F}_{44}$	
$GeBr_4$	- 0.06	2.03	-0.08	0.14	2.03	- 0.08	0.14 E	2, 3
GeI_4	- 0.06	1.563	-0.074	0.103	1.20 1.414	0.00 - 0.047	0.16* 0.117	6 8
CBr_4	- 0.05	2.559	-0.387	0.287	3.36	0.00	0.237*	10
CI_4	- 0.04	1.883	-0.286	0.203	1.49	- 0.21	0.23	13
$HfCl_4$	- 0.01	2.358	-0.012	0.064	2.287 2.315	- 0.029 - 0.007	0.112 0.050	5 7
$HfBr_4$	- 0.02/ - 0.03	1.693/ 1.676	-0.015/ -0.004	0.049/ 0.049	1.640	- 0.042	0.058	5
HfI_4	- 0.03	1.300	-0.014	0.041	1.257	- 0.031	0.057	5
ZrF_4	- 0.02	3.893	-0.014	0.141	3.771 3.785	- 0.084 0.034	0.097 0.164	5 7
$ZrCl_4$	- 0.03	2.435	-0.010	0.082	2.299	- 0.096	0.132	5
$ZrBr_4$	- 0.04	2.032	-0.020	0.071	2.004	- 0.045	0.123	5

(contd ...)

Table 5.2 (contd).

Molecule	e minimum value of $F_{44}\Sigma_{44}$	Force fields						Reference
		Present work			Previous result			
		F_{33}	F_{34}	F_{44}	F_{33}	F_{34}	F_{44}	
ZrI_4	- 0.05	1.138	- 0.023	0.051	1.138 1.116	- 0.074 - 0.011	0.005 0.153	5 7
PbF_4	- 0.01	3.239	- 0.013	0.149	3.148 3.177	- 0.051 - 0.042	0.154 0.095	5 7
$PbCl_4$	- 0.02	1.969	- 0.004	0.075	1.99 2.01	- 0.050 0.00	0.119 0.06*	5 6
$PbBr_4$	- 0.05	1.649	- 0.021	0.075	1.582	- 0.055	0.046	5
PbI_4	- 0.04	1.144	- 0.012	0.046	1.116 1.116	- 0.036 - 0.008	0.025 0.072	5 7
CH_4	- 0.02	5.320	- 0.033	0.456	5.383	- 0.206	0.458E	2, 3
CD_4	- 0.04	5.266	- 0.054	0.461				
CT_4	- 0.05	5.257	- 0.090	0.463				
SiH_4	- 0.01	3.028	- 0.004	0.240	3.032	- 0.025	0.240E	2, 3
SiD_4	- 0.02	3.024	- 0.008	0.240				
SiT_4	- 0.02	3.031	- 0.026	0.240				

(contd ...)

Table 5.2 (contd.)

Molecule	e minimum value of $F_{44}\Sigma_{44}$	Force fields						Reference
		Present work			Previous result			
		F_{33}	F_{34}	F_{44}	F_{33}	F_{34}	F_{44}	
GeH_4	0.00	2.809	- 0.007	0.205	2.807	- 0.083	0.2088	2, 3
GeD_4	- 0.01	2.802	0.002	0.206				
GeT_4	- 0.01	2.800	- 0.005	0.206				
SnH_4	0.00	2.267	- 0.003	0.141	2.17	0.00	0.156*	9
SnD_4	0.00	2.264	- 0.006	0.141				
SnT_4	0.00	2.262	- 0.009	0.141				

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CHAPTER VI

AVERAGE BENDING ENERGY CRITERION: FORCE FIELDS OF SOME PYRAMIDAL XY_3 TYPE MOLECULES

The force fields of several molecules of the pyramidal XY_3 type are evaluated using the average bending energy criterion developed in the three preceeding chapters. The results are in good agreement with those published earlier in the literature.

Pyramidal XY_3 molecules

Pyramidal XY_3 molecules of the C_{3v} symmetry point group posses the geometry illustrated in Fig. (6.0). By group theoretical considerations (1,2) the six normal vibrations of a molecule of this type are found to be distributed under the irreducible representations $2\,A_1 + 2\,E$. It is known that one A_1 species and one E species vibration each is involved in the stretching and in the bending vibrations of the molecule.

The potential energy function of the general valence type for the XY_3 pyramidal molecule is given by

$$\begin{aligned}
2V = {} & f_r\,(\Delta r_1^2 + \Delta r_2^2 + \Delta r_3^2) + \\
& r^2 f_\alpha\,(\Delta \alpha_{12}^2 + \Delta \alpha_{23}^2 + \Delta \alpha_{31}^2) + \\
& 2 f_{rr}\,(\Delta r_1 \Delta r_2 + \Delta r_2 \Delta r_3 + \Delta r_3 \Delta r_1) \\
& + 2 r f_{r\alpha} \Big[\Delta r_1 (\Delta \alpha_{31} + \Delta \alpha_{12}) + \\
& \Delta r_2 (\Delta \alpha_{12} + \Delta \alpha_{23}) + \Delta r_3 \\
& (\Delta \alpha_{23} + \Delta \alpha_{31}) \Big] + 2 r f_{r\alpha}' \\
& (\Delta r_1 \Delta \alpha_{32} + \Delta r_2 \Delta \alpha_{31} + \Delta r_3 \\
& \Delta \alpha_{21}) + 2 r^2 f_{\alpha\alpha}\,(\Delta \alpha_{32} \Delta \alpha_{13} + \\
& \Delta \alpha_{13} \Delta \alpha_{21} + \Delta \alpha_{21} \Delta \alpha_{32})
\end{aligned}$$

(6.1)

On evaluating averages, we have

$$\langle 2V \rangle = 2 f_r \sigma_r + 3 f_\alpha \sigma_\alpha + 6 f_{rr} \sigma_{rr} + 6 f_{\alpha\alpha} \sigma_{\alpha\alpha} + 12 f_{r\alpha} \sigma_{r\alpha} + 6 f_{r\alpha'} \sigma_{r\alpha'} \qquad (6.2)$$

where $\sigma_r = \langle \Delta r_i^2 \rangle$

$\sigma_\alpha = r^2 \langle \Delta \alpha_{ij}^2 \rangle$

These are mean square amplitude quantities evaluated at absolute zero. The following set of symmetry coordinates has been utilised in the calculation: (3)

$$S_1 (A_1) = 3^{-1/2} (\Delta r_1 + \Delta r_2 + \Delta r_3)$$

$$S_2 (A_1) = 3^{-1/2} r (\Delta \alpha_{32} + \Delta \alpha_{31} + \Delta \alpha_{12})$$

$$S_{3a} (E) = 6^{-1/2} (2 \Delta r_1 - \Delta r_2 - \Delta r_3)$$

$$S_{4a} (E) = 6^{-1/2} r (2 \Delta \alpha_{32} - \Delta \alpha_{31} - \Delta \alpha_{12})$$

$$S_{3b} (E) = 2^{-1/2} (\Delta r_2 - \Delta r_3)$$

$$S_{4b} (E) = 2^{-1/2} r (\Delta \alpha_{31} - \Delta \alpha_{12})$$

From eq. (6.2) the total average bending energy is given by

$$\langle 2 V_\alpha \rangle = 3 (f_\alpha \sigma_\alpha + 2 f_{\alpha\alpha} \sigma_{\alpha\alpha}) \qquad (6.3)$$

Using symmetry coordinates the pure bending contribution is worked out to be

$$F_{22}\,\Sigma_{22} + 2\,F_{44}\,\Sigma_{44} \qquad (6.4)$$

where the factor 2 accounts for double degeneracy of the E species bending vibration. Substituting the relations (3)

$$\begin{aligned} F_{22}\ (A_1) &= f_{\alpha} + 2\,f_{\alpha\alpha} \\ F_{44}\ (E) &= f_{\alpha} - f_{\alpha\alpha} \qquad (6.5) \\ \Sigma_{22}\ (A_1) &= \sigma_{\alpha} + 2\,\sigma_{\alpha\alpha} \\ \Sigma_{44}\ (E) &= \sigma_{\alpha} - \sigma_{\alpha\alpha} \end{aligned}$$

in eq.(6.4) we obtain

$$F_{22}\,\Sigma_{22} + 2\,F_{44}\,\Sigma_{44} = \langle 2\,V_{\alpha} \rangle$$

Since $F_{22}\,\Sigma_{22}$ and $F_{44}\,\Sigma_{44}$ belong to the A_1 and E species, respectively, each of these quantities is minimised with respect to the corresponding parameter. The parameter representation of F and Σ of second order species is discussed in Refs. (1) and (5). Thus, the A_1 species force field is assumed to correspond to the minimum of $F_{22}\,\Sigma_{22}$, while the E species force field depends on the minimum of $F_{44}\,\Sigma_{44}$. This procedure has been successfully applied to a large number of pyramidal XY_3 systems.

The G elements are given by the relations (3)

$$\begin{aligned} G_{11}\ (A_1) &= (\,4\cos^2\alpha - 1)\,\mu_x + \mu_y \\ G_{12}\ (A_1) &= -2\,(\,4\cos^2\alpha - 1)\,\mu_x \tan\alpha \end{aligned}$$

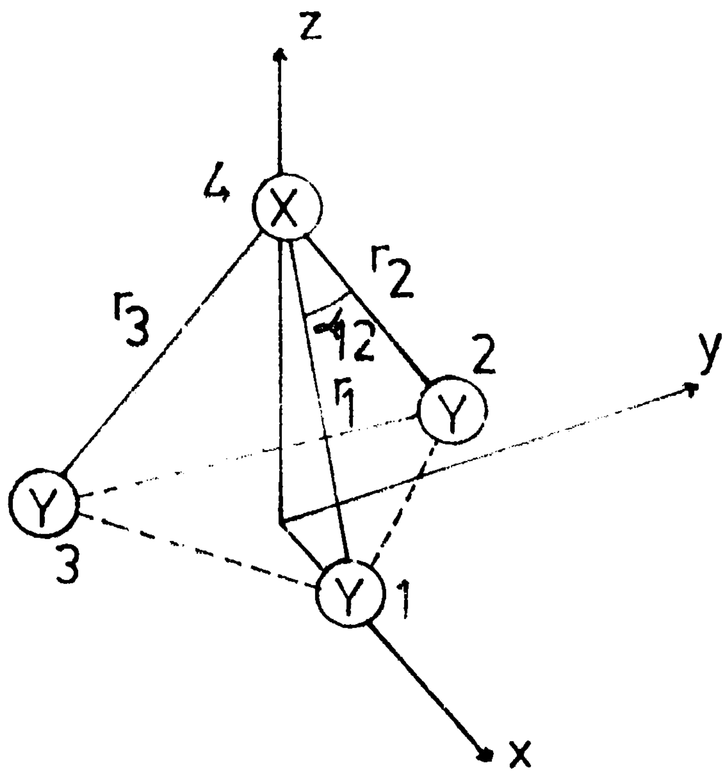


Fig. (6.0) Pyramidal XY_3 Model (Symmetry C_{3v})

$$G_{22}\ (A_1) = (4 - \sec^2\alpha)\ (4\mu_x \sin^2\alpha + \mu_y)$$

$$G_{33}\ (E) = 2\mu_x \sin^2\alpha + \mu_y$$

$$G_{34}\ (E) = 2\mu_x \sin^2\alpha\ \tan\alpha$$

$$G_{44}\ (E) = 2\mu_x + \sin^2\alpha\ \tan^2\alpha + (1 + 1/2 \sec^2\alpha)\mu_y$$

where 2α is the interbond angle μ_x and μ_y represent the reciprocal masses of the X and Y atoms respectively. Structural data and the frequencies (harmonic, wherever available) employed in this calculations are given in Table 6.1 and 6.2. Values of the interbond angle are taken from Ref. (6).

Results and discussion

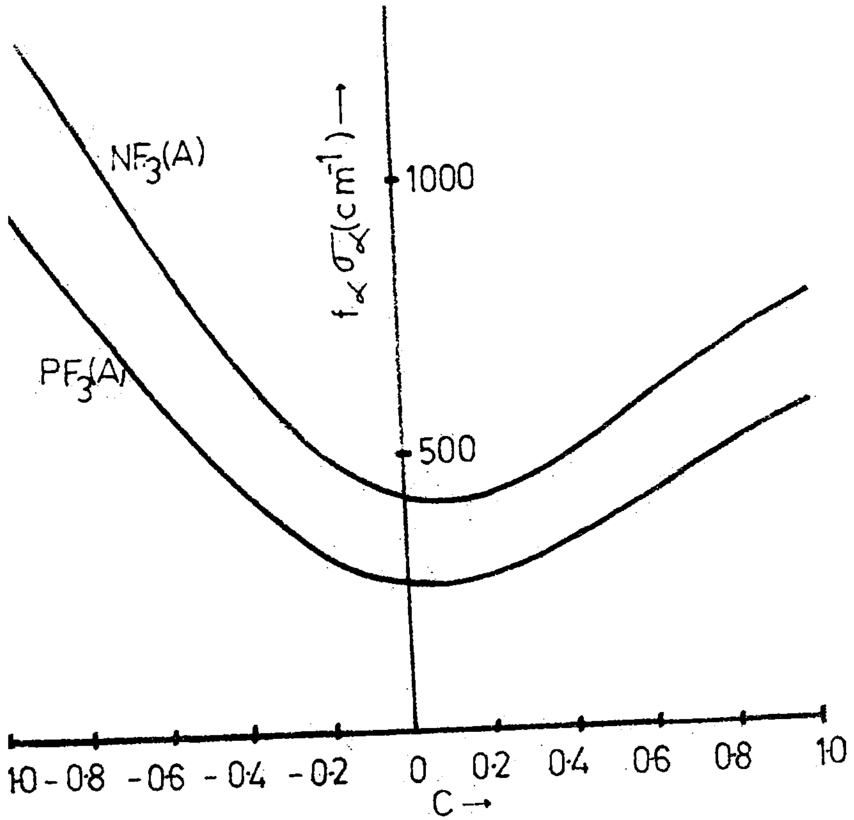
The force constants obtained are tabulated in Table 6.3 and 6.4 for the A_1 and E species separately, and these results are compared with available standard values. The agreement between the two sets of data is very good. Moreover, just as in the case of XY_2 (C_{2v}), XY_3 (D_{3h}), XY_4 (T_d) molecules, the isotopic invariance is very prominent for XY_3 (C_{3v}) systems as well.

The force constants calculated using the present criterion are better for the E species than for the A_1 species. Again there is marked deviation of the interaction force constants from the exact values in the case of hydrides. A similar trend has already been noted for XY_4 (T_d) and XY_2 (C_{2v}) type hydride molecules.

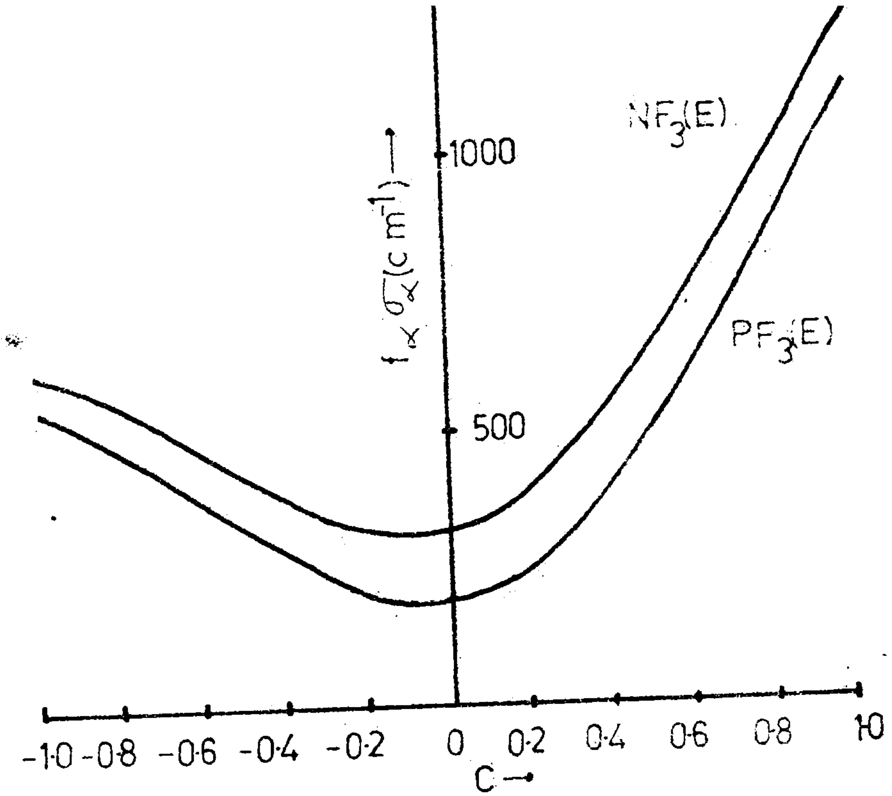
In Figs. (6.1) to (6.4) are shown the variation of the average bending energy for the A_1 and E species of the pyramidal XY_3 molecules studied. Figs. (6.5) and (6.6) show the variation of the bending energy terms $F_{22}\Sigma_{22}$ and $F_{44}\Sigma_{44}$ in NH_3 - ND_3 - NT_3 group for the A_1 and E species.

Figs. (6.1) - (6.4). Average bending energy variation in various XY_3 (C_{3v}) type molecular species.

Figs. (6.5 and (6.6). Variation of average bending energy terms $F_{22}\Sigma_{22}$ and $F_{44}\Sigma_{44}$ for isotopic species of ammonia.


NF3(A)
PF3(A)
$f_\alpha \sigma_\alpha$ (cm^{-1}) →
1000
500
1·0 -0·8 -0·6 -0·4 -0·2 0 0·2 0·4 0·6 0·8 1·0
C →

Fig·6·1·


NF3(E)
PF3(E)
$f_\alpha \sigma_\alpha$ (cm^{-1}) →
1000
500
-1·0 -0·8 -0·6 -0·4 -0·2 0 0·2 0·4 0·6 0·8 1·0
C →

Fig·6·2·

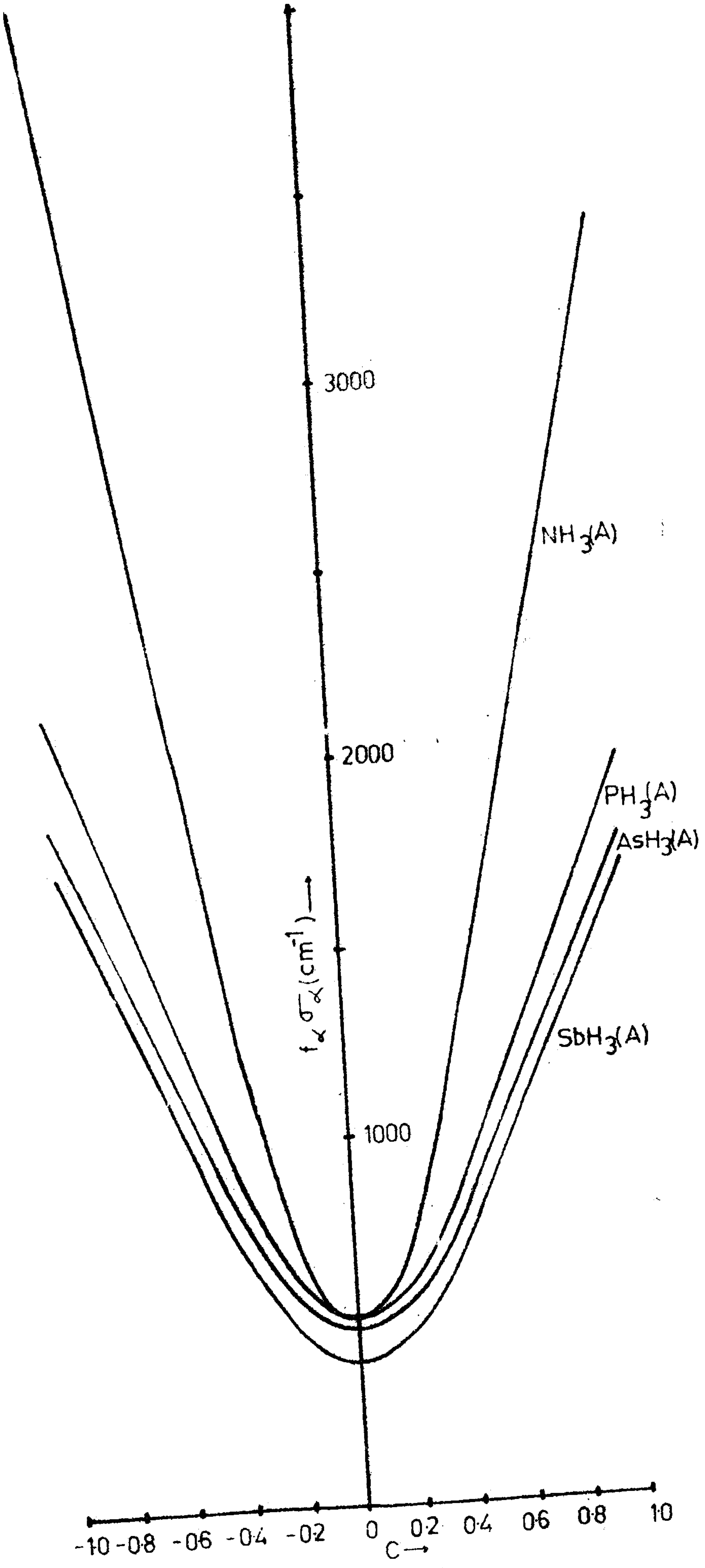

3000
2000
1000
$f_\alpha \sigma_\alpha (cm^{-1})$ →
NH$_3$(A)
PH$_3$(A)
AsH$_3$(A)
SbH$_3$(A)
-1·0 -0·8 -0·6 -0·4 -0·2 0 0·2 0·4 0·6 0·8 1·0
C →

Fig.6·3

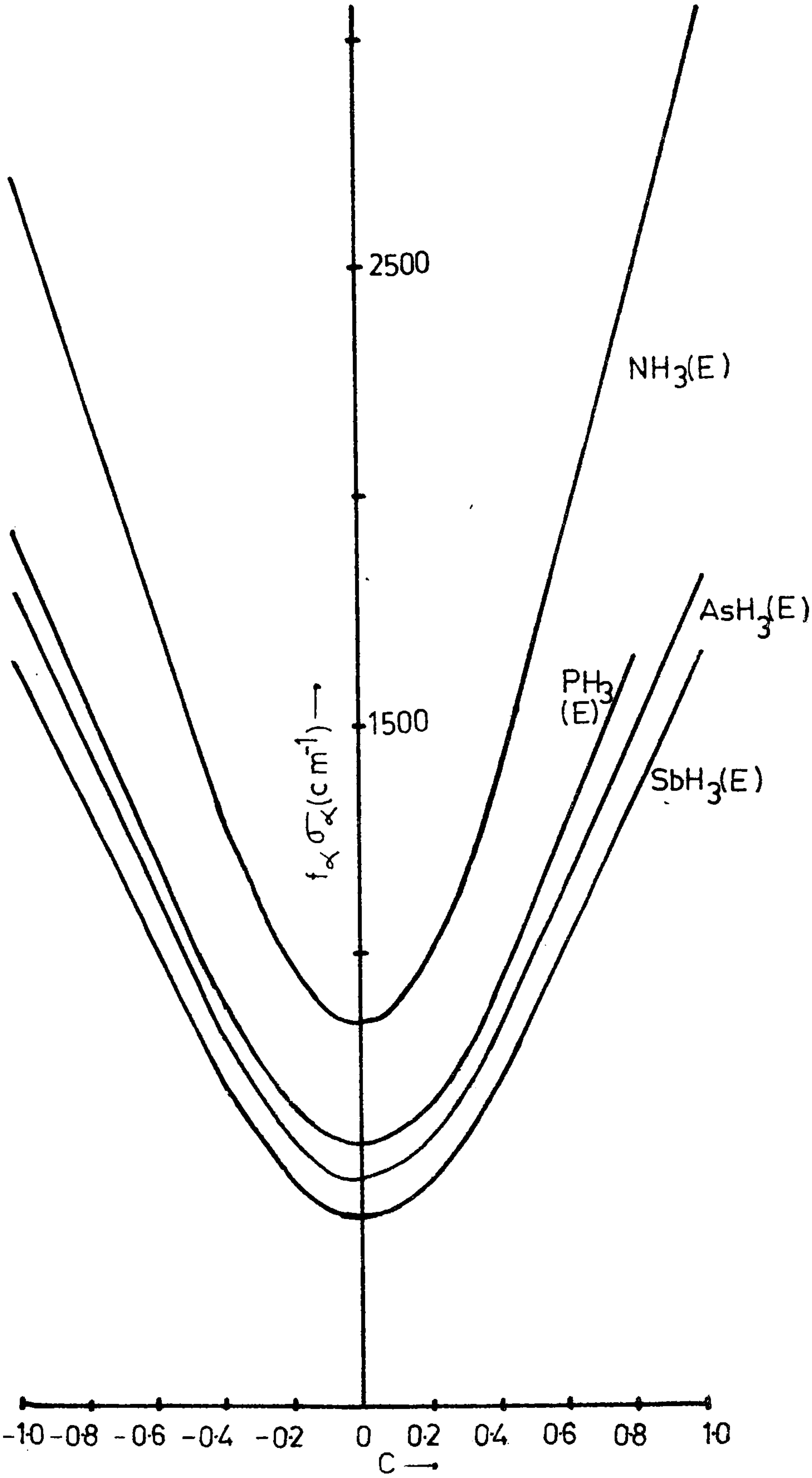

2500
1500
$f_\alpha \sigma_\alpha (cm^{-1})$ →
$NH_3(E)$
$AsH_3(E)$
PH_3 (E)
$SbH_3(E)$
-1·0
-0·8
-0·6
-0·4
-0·2
0
0·2
0·4
0·6
0·8
1·0
C →

Fig. 6·4·

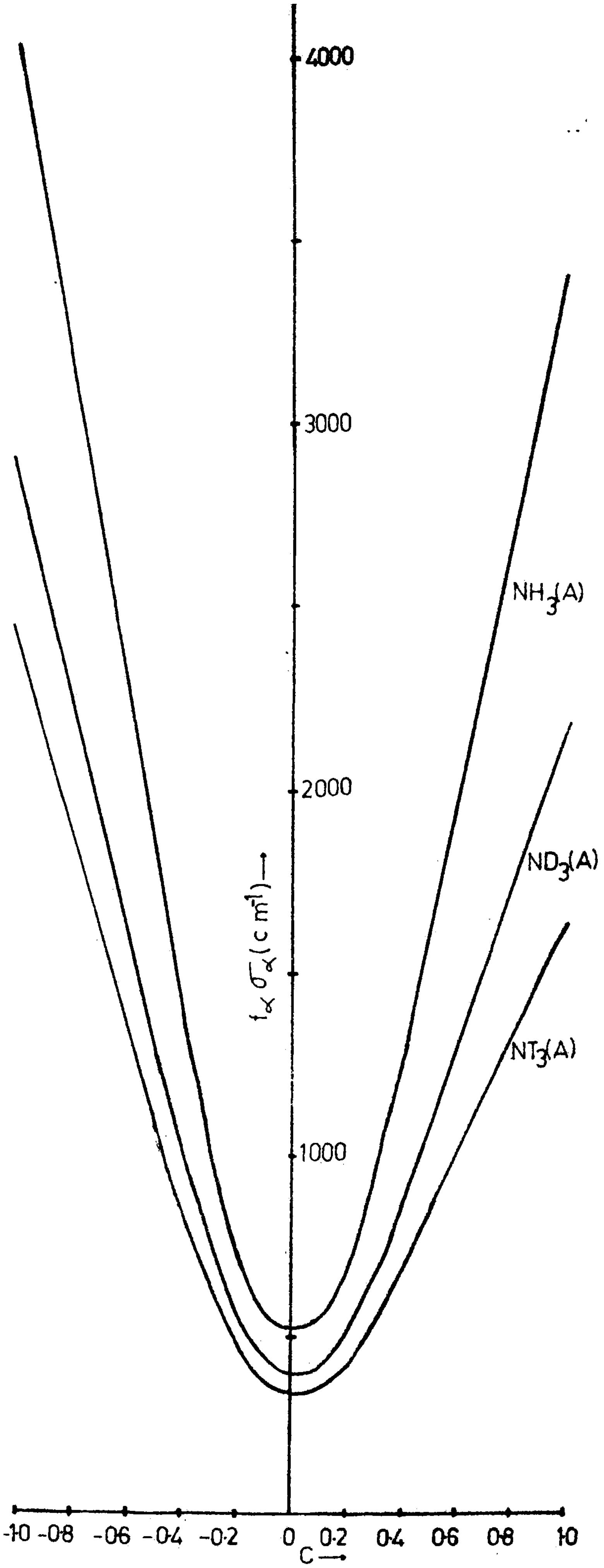

4000
3000
2000
1000
$f_\alpha \sigma_\alpha$ (cm^{-1}) ⟶
NH$_3$(A)
ND$_3$(A)
NT$_3$(A)
-1.0 -0.8 -0.6 -0.4 -0.2 0 0.2 0.4 0.6 0.8 1.0
C ⟶

Fig.6.5.

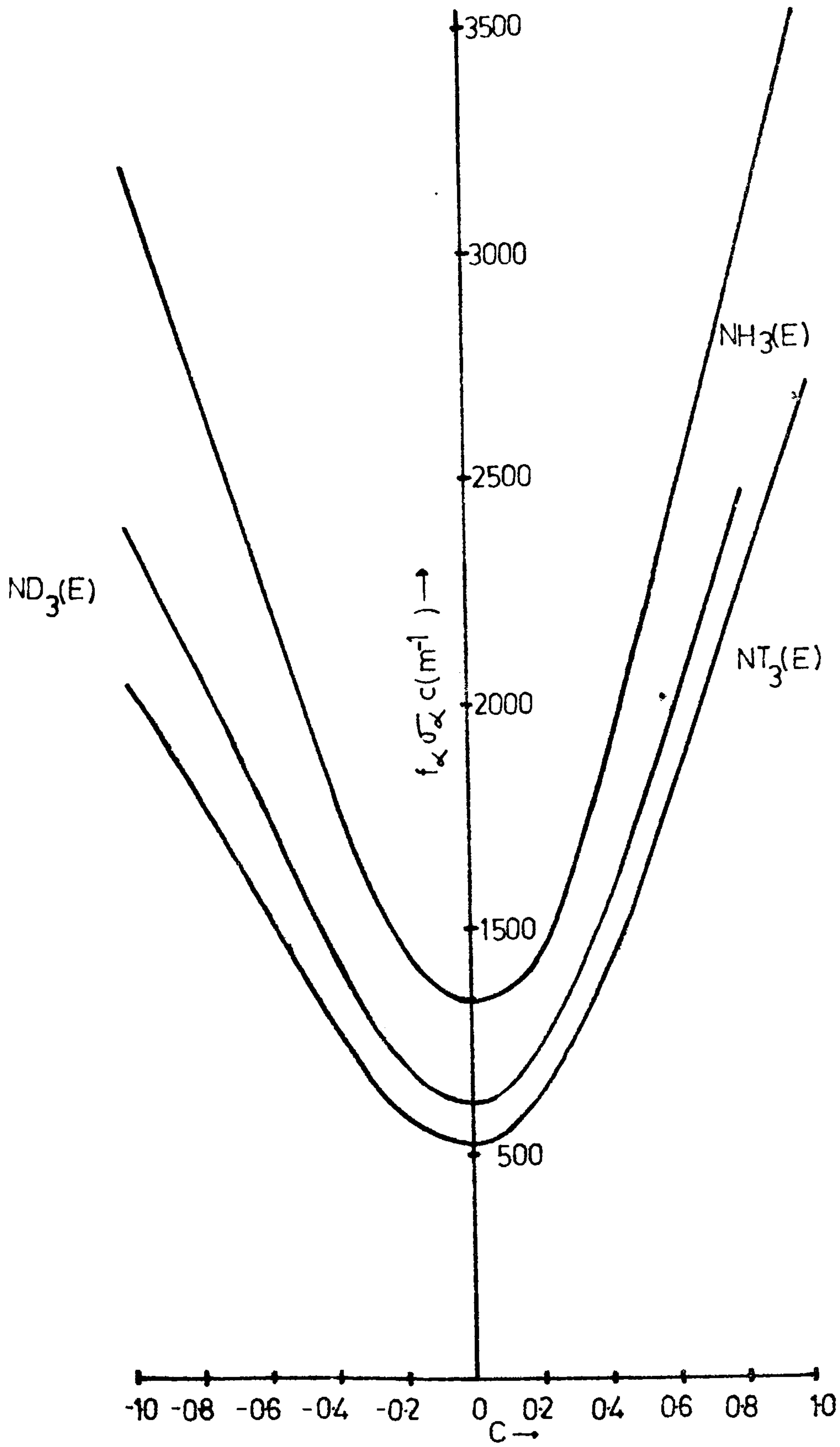

3500
3000
2500
2000
1500
500
$f_\alpha \sigma_\alpha c (m^{-1})$
NH3(E)
ND3(E)
NT3(E)
-1·0 -0·8 -0·6 -0·4 -0·2 0 0·2 0·4 0·6 0·8 1·0
C

Fig. 6·6·

Table 6.1

Frequencies and structural data for the A_1 species vibration of XY_3 (C_{3v}) molecules

Molecule	G_{11}	G_{12}	G_{22}	Interbond angle 2α	T^{-1}_{11}	T^{-1}_{12}	T^{-1}_{22}	ω_1 (cm^{-1})	ω_2 (cm^{-1})	Reference
NF_3	0.0947	− 0.1043	0.3306	102° 9'	3.2488	2.3709	2.1529	1006.97	644.84	7
PF_3	0.0737	− 0.0502	0.2029	100°	3.6853	1.6596	2.4352	892.0	487.0	9
NH_3	1.0219	− 0.0801	1.3811	107°	0.9892	0.0669	0.8529	3504.0	1031.0	9
ND_3	0.5261	− 0.0801	0.7993	107°	1.3786	0.1716	1.1271	2496.4	785.7	9
NT_3	0.3612	− 0.0801	0.6058	107°	1.6639	0.2893	1.3041	2054.8	683.6	9
PH_3	1.0206	− 0.0603	1.9838	93°30'	0.9899	0.0420	0.7106	2448.0	1042.0	9
PD_3	0.5248	− 0.0603	1.0567	93°30'	1.3803	0.1121	0.9760	1763.8	755.1	9
PT_3	0.3599	− 0.0603	0.7482	93°30'	1.6669	0.1949	1.1640	1467.5	630.2	9
AsH_3	1.0047	− 0.0257	1.9658	92°	0.9977	0.0183	0.7133	2204.0	974.0	9
AsD_3	0.5089	− 0.0257	1.0103	92°	1.4018	0.0503	0.9955	1573.6	695.7	9
AsT_3	0.3440	− 0.0257	0.6923	92°	1.7050	0.0899	1.2035	1297.7	573.7	9
SbH_3	1.0001	− 0.0161	1.9642	91°30'	0.9999	0.0115	0.7136	1986.0	796.0	9
SbD_3	0.5043	− 0.0161	0.9993	91°30'	1.4081	0.0319	1.0001	1412.8	566.8	9
SbT_3	0.3394	− 0.0161	0.6783	91°30'	1.7165	0.0576	1.2149	1160.9	465.9	9

Table 6.2

Frequencies and structural data for the E species vibration of XY_3 (C_{3v}) molecules

Molecule	G_{33}	G_{34}	G_{44}	F_{33}	F_{34}	F_{44}	ω_1 (cm^{-1})	ω_2 (cm^{-1})	Reference
$N F_3$	0.1391	0.1071	0.2520	2.6814	$-$ 1.8683	2.4288	886.34	492.7	7
$P F_3$	0.0905	0.0452	0.1701	3.3237	$-$ 1.2983	2.6027	860.0	344.0	9
$N H_3$	1.0845	0.1247	2.5630	0.9603	$-$ 0.0720	0.6264	3592.0	1690.0	9
$N D_3$	0.5888	0.1247	1.3667	1.3042	$-$ 0.1829	0.8638	2643.2	1226.7	9
$N T_3$	0.4238	0.1247	0.9687	1.5361	$-$ 0.3047	1.0359	2242.1	1022.9	9
$P H_3$	1.0265	0.0364	2.0876	0.9870	$-$ 0.0246	0.6923	2457.0	1154.0	9
$P D_3$	0.5308	0.0364	1.0639	1.3726	$-$ 0.0666	0.9706	1763.3	825.3	9
$P T_3$	0.3658	0.0364	0.7234	1.6534	$-$ 0.1173	1.1787	1466.3	678.0	9
$As H_3$	1.0060	0.0140	2.0552	0.9970	$-$ 0.0099	0.7010	2225.0	1012.0	9
$As D_3$	0.5103	0.0143	1.0258	1.3999	$-$ 0.0277	0.9875	1583.7	718.7	9
$As T_3$	0.3454	0.0143	0.5899	1.7016	$-$ 0.0499	1.2044	1302.1	589.6	9
$Sb H_3$	1.0007	0.0087	2.0201	0.9996	$-$ 0.0061	0.7036	1976.0	845.0	9
$Sb D_3$	0.5050	0.0087	1.0153	1.4072	$-$ 0.0171	0.9925	1403.5	599.1	9
$Sb T_3$	0.3400	0.0087	0.6810	1.7149	$-$ 0.0311	1.2120	1151.6	490.6	9

Table 6.3

A_1 species force fields of XY_3 (C_{3v}) type molecules (in md/Å)

Molecule	c minimum	Force constants						Reference
		Present work			Previous result			
		F_{11}	F_{12}	F_{22}	F_{11}	F_{12}	F_{22}	
NF_3	0.20	6.571	0.845	1.198	6.204	0.640	1.28	11
					6.290	0.642	1.24	12
					6.131±0.221	0.632±0.042	1.288±0.041	10
PF_3	0.06	6.491	0.393	0.836	6.180	0.357	0.815	13, 14
					6.18	0.313	0.819	12
					6.2	0.41	0.80	15
NH_3	0.00	7.082	0.036	0.455	7.120	0.326	0.454	11
ND_3	0.01	6.973	0.019	0.462				
NT_3	0.01	6.888	0.056	0.469				
PH_3	0.00	3.461	0.019	0.323	3.442	0.302	0.353	11
PD_3	0.01	3.492	0.017	0.320				
PT_3	0.01	3.527	0.033	0.317				
AsH_3	0.00	2.849	0.007	0.284	2.785	0.312	0.300	13, 14
AsD_3	0.00	2.867	0.014	0.284				
AsT_3	0.01	2.885	0.005	0.281				
SbH_3	0.00	2.324	0.003	0.190	2.267	-0.200	0.215	12
SbD_3	0.00	2.332	0.006	0.190				
SbT_3	0.00	2.339	0.009	0.190				

Table 6.4

E species force fields of XY_3 (C_{3v}) type molecules (in md/Å)

Molecule	e minimum	Force constants						Reference
		Present work			Previous result			
		F_{33}	F_{34}	F_{44}	F_{33}	F_{34}	F_{44}	
NF_3	−0.08	3.565	−0.488	0.856	3.412	−0.416	0.866	8
					3.404 ± 0.101	−0.329 ± 0.043	0.899 ± 0.022	10
					3.478	−0.368	0.887	11
PF_3	−0.04	5.052	−0.111	0.476	4.930	−0.175	0.492	8
					4.882	−0.119	0.495	11
					4.980	−0.190	0.500	15
NH_3	−0.01	7.026	−0.040	0.661	6.469	−0.150	0.616	8
					6.982	−0.024	0.666	11
					7.038	−0.174	0.665	12
					6.965	0.000	0.666	13,14
ND_3	−0.02	7.050	−0.067	0.662				
NT_3	−0.02	7.087	−0.120	0.662				
PH_3	0.00	3.465	−0.013	0.376	3.284	−0.052	0.376	11
					3.466	−0.040	0.376	12
					3.270	−0.010	0.393	13,14
PD_3	−0.01	3.462	−0.007	0.376				
PT_3	−0.01	3.466	−0.018	0.376				
AsH_3	0.00	2.899	−0.004	0.297	2.895	−0.074	0.300	11
					2.892	−0.100	0.301	12

(contd ...)

Table 6.4 (contd.)

Molecule	θ minimum	Force constants						Reference
		Present work			Previous result			
		F_{33}	F_{34}	F_{44}	F_{33}	F_{34}	F_{44}	
As D_3	0.00	2.896	−0.008	0.297				
As T_3	−0.01	2.891	−0.004	0.297				
Sb H_3	0.00	2.299	−0.002	0.208	2.299	−0.013	0.208	11
					2.297	−0.020	0.208	12
Sb D_3	0.00	2.302	−0.005	0.208				
Sb T_3	0.00	2.303	−0.005	0.208				

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CHAPTER VII

AVERAGE BENDING ENERGY CRITERION: APPLICATION TO THE METAL HEXAFLUORIDES OF THE XY_6 (O_h) TYPE

The average bending energy criterion developed and applied in the three preceding chapters of the present thesis has been extended to the case of metal hexafluoride molecules of the octahedral point symmetry group. The results are in satisfactory agreement with values reported earlier in the literature.

Metalhexafluorides

The octahedral XY_6 molecular model belonging to the O_h point group is illustrated in Fig. (7.0). The potential energy function of the general valence type may be written as

$$\begin{aligned}
2V = & \Big[f_r \quad (\Delta r_1)^2 + (\Delta r_2)^2 + (\Delta r_3)^2 \\
& + (\Delta r_4)^2 + (\Delta r_5)^2 + (\Delta r_6)^2 \Big] \\
& + 2 f_{rr} \Big[(\Delta r_3 + \Delta r_6)(\Delta r_1 + \Delta r_2 + \Delta r_4 \\
& + \Delta r_5) + (\Delta r_2 + \Delta r_5)(\Delta r_1 + \Delta r_4) \Big] \\
& + 2 f_{rr'} \Big[(\Delta r_1)(\Delta r_4) + (\Delta r_2)(\Delta r_5) \\
& + (\Delta r_3)(\Delta r_6) \Big] \\
& + 2 r f_{r\alpha} \Big[\Delta r_1 (\Delta\alpha_{12} + \Delta\alpha_{13} + \Delta\alpha_{15} + \Delta\alpha_{16}) \\
& + (\Delta r_2)(\Delta\alpha_{12} + \Delta\alpha_{23} + \Delta\alpha_{24} + \Delta\alpha_{26}) \\
& + (\Delta r_3)(\Delta\alpha_{13} + \Delta\alpha_{23} + \Delta\alpha_{34} + \Delta\alpha_{35}) \\
& + (\Delta r_4)(\Delta\alpha_{24} + \Delta\alpha_{34} + \Delta\alpha_{45} + \Delta\alpha_{46}) \\
& + (\Delta r_5)(\Delta\alpha_{15} + \Delta\alpha_{35} + \Delta\alpha_{45} + \Delta\alpha_{56}) \\
& + (\Delta r_6)(\Delta\alpha_{16} + \Delta\alpha_{26} + \Delta\alpha_{46} + \Delta\alpha_{56}) \Big]
\end{aligned}$$

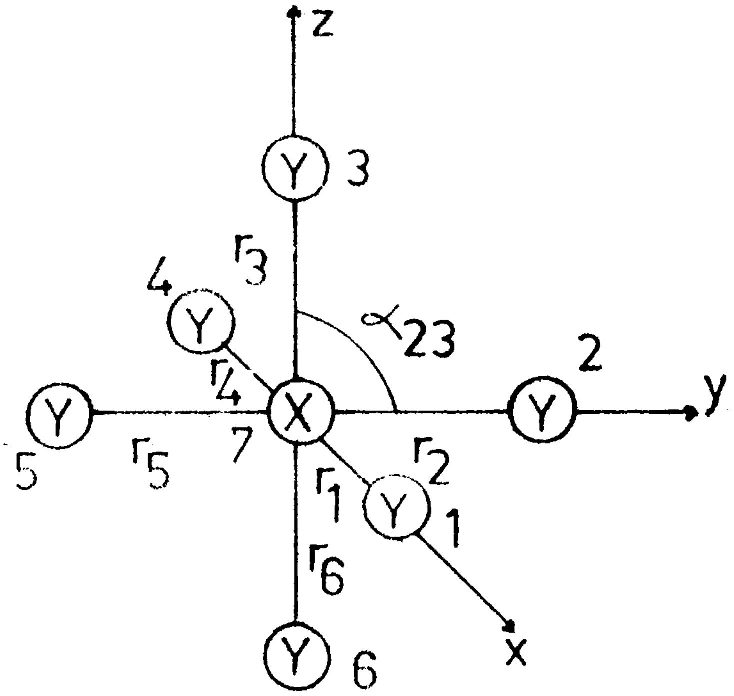


Fig.(7.0)Octahedral XY_6 Molecular Model
(Symmetry O_h)

$$+ 2\,r\,f_{r\alpha'} \Big[(\Delta r_1 + \Delta r_6)(\Delta\alpha_{12} + \Delta\alpha_{15} + \Delta\alpha_{24} + \Delta\alpha_{45}) + (\Delta r_2 + \Delta r_5)(\Delta\alpha_{13} + \Delta\alpha_{16} + \Delta\alpha_{34} + \Delta\alpha_{46})$$

$$+ (\Delta r_1 + \Delta r_4)(\Delta\alpha_{23} + \Delta\alpha_{26} + \Delta\alpha_{35} + \Delta\alpha_{56}) \Big]$$

$$+ 2\,r\,f_{r\alpha''} \Big[(\Delta r_1)(\Delta\alpha_{24} + \Delta\alpha_{34} + \Delta\alpha_{45} + \Delta\alpha_{46})$$

$$+ (\Delta r_2)(\Delta\alpha_{15} + \Delta\alpha_{35} + \Delta\alpha_{45} + \Delta\alpha_{56})$$

$$+ (\Delta r_3)(\Delta\alpha_{16} + \Delta\alpha_{26} + \Delta\alpha_{46} + \Delta\alpha_{56})$$

$$+ (\Delta r_4)(\Delta\alpha_{12} + \Delta\alpha_{13} + \Delta\alpha_{15} + \Delta\alpha_{16})$$

$$+ (\Delta r_5)(\Delta\alpha_{12} + \Delta\alpha_{23} + \Delta\alpha_{24} + \Delta\alpha_{26})$$

$$+ (\Delta r_6)(\Delta\alpha_{13} + \Delta\alpha_{23} + \Delta\alpha_{34} + \Delta\alpha_{35}) \Big]$$

$$+ r^2 f_{\alpha} \Big[(\Delta\alpha_{12})^2 + (\Delta\alpha_{13})^2 + (\Delta\alpha_{15})^2 + (\Delta\alpha_{16})^2$$

$$+ (\Delta\alpha_{23})^2 + (\Delta\alpha\, 24)^2 + (\Delta\alpha_{26})^2 + (\Delta\alpha_{34})^2$$

$$+ (\Delta\alpha_{35})^2 + (\Delta\alpha_{45})^2 + (\Delta\alpha_{46})^2 + (\Delta\alpha_{56})^2 \Big]$$

$$+ 2\,r^2 f_{\alpha\alpha} \Big[(\Delta\alpha_{13} + \Delta\alpha_{16})(\Delta\alpha_{12} + \Delta\alpha\, 15)$$

$$+ (\Delta\alpha_{23})(\Delta\alpha_{12} + \Delta\alpha_{13} + \Delta\alpha_{24})$$

$$+ (\Delta\alpha_{26})(\Delta\alpha_{12} + \Delta\alpha_{16} + \Delta\alpha_{24})$$

$$+ (\Delta\alpha_{34}) (\Delta\alpha_{23} + \Delta\alpha_{24} + \Delta\alpha_{45})$$

$$+ (\Delta\alpha_{35}) (\Delta\alpha_{13} + \Delta\alpha_{15} + \Delta\alpha_{34} + \Delta\alpha_{45})$$

$$+ (\Delta\alpha_{46}) (\Delta\alpha_{24} + \Delta\alpha_{26} + \Delta\alpha_{45})$$

$$+ (\Delta\alpha_{56}) (\Delta\alpha_{15} + \Delta\alpha_{16} + \Delta\alpha_{45} + \Delta\alpha_{46}) \Big]$$

$$+ 2 r^2 f_{\alpha\alpha'} \Big[(\Delta\alpha_{12} + \Delta\alpha_{45}) (\Delta\alpha_{15} + \Delta\alpha_{24})$$

$$+ (\Delta\alpha_{13} + \Delta\alpha_{46}) (\Delta\alpha_{16} + \Delta\alpha_{34})$$

$$+ (\Delta\alpha_{23} + \Delta\alpha_{56}) (\Delta\alpha_{26} + \Delta\alpha_{35}) \Big]$$

$$+ 2 r^2 f_{\alpha\alpha''} \Big[(\Delta\alpha_{23}) (\Delta\alpha_{15} + \Delta\alpha_{16} + \Delta\alpha_{46})$$

$$+ (\Delta\alpha_{24}) (\Delta\alpha_{13} + \Delta\alpha_{16} + \Delta\alpha_{56})$$

$$+ (\Delta\alpha_{26}) (\Delta\alpha_{13} + \Delta\alpha_{15})$$

$$+ (\Delta\alpha_{34}) (\Delta\alpha_{12} + \Delta\alpha_{15} + \Delta\alpha_{26})$$

$$+ (\Delta\alpha_{35}) (\Delta\alpha_{12} + \Delta\alpha_{16} + \Delta\alpha_{24})$$

$$+ (\Delta\alpha_{45}) (\Delta\alpha_{13} + \Delta\alpha_{16} + \Delta\alpha_{26})$$

$$+ (\Delta\alpha_{46}) (\Delta\alpha_{12} + \Delta\alpha_{15} + \Delta\alpha_{35})$$

$$+ (\Delta\alpha_{56}) (\Delta\alpha_{12} + \Delta\alpha_{13} + \Delta\alpha_{34}) \Big]$$

$$+ 2 r^2 f_{\alpha\alpha'''} \Big[(\Delta\alpha_{24}) (\Delta\alpha_{15}) + (\Delta\alpha_{34}) (\Delta\alpha_{16})$$

$$+ (\Delta\alpha_{35})(\Delta\alpha_{26}) + (\Delta\alpha_{45})(\Delta\alpha_{12})$$

$$+ (\Delta\alpha_{46})(\Delta\alpha_{13}) + (\Delta\alpha_{56})(\Delta\alpha_{23}) \Big] \qquad (7.1)$$

where f_r represents the XY stretching force constant, f_{rr} the stretch-stretch interaction when there is an angle of 90° between the two stretching bonds, f_{rr}', the stretch-stretch interaction when the two bonds are opposite, $f_{r\alpha}$ the stretch-bend interaction when the stretching bond is also one of the bending bonds, $f_{r\alpha}'$ the stretch-bend interaction when the stretching bond is perpendicular to both bending bonds, $f_r{}''$ the stretch-bend interaction when the stretching bond is perpendicular to one and opposite to the other bending bond, f_α the force associated with bending, $f_{\alpha\alpha}$ the bend-bend interaction when one bond is common to both bending pairs and the two others are perpendicular, $f_{\alpha\alpha}'$ the bend-bend interaction when one bond is common to both bending pairs and the two others are opposite, $f_{\alpha\alpha}''$ the bend-bend interaction when one bond of one pair is opposite to a bond of the other pair, while the other bonds are perpendicular to each other and $f_{\alpha\alpha}'''$ the bend-bend interaction when the two bending angles are opposite to each other. r is the equilibrium X - Y distance. The average potential energy is given by

$$\langle 2V\rangle = 6\,(\, f_r\sigma_r + 4\, f_{rr}\sigma_{rr}$$

$$+ f_{rr}' \sigma_{rr}' + 8 f_{r\alpha} \sigma_{r\alpha}$$
$$+ 8 f_{r\alpha}' \sigma_{r\alpha}' + 8 f_{r\alpha}'' \sigma_{r\alpha}''$$
$$+ 2 f_{\alpha} \sigma_{\alpha} + 4 f_{\alpha\alpha}' \sigma_{\alpha\alpha}'$$
$$+ 2 f_{\alpha\alpha}''' \sigma_{\alpha\alpha}''' + 8 f_{\alpha\alpha} \sigma_{\alpha\alpha} + 8 f_{\alpha\alpha}'' \sigma_{\alpha\alpha}'') \qquad (7.2)$$

where the quantities σ_{ij} are the mean square amplitudes evaluated at absolute zero.

$$\sigma_r = \langle \Delta r_i^2 \rangle$$
$$\sigma_\alpha = r^2 \langle \Delta \alpha_{ij}^2 \rangle$$

separating the total bending energy contribution from this, we get

$$\langle 2 V_\alpha \rangle = 12 \Big[f_\alpha \sigma_\alpha + 4 f_{\alpha\alpha} \sigma_{\alpha\alpha}$$
$$+ 4 f_{\alpha\alpha}'' \sigma_{\alpha\alpha}'' + 2 f_{\alpha\alpha}' \sigma_{\alpha\alpha}'$$
$$+ f_{\alpha\alpha}''' \sigma_{\alpha\alpha}''' \Big] \qquad (7.3)$$

Octahedral molecules possess six fundamental modes of vibration, three of which are Raman-active only [ν_1 (A_{1g}), ν_2 (E_g) and ν_5 (F_{2g})], two of which are infrared-active only [ν_3 (F_{1u}) and ν_4 (F_{1u})], and the sixth one [ν_6 (F_{2u})] is inactive. Of these the F_{1u} species is a second order species, while the other species are of first order. A convenient set of symmetry coordinates transforming according to the characters of the irreducible representations of the point group are listed below.

$$S_1\ (A_{1g}) = 6^{-1/2}\,(\Delta r_1 + \Delta r_2 + \Delta r_3 + \Delta r_4 + \Delta r_5 + \Delta r_6)$$

$$S_{2a}\ (E_g) = 12^{-1/2}\,(\Delta r_1 + \Delta r_2 - 2\,\Delta r_3 + \Delta r_4 + \Delta r_5 - 2\,\Delta r_6)$$

$$S_{2b}\ (E_g) = 1/2\,(\Delta r_2 - \Delta r_1 + \Delta r_5 - \Delta r_4)$$

$$S_{3a}\ (F_{2g}) = 1/2\, r\,(\Delta\alpha_{26} + \Delta\alpha_{35} - \Delta\alpha_{23} - \Delta\alpha_{56})$$

$$S_{3b}\ (F_{2g}) = 1/2\, r\,(\Delta\alpha_{16} + \Delta\alpha_{34} - \Delta\alpha_{13} - \Delta\alpha_{46})$$

$$S_{3c}\ (F_{2g}) = 1/2\, r\,(\Delta\alpha_{15} + \Delta\alpha_{24} - \Delta\alpha_{12} - \Delta\alpha_{45})$$

$$S_{4a}\ (F_{1u}) = 2^{-1/2}\,(\Delta r_1 - \Delta r_4)$$

$$S_{5a}\ (F_{1u}) = 8^{-1/2}\, r\,(\Delta\alpha_{24} + \Delta\alpha_{34} + \Delta\alpha_{45} + \Delta\alpha_{46} - \Delta\alpha_{12} - \Delta\alpha_{13} - \Delta\alpha_{15} - \Delta\alpha_{16})$$

$$S_{4b}\ (F_{1u}) = 2^{-1/2}\,(\Delta r_2 - \Delta r_5)$$

$$S_{5b}\ (F_{1u}) = 8^{-1/2}\, r\,(\Delta\alpha_{15} + \Delta\alpha_{35} + \Delta\alpha_{45} + \Delta\alpha_{56} - \Delta\alpha_{12} - \Delta\alpha_{23} - \Delta\alpha_{24} - \Delta\alpha_{26})$$

$$S_{4c}\ (F_{1u}) = 2^{-1/2}\,(\Delta r_3 - \Delta r_6)$$

$$S_{5c}\ (F_{1u}) = 8^{-1/2}\, r\, (\Delta\alpha_{16} + \Delta\alpha_{26} + \Delta\alpha_{46} + \Delta\alpha_{56}$$

$$- \Delta\alpha_{13} - \Delta\alpha_{23} - \Delta\alpha_{34} - \Delta\alpha_{35})$$

$$S_{6a}\ (F_{2u}) = 8^{-1/2}\, r\, (\Delta\alpha_{12} - \Delta\alpha_{13} + \Delta\alpha_{15} - \Delta\alpha_{16}$$

$$- \Delta\alpha_{24} + \Delta\alpha_{34} - \Delta\alpha_{45} + \Delta\alpha_{46})$$

$$S_{6b}\ (F_{2u}) = 8^{-1/2}\, r\, (\Delta\alpha_{15} - \Delta\alpha_{35} + \Delta\alpha_{45} - \Delta\alpha_{56}$$

$$- \Delta\alpha_{12} + \Delta\alpha_{23} - \Delta\alpha_{24} + \Delta\alpha_{26})$$

$$S_{6c}\ (F_{2u}) = 8^{-1/2}\, r\, (\Delta\alpha_{13} - \Delta\alpha_{23} + \Delta\alpha_{34} - \Delta\alpha_{35} - \Delta\alpha_{16}$$

$$+ \Delta\alpha_{26} - \Delta\alpha_{46} + \Delta\alpha_{56})$$

The symmetry force constants F_{ij} and symmetry mean square amplitudes Σ_{ij}. Corresponding to the above set of symmetry coordinates are given by (1)

$$F_{11}\ (A_{1g}) = f_r + 4 f_{rr} + f_{rr}'$$

$$F_{22}\ (E_g) = f_r - 2 f_{rr} + f_{rr}'$$

$$F_{33}\ (F_{2g}) = f_\alpha - 2 f_{\alpha\alpha}' + f_{\alpha\alpha}'''$$

$$F_{44}\ (F_{1u}) = f_r - f_{rr}'$$

$$F_{45}\ (F_{1u}) = 2 (f_{r\alpha} - f_{r\alpha}'')$$

$$F_{55}\ (F_{1u}) = f_\alpha + 2 f_{\alpha\alpha} - 2 f_{\alpha\alpha}'' - f_{\alpha\alpha}'''$$

$$F_{66}\ (F_{2u}) = f_\alpha - 2 f_{\alpha\alpha} + 2 f_{\alpha\alpha}'' - f_{\alpha\alpha}'''$$

and

$$
\begin{aligned}
\Sigma_{11} \quad (A_{1g}) &= \sigma_r + 4\,\sigma_{rr} + \sigma_{rr'} \\
\Sigma_{22} \quad (E_g) &= \sigma_r - 2\,\sigma_{rr} + \sigma_{rr'} \\
\Sigma_{33} \quad (F_{2g}) &= \sigma_\alpha - 2\,\sigma_{\alpha\alpha'} + \sigma_{\alpha\alpha'''} \\
\Sigma_{44} \quad (F_{1u}) &= \sigma_r - \sigma_{rr'} \\
\Sigma_{45} \quad (F_{1u}) &= 2\,(\sigma_{r\alpha} - \sigma_{r\alpha''}) \\
\Sigma_{55} \quad (F_{1u}) &= \sigma_\alpha + 2\,\sigma_{\alpha\alpha} - 2\,\sigma_{\alpha\alpha''} - \sigma_{\alpha\alpha'''} \\
\Sigma_{66} \quad (F_{2u}) &= \sigma_\alpha - 2\,\sigma_{\alpha\alpha} + 2\,\sigma_{\alpha\alpha''} - \sigma_{\alpha\alpha'''}
\end{aligned}
\qquad (7.4)
$$

The G matrix belonging to the F_{1u} species (1) is written as

$$
\begin{pmatrix} G_{44} & G_{45} \\ G_{45} & G_{55} \end{pmatrix} = \begin{pmatrix} 2\mu_M + F & -4\mu_M \\ -4\mu_M & 8\mu_M + 2\mu_F \end{pmatrix}
$$

where M refers to the metal atom, F to the fluoride and μ is the reciprocal mass. The average potential energy in the symmetry coordinate representation is given by

$$
\begin{aligned}
\langle 2V \rangle = {} & F_{11}\,\Sigma_{11} + 2\,F_{22}\,\Sigma_{22} + 3\,F_{33}\,\Sigma_{33} \\
& + 3\,(F_{44}\,\Sigma_{44} + 3\,F_{45}\,\Sigma_{45} + F_{55}\,\Sigma_{55}) \\
& + 3\,F_{66}\,\Sigma_{66}
\end{aligned}
\qquad (7.5)
$$

Now the average zero point bending energy alone may be written as

$$\langle 2 V_\alpha \rangle = 3 (F_{33}\, \Sigma_{33} + F_{55}\, \Sigma_{55} + F_{66}\, \Sigma_{66}) \tag{7.6}$$

Substituting from eqs. (7.4), eq. (7.6) ~~is~~ becomes

$$\begin{aligned} \langle 2 V_\alpha \rangle = 3 \Big[\; & 3 f_\alpha \sigma_\alpha - 2 f_\alpha \sigma_{\alpha\alpha}{}' - f_\alpha \sigma_{\alpha\alpha}{}''' \\ & - 2 f_{\alpha\alpha}{}' \sigma_\alpha + 4 f_{\alpha\alpha}{}' \sigma_{\alpha\alpha}{}' - 2 f_{\alpha\alpha}{}' \sigma_{\alpha\alpha}{}''' \\ & - f_{\alpha\alpha}{}''' \sigma_\alpha - 2 f_{\alpha\alpha}{}''' \sigma_{\alpha\alpha}{}' \\ & + 3 f_{\alpha\alpha}{}''' \sigma_{\alpha\alpha}{}''' + 8 f_{\alpha\alpha} \sigma_{\alpha\alpha} \\ & - 8 f_{\alpha\alpha} \sigma_{\alpha\alpha}{}'' - 8 f_{\alpha\alpha}{}'' \sigma_{\alpha\alpha} \\ & + 8 f_{\alpha\alpha}{}'' \sigma_{\alpha\alpha}{}'' \Big] \end{aligned} \tag{7.7}$$

There is one redundant coordinate belonging to the A_{1g} species:

$$\begin{aligned} & 12^{-1/2}\, r\, (\Delta\alpha_{12} + \Delta\alpha_{13} + \Delta\alpha_{23} + \Delta\alpha_{15} + \Delta\alpha_{16} \\ & + \Delta\alpha_{26} + \Delta\alpha_{24} + \Delta\alpha_{34} + \Delta\alpha_{35} + \Delta\alpha_{45} + \Delta\alpha_{46} \\ & + \Delta\alpha_{56}) = 0 \end{aligned} \tag{7.8}$$

In the E_g species we have the redundant coordinates

$$\begin{aligned} & 24^{-1/2}\, r\, (2\Delta\alpha_{12} - \Delta\alpha_{13} - \Delta\alpha_{23} + 2\Delta\alpha_{15} \\ & - \Delta\alpha_{16} - \Delta\alpha_{26} + 2\Delta\alpha_{24} - \Delta\alpha_{34} - \Delta\alpha_{35} \\ & + 2\Delta\alpha_{45} - \Delta\alpha_{46} - \Delta\alpha_{56}) = 0 \end{aligned} \tag{7.9a}$$

and

$$8^{-1/2}\ r\ (\Delta\alpha_{23} - \Delta\alpha_{13} + \Delta\alpha_{26} - \Delta\alpha_{16} + \Delta\alpha_{35} - \Delta\alpha_{34} + \Delta\alpha_{56} - \Delta\alpha_{46}) = 0 \qquad (7.9b)$$

On taking the mean-square of (7.8) as well as ~~that of~~ (7.9a) or (7.9b), the following constraints are obtained

$$-\sigma_{\alpha\alpha}''' = \sigma_{\alpha} - 2\,\sigma_{\alpha\alpha} + 2\,\sigma_{\alpha\alpha}' - 2\,\sigma_{\alpha\alpha}'' \qquad (7.10)$$

and

$$-\sigma_{\alpha\alpha}''' = \sigma_{\alpha} + 4\,\sigma_{\alpha\alpha} + 2\,\sigma_{\alpha\alpha}' + 4\,\sigma_{\alpha\alpha}'' \qquad (7.11)$$

From these two equations we get the conditions

$$\sigma_{\alpha\alpha} = -\sigma_{\alpha\alpha}''$$

$$-\sigma_{\alpha\alpha}''' = \sigma_{\alpha} + 2\,\sigma_{\alpha\alpha}'$$

Using these two conditions in eq. (7.7)

$$3\,(F_{33}\,\Sigma_{33} + F_{55}\,\Sigma_{55} + F_{66}\,\Sigma_{66}) = 12\left[f_{\alpha}\sigma_{\alpha} + 4\,f_{\alpha\alpha}\,\sigma_{\alpha\alpha} + 4\,f_{\alpha\alpha}''\,\sigma_{\alpha\alpha}'' + 2\,f_{\alpha\alpha}'\,\sigma_{\alpha\alpha}' + f_{\alpha\alpha}'''\,\sigma_{\alpha\alpha}'''\right] = \langle 2\,V_{\alpha}\rangle$$

as is given by eq. (7.3). The criterion is to minimise the term $F_{55}\,\Sigma_{55}$ which belongs to the F_{1u} species. F_{ij} and Σ_{ij}

are parametrised and the value c_{min} of the parameter corresponding to the minimum of $F_{55}\,\Sigma_{55}$ is noted. Force constants are calculated using the value $c = c_{min}$. In Table 7.1 are entered the frequencies (harmonic, wherever available) and structural data of the molecules.

Results and discussion

Figs. (7.1)to (7.5) give the variation of the average bending energy term $F_{55}\,\Sigma_{55}$ with parameter c for the various XY_6 molecules of octahedral symmetry. In Table 7.2 the symmetry force constants of some 12 metal|hexafluoride molecules of the MF_6 type (M = S, Se, Te, Mo, Rh, W, Re, Os, Ir, Pt, U and Np) are reported against values taken from the literature. Entries carrying the label 'E' in Table 7.2 correspond to determinations using additional experimental data. Such reliable force fields are available only for UF_6, MoF_6 and WF_6 (5, 6). While there is excellent agreement between the diagonal force constants obtained by the present method and those based on exact methods, the values of the interaction force constant F_{45} differ slightly in the two approaches. These force fields reproduce the frequencies exactly while the corresponding coriolis constants deviate slightly from the experimental values. Thus for UF_6 the calculated zeta values are $\zeta_3 = 0.12$ and $\zeta_4 = 0.364$ while those of McDowell's' (6) are $\zeta_3 = 0.20 \pm 0.04$ and $\zeta_4 = 0.29 \pm 0.03$. The calculated values of ζ_3 and ζ_4 in the case of WF_6 are 0.43 and 0.156 respectively while Bosworth et.al.

(7) report the value $\zeta_4 = 0.12$. And the ζ_3 and ζ_4 values for Mo F_6 obtained are 0.22 and 0.256 respectively, while the experimental values are 0.21 and 0.288 (5).

The previous force fields in Table 7.2 for S F_6, Se F_6 and Te F_6 with which comparison is made first are those determined from the zeta constants of these molecules (2). The ζ_3 and ζ_4 values for S F_6 and Te F_6 are -0.33, 0.83 and 0.28, 0.18 respectively. For Se F_6, ζ_3 is given as 0.21.

Figs. (7.1) - (7.5). Relationship between average bending energy term $F_{55}\ \Sigma_{55}$ with parameter for various XY_6 type molecules of octahedral symmetry.

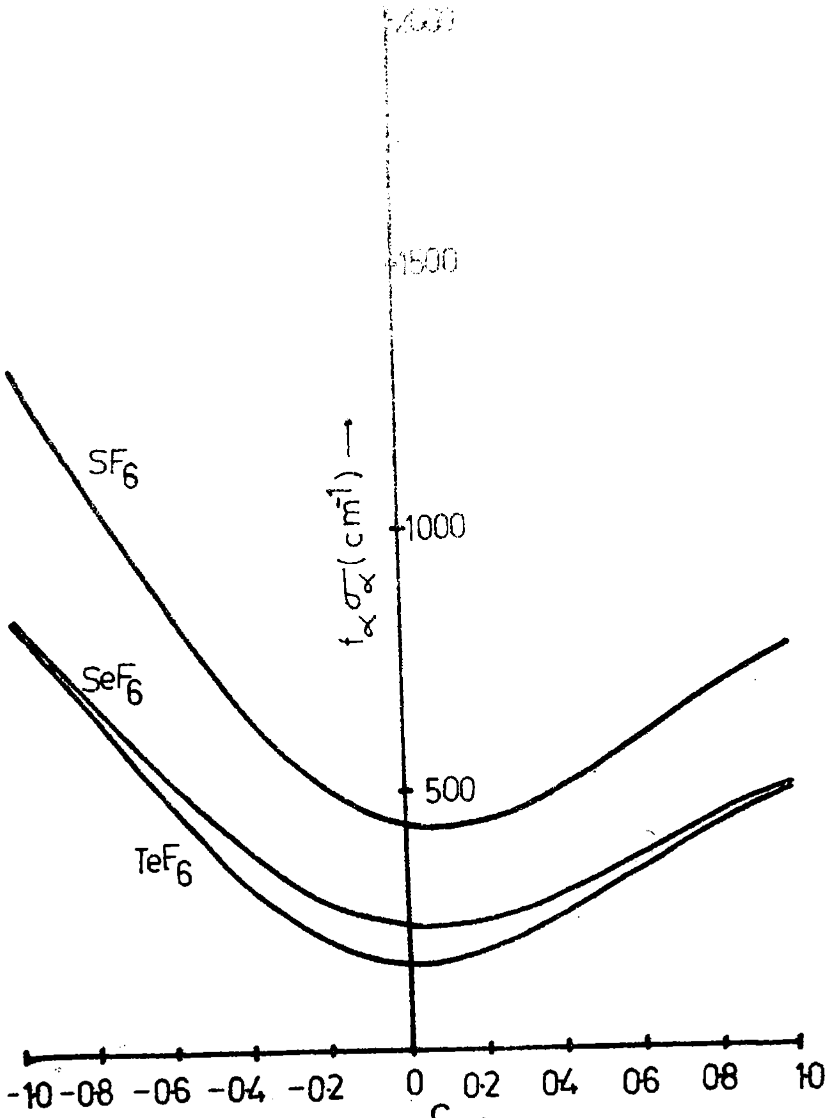

2000
1500
1000
500
$t_\gamma \sigma_\gamma (cm^{-1}) \rightarrow$
SF_6
SeF_6
TeF_6
-1·0
-0·8
-0·6
-0·4
-0·2
0
0·2
0·4
0·6
0·8
1·0
C →

Fig. 7.1.

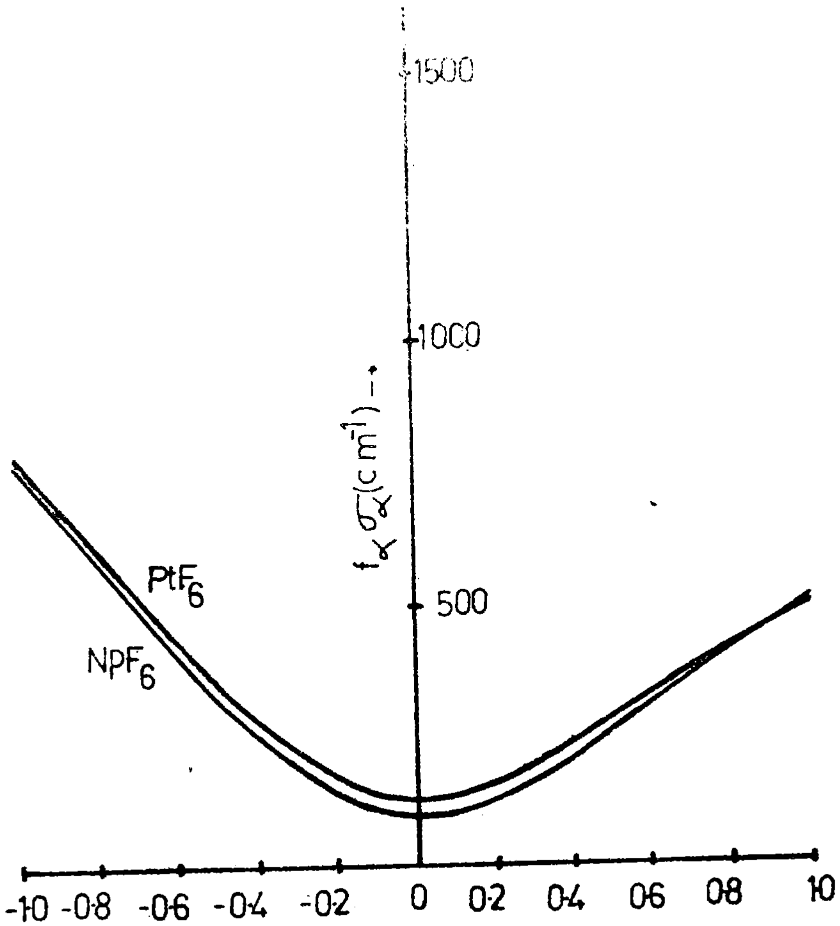
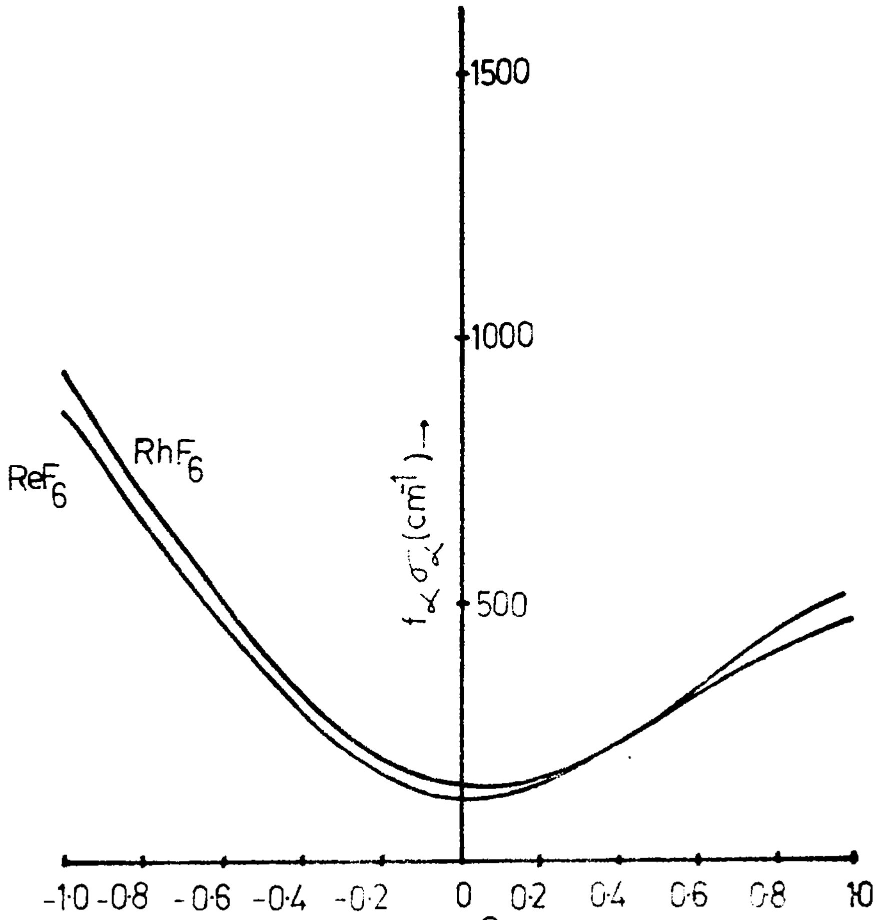
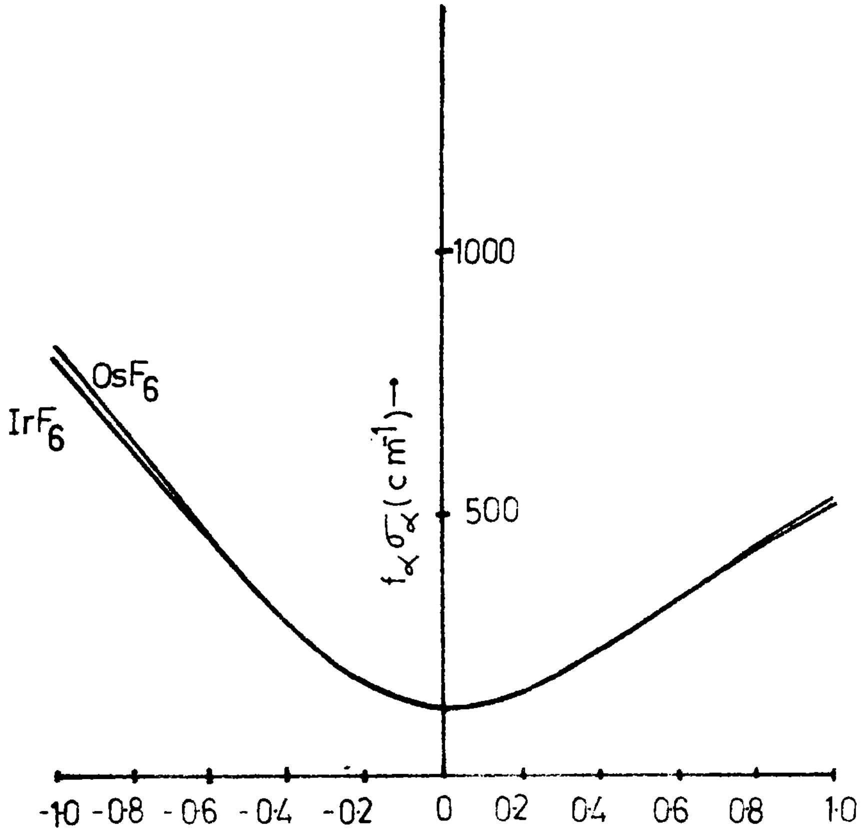

1500
1000
500
$t_\gamma \sigma_\gamma (cm^{-1}) \rightarrow$
PtF_6
NpF_6
-1·0
-0·8
-0·6
-0·4
-0·2
0
0·2
0·4
0·6
0·8
1·0
C →

Fig. 7.2.



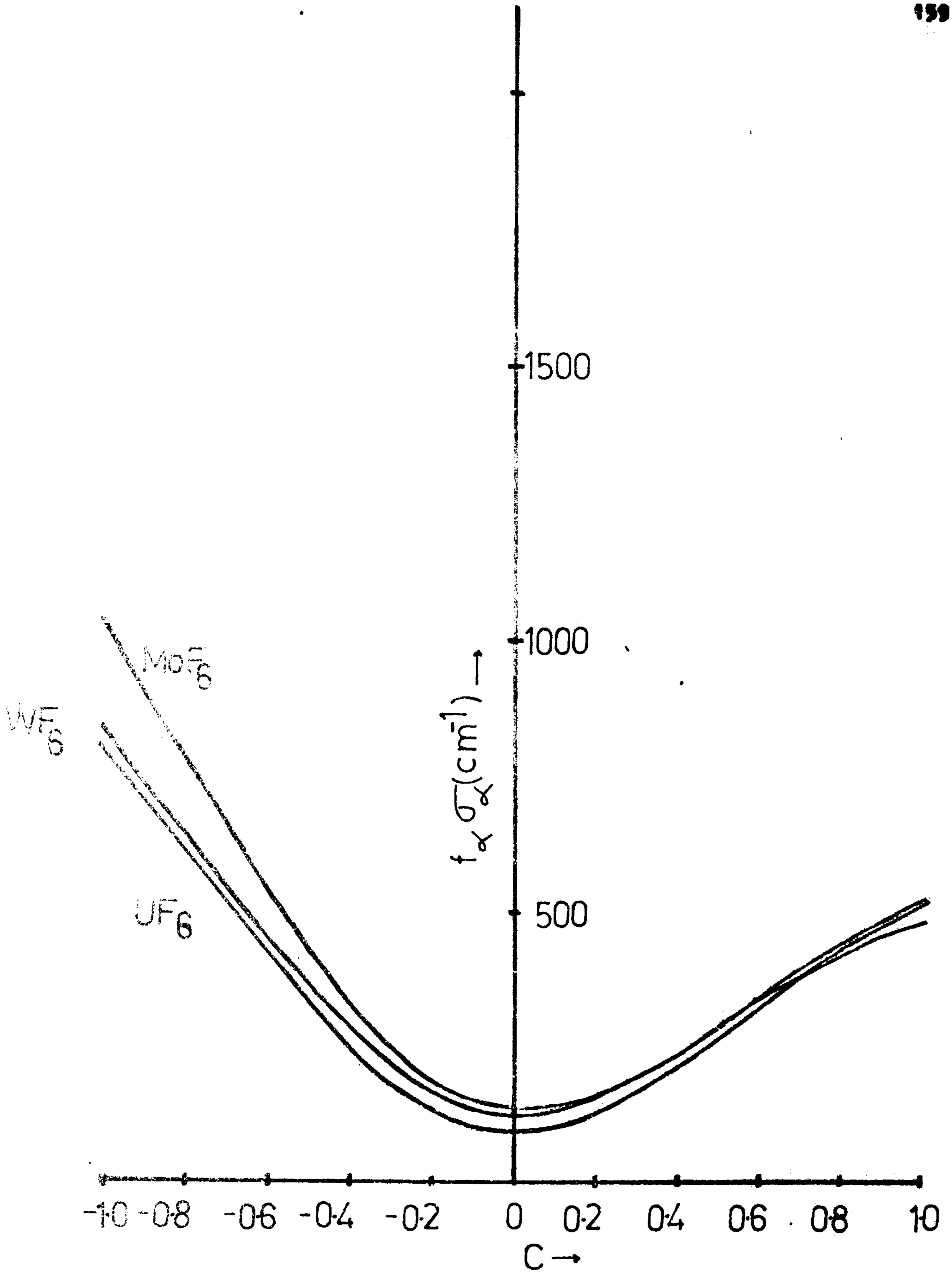
1500
1000
500
$f_\alpha \sigma_\alpha (cm^{-1})$ →
RhF$_6$
ReF$_6$
-1·0 -0·8 -0·6 -0·4 -0·2 0 0·2 0·4 0·6 0·8 1·0
C →

Fig·7·3·



1000
500
$f_\alpha \sigma_\alpha (cm^{-1})$ →
OsF$_6$
IrF$_6$
-1·0 -0·8 -0·6 -0·4 -0·2 0 0·2 0·4 0·6 0·8 1·0
C →

Fig·7·4


1500
1000
500
$f_\alpha \sigma_\alpha (cm^{-1}) \rightarrow$
MoF6
WF6
UF6
-1·0
-0·8
-0·6
-0·4
-0·2
0
0·2
0·4
0·6
0·8
1·0
C →

Fig·7·5·

Table 7.1

Frequencies and structural data of the XY_6 (O_h) molecules

Molecule*	G_{44}	G_{45}	G_{55}	T^{-1}_{44}	T^{-1}_{45}	T^{-1}_{55}	ω_1 (cm^{-1})	ω_2 (cm^{-1})
$S F_6$	0.1152	-0.1251	0.3555	2.9464	2.3176	2.1339	940.0	615.0
$Se F_6$	0.0777	-0.0501	0.2054	3.5884	1.5490	2.4054	780.0	437.0
$Te F_6$	0.0680	-0.0508	0.1669	3.8339	1.1574	2.5572	752.0	327.0
$Mo F_6$	0.0731	-0.0409	0.1870	3.6996	1.3802	2.4683	741.0	264.0
$Rh F_6$	0.0721	-0.0389	0.1330	3.7249	1.3398	2.4841	724.0	283.0
$W F_6$	0.0635	-0.0217	0.1488	3.9681	0.9108	2.6601	712.0	256.0
$Re F_6$	0.0633	-0.0214	0.1481	3.9756	0.9001	2.6647	715.0	257.0
$Os F_6$	0.0631	-0.0208	0.1469	3.9824	0.8830	2.6720	720.0	268.0
$Ir F_6$	0.0630	-0.0207	0.1467	3.9841	0.8797	2.6735	718.0	276.0
$Pt F_6$	0.0629	-0.0205	0.1465	3.9874	0.8730	2.6763	705.0	273.0
$U F_6$	0.0610	-0.0168	0.1389	4.0476	0.7513	2.7292	626.0	189.0
$Np F_6$	0.0611	-0.0169	0.1390	4.0465	0.7538	2.7281	624.0	200.0

* Frequencies are taken from Ref. (1)

Table 7.2

F_{55} Σ_{55} minimum force constant elements of the XY_6 molecules

(in md/Å)

Molecule	ε minimum	Force constants						Reference
		Present work			Previous result			
		F_{44}	F_{45}	F_{55}	F_{44}	F_{45}	F_{55}	
SF_6	0.09	5.345	0.947	1.026	4.75 ± 0.15	0.74 ± 0.05	1.10 ± 0.05	2
					5.14	0.78	1.02	3
SeF_6	0.06	4.713	0.295	0.655	4.88 ± 0.10	0.44 ± 0.05	0.64 ± 0.01	2
					4.91	0.33	0.66	3
TeF_6	0.03	4.307	0.108	0.414	4.98 ± 0.10	0.24 ± 0.05	0.40 ± 0.05	2
					5.07	0.22	0.41	3
MoF_6	0.05	4.416	0.063	0.252	4.38	0.06	0.251*	4*
					4.65	0.25	0.253	5
					5.132	0.414	0.262	1
WF_6	0.02	5.022	0.035	0.276	4.71	0.06	0.273*	4
					4.81	0.18	0.263	5
					5.55	0.43	0.29	1
ReF_6	0.02	4.748	0.038	0.277	4.78	0.06	0.238*	4
					3.595	0.655	0.169	1
UF_6	0.01	3.792	0.020	0.157	3.76	0.06	0.145*	4
					3.84 ± 0.08	−0.04 ± 0.05	0.154 ± 0.013	6
					3.74	−0.04	0.153	5
					3.77	0.498	0.114	1

(Contd ...)

Table 7.2 (contd.)

Molecule	e minimum	Force constants						Reference
		Present work			Previous result			
		F_{44}	F_{45}	F_{55}	F_{44}	F_{45}	F_{55}	
Np F_6	0.01	3.757	0.026	0.176	3.77 3.644	0.06 0.430	0.177* 0.119	4 1
Rh F_6	0.04	4.260	0.062	0.294	4.139	0.146	0.224	1
Os F_6	0.02	4.838	0.044	0.303	4.85	0.06*		4
Ir F_6	0.02	4.818	0.051	0.322	4.81	0.06	0.320*	4
Pt F_6	0.02	4.653	0.050	0.315	4.69 4.294	0.06 0.208	0.314* 0.164	4 1

* ($f_{d\alpha} - \rho$) is assumed to be 0.03 so that $F_{34} = 2 (f_{d\alpha} - \rho) = 0.06$ for all the molecules.

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CHAPTER VIII

AVERAGE BENDING ENERGY CRITERION: GENERAL DISCUSSION

The principal features of the results obtained using the average bending energy criterion for more than a hundred molecular species of the XY_n type are summarised. It is pointed out that this criterion is most effective in non-hydride molecules exhibiting the orbital following effect.

In chapter III the variation of the various terms in the average potential energy due to zero point vibrations has been plotted and their maxima and minima examined. From this analysis it emerged that for all the 23 molecules of the XY_2 type examined, there exists a valid 'c minimum' near zero for the bending energy term $f_\alpha \sigma_\alpha$ that would give a force field in good agreement with that fixed exactly with the help of additional data. While the force fields of nonhydride XY_2 (C_{2v}) type molecules are in complete agreement, the off-diagonal elements $f_{r\alpha}$ of hydride molecules deviate slightly from standard values, despite the fact that the diagonal elements are in perfect agreement. Even for the $f_{r\alpha}$ elements of hydrides, the standard values reported have enough range to accommodate the value calculated using the average bending energy criterion well inside the range.

However, an attempt has been made to see whether it is possible to fix the off-diagonal elements still more exactly in such cases. It is found that if the bending energy is "redefined" by adding 50% weighted stretch-bend interaction energy to $f_\alpha \sigma_\alpha$ i.e., $f_\alpha \sigma_\alpha + 2 f_{r\alpha} \sigma_{r\alpha}$, the minimum corresponding to the new bending energy gives excellent force fields (Table 8.1). The variation of the redefined bending energy in the case of XY_2 (C_{2v}) type hydrides is represented in Fig (8.1). A detailed investigation shows that neither the total average interaction energy $2 f_{rr}\sigma_{rr} + 4 f_{r\alpha}\sigma_{r\alpha}$ nor $f_{\alpha}\sigma_{\alpha} + 4 f_{r\alpha}\sigma_{r\alpha}$ possesses any physical significance.

In chapters IV - VII the average bending energy criterion has been successfully applied to XY_3 planar molecules of D_{3h} symmetry, tetrahedral XY_4 molecules of T_d symmetry, XY_3 pyramidal molecules of C_{3v} symmetry, and octahedral XY_6 molecules of O_h symmetry. In all these cases, the average bending energy criterion serves as a unique criterion for evaluating a force field in satisfactory agreement with that fixed using additional experimental inputs other than frequencies. This criterion stands distinct from and superior to various other approximations that have appeared in the literature. Given harmonic frequencies, the average bending energy hypothesis leads to excellent force fields. It is verified that the force fields obtained for isotopically substituted molecules are more or less the same and hence are in accord with the Born-Oppenheimer approximation (1). The lower the mixing of vibrations, the better is the agreement in respect of isotopic invariance. The force field parameter c turns out to be the same for isotopic substitutents except for hydrides.

This criterion differs from Müller's approximation (2-6) as can be easily verified by calculating the L matrix elements in any case. For example in the case of $N O_2$, the values obtained by the two methods are compared below

$$\begin{pmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{pmatrix} = \begin{pmatrix} 0.264 & 0.055 \\ -0.278 & 0.549 \end{pmatrix}$$

(Present method)

$$\begin{pmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{pmatrix} = \begin{pmatrix} 0.290 & 0 \\ -0.250 & 0.552 \end{pmatrix}$$

(Müller's approximation)

The average bending energy minimisation is an energy minimisation method and stands distinct from force field extremisation (7) and eigenvalue minimisation (Chapter II of the present thesis), yielding far more satisfactory results than either of them.

It is observed that the off-diagonal elements of the force constant matrix for hydride molecules of the XY_2 (C_{2v}), XY_3 (C_{3v}), XY_4 (T_d) types differ from the exact values, and in the case of XY_2 (C_{2v}) hydride molecules, best agreement could be brought about only by redefining the average bending energy. In the XY_4(T_d) and XY_3 (C_{3v}) cases such a redefinition does not work.

The essence of the average bending energy hypothesis is that the normal vibrations of XY_n type molecules occur in such a way that the average zero point potential energy contribution from the bending deformation is quite close to its minimum possible value. A plausible explanation for the effectiveness of this criterion may be attempted on the basis of the concept of rehybridisation developed by Linnet and Wheatley (8) in connection with their Orbital Valence Force Field Model. According to them, the condition for minimum potential energy is the maximum overlap between bond-forming orbitals of the atoms in the molecule. In a bending vibration, overlap between the bonding orbitals of the central atom and the terminal atoms can be increased either by rotation of the bond-forming orbitals of the central atom as a whole, or yet another possibility is by the orbital following effect. In the latter case, the orbitals of the central atom, by changing their hybridisation ratios might alter the angles they make with one another in such a way as to follow the movements of the outer atoms during a bending vibration. Such a possibility was pointed out by Penny (9). If the bond-forming orbitals of the central atom change their hybridisation, the new distribution of these orbitals must be of higher energy as this configuration is different from that of equilibrium (8, 9). The molecule can adjust its normal vibration so that the increase in energy associated with the rehybridisation is a minimum and hence the success of the average bending energy criterion. The most important conclusion is that bending vibrations will occur more easily in certain molecules if the bonding orbitals are able to follow the movement of the atoms by change of hybridisation. It is, however, possible to follow the atoms during certain vibrations but impossible for them to follow the atoms during other vibrations, because change of hybridisation in the required sense is not possible (8).

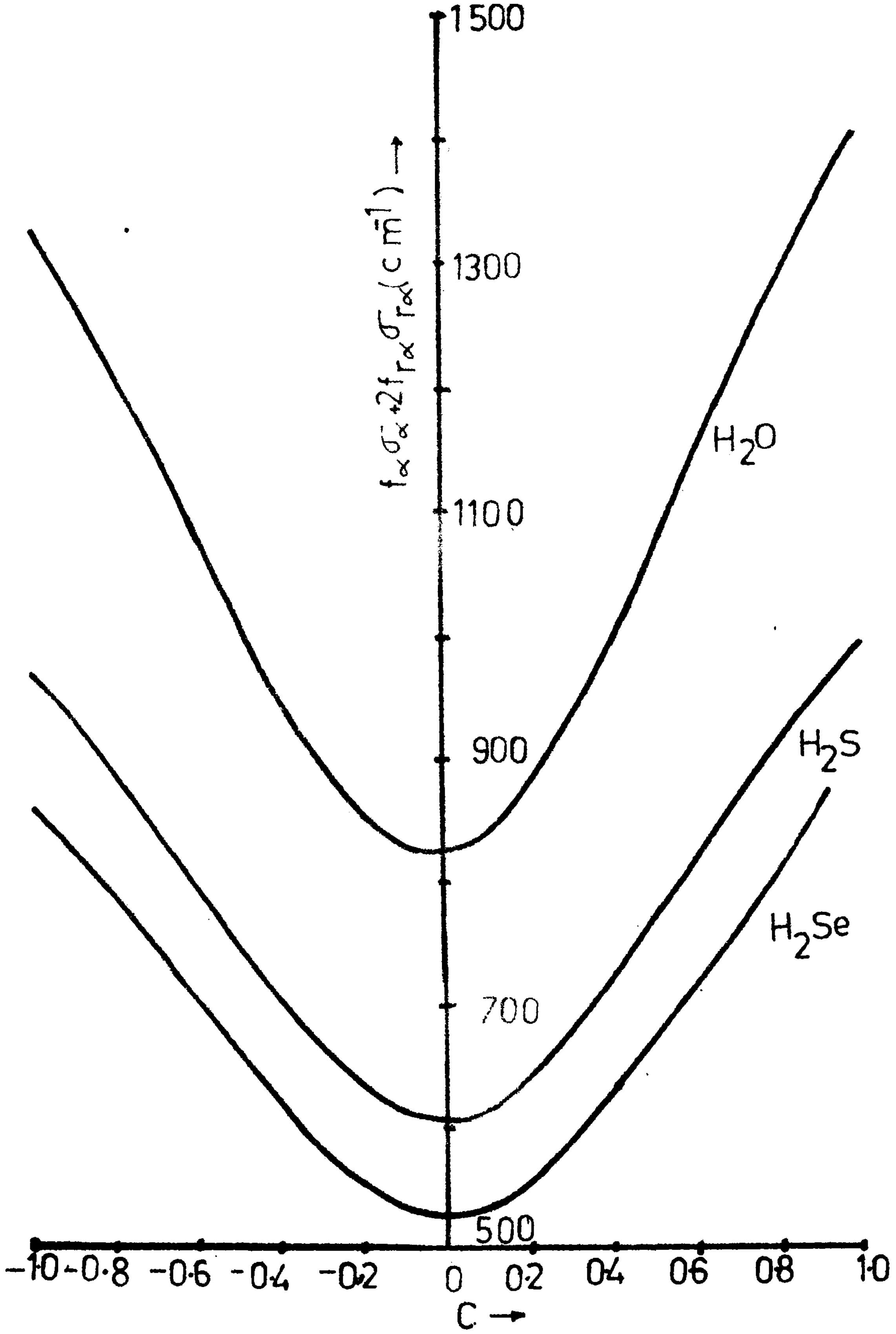
The orbital following effect during bending vibration exists in symmetrical XY_2 and XY_4 (T_d) molecules (8, 10). For these molecules excellent force fields are obtained by the average bending energy criterion. For XY_3 (D_{3h}) also the results are in complete agreement with the exact values, since, when there is a distortion of the molecule, the bond-forming orbitals of the X atom will rotate about X to give the greatest overlap with the bond-forming orbitals of the three other Y atoms (11). This will happen at all stages of the vibration and thus the contribution of the angular part of the potential energy is modified. In the case of XY_3 (C_{3v}) molecules, the force fields obtained for the E species vibrations are better than that for the A_1 species, as has been reported earlier (12, 13). This may be correlated with the assumption that rehybridisation and changes in spatial distribution of orbitals can render certain distortions easier by a partial accommodation of the orbitals to distortion (10). There is no orbital following in the F_{1u} species of the XY_6 (O_h) model molecules (14). Thus the calculated force constants, particularly the off-diagonal force constant elements are not sufficiently accurate. McDowell et.al (15, 16) fix the off-diagonal force constant F_{45} of UF_6 for the F_{1u} species to be -0.04, while the average bending energy criterion gives a value + 0.02. For XeF_6 and WF_6 the calculated values of F_{45} are 0.065 and 0.035 respectively, while the exact values are 0.25 and 0.18 (15). Hence it may be concluded that the average bending energy criterion holds extremely well in cases exhibiting the orbital following effect or the rotation of the bond-forming orbitals of the central atom as a whole.

Further, the observed lack of success of the bending energy criterion for hydrides may be attributed to low electronegativity of the terminal hydrogen atoms which reduces the effectiveness of the orbital following phenomenon.

The method is successful for XY_n type molecules, especially in the case of nonhydrides. On the whole, the agreement is satisfactory. For cases with more than one bending coordinate, the average bending energy may not be divisible for each coordinate and the degree of the vibrational species in which the bending modes appear would exceed two. This requires the introduction of more than one parameter for the representation of the force field, and the average bending energy would turn out to be a very complicated function.

In conclusion, it may be mentioned that while the variation method has been found to be successful for XY_2 (C_{2v}) type hydrides of low mass ratio, the average bending energy criterion yields very reliable force fields in the case of non hydrides belonging to various geometries of the XY_n type. The two methods thus seem to be complementary to each other.

Fig. (8.1). Plot of redefined average bending energy, $f_{\alpha}\sigma_{\alpha} + 2\, f_{r\alpha} \quad r\alpha$, for H_2O, H_2S and H_2Se in the range $-1 \leq e \leq +1$



1500
1300
1100
900
700
500
$f_\alpha \sigma_\alpha + 2 f_{r\alpha} \sigma_{r\alpha}$ (c m^{-1}) →
H_2O
H_2S
H_2Se
−1·0
−0·8
−0·6
−0·4
−0·2
0
0·2
0·4
0·6
0·8
1·0
C →

Fig·8·1·

Table 8.1

Force fields of bent symmetrical XY_2 type molecules determined by the $f_\alpha \sigma_\alpha$ + $2 f_{r\alpha} \sigma_{r\alpha}$ minimum condition (in md/Å)

Molecule	e value at minimum	f_r Present work	f_r Previous result	f_{rr} Present work	f_{rr} Previous result	f_α Present work	f_α Previous result	$f_{r\alpha}$ Present work	$f_{r\alpha}$ Previous result	Reference
H_2O	- 0.05	8.452	8.454±0.001 8.449±0.012	-0.105	-0.101±0.002 -0.107±0.012	0.753	0.759±0.002 0.769±0.018	0.144	0.251±0.018 0.200±0.199	17 18
D_2O	- 0.05	8.457	8.454±0.003 8.472±0.028	-0.098	-0.105±0.005 -0.085±0.055	0.763	0.760±0.004 0.764±0.010	0.249	0.235±0.034 0.192±0.177	17 18
T_2O	-0.08	8.488		-0.068		0.777		0.382		
H_2S	- 0.02	4.285	4.280±0.003	-0.011	-0.017±0.007	0.425	0.435±0.006	0.047	0.148±0.038	17
D_2S	- 0.03	4.275	4.280±0.003	-0.021	-0.017±0.006	0.428	0.434±0.006	0.076	0.144±0.038	17
T_2S	- 0.04	4.306		0.010		0.430		0.106		
H_2Se	- 0.01	3.509	3.509±0.005	-0.021	-0.022±0.001	0.328	0.331±0.001	0.018	0.023±0.022	17
D_2Se	- 0.01	3.542	3.544±0.001	-0.060	-0.058±0.002	0.328	0.331±0.001	0.022	0.054±0.022	17
T_2Se	- 0.02	3.505		-0.024		0.329		0.040		

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