STUDIES IN MOLECULAR SPECTROSCOPY

(I) Approximation Methods in Molecular Internal Mechanics
(II) Infrared Spectral Studies of Ternary Liquid Systems and Polymer Thin Film.

By

ANNIE JOSEPH VALLAMATTOM M. Sc.

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of the requirements for the degree
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University of Cochin
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DECLARATION

Certified that the work presented in this thesis is based on the original work done by me under the guidance of Dr.M.G. Krishna Pillai, in the Department of Physics, Cochin University, and has not been included in any other thesis submitted previously for the award of any degree.

Annie Joseph V.

Cochin - 22
25 November 1978

Annie Joseph Vallamattam.

CERTIFICATE

Certified that the work reported in the present thesis is based on the bonafide work done by Smt. Annie Joseph Vallamattam, research scholar, under my guidance in the Department of Physics, Cochin University, and has not been included in any other thesis submitted previously for the award of any degree.

M. G. Krishna Pillai

Cochin - 22
25, November 1978

M.G. Krishna Pillai
Supervising Teacher.

CONTENTS

PREFACE AND ACKNOWLEDGEMENTS

The investigations presented in this thesis were carried out by the author as a full-time research scholar in the Physics Department of the Cochin University during 1975-78.

This thesis is divided into two parts. The first part deals with some studies in molecular mechanics using spectroscopic data and has four chapters in it. Certain approximation methods for the evaluation of molecular force fields are herein developed. The second part, which consists of the last two chapters, deals with infrared spectral studies of ternany liquid systems and a polymer film prepared by glow discharge method.

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

Chapter II, III and IV present parameter representation of harmonic force fields of some XY_3,

XY_2 and XY_4 and XY_3Z type molecules. In Chapter II a graphical method making use of isotopic frequencies is presented. Since it is often not possible to have a unique solution of the force field even with the help of three sets of isotopic frequencies, a new criterion called the "method of equal co-ordinates" is developed to fix the exact force field, in the case of multiple solutions. Using this criterion in the parameter formulation harmonic force fields of ammonia, phosphine and arsine are evaluated. In Chapter III the relationship between the parameter and mass ratio of several molecules is studied. With the help of this, the force fields, mean amplitudes of vibration and coriolis constants of several bent XY_2 and tetrahedral XY_4 type molecules are obtained. Chapter IV presents a new approximation scheme termed "Hybrid High Low Frequency Separation Method" for a third order vibrational problem. This method has been applied successfully to several molecules belonging to the XY_3Z type model.

The last two chapters report some experimental work. In Chapter V an easy method for the evaluation of association constants for a few ternary liquid systems is developed with the help of ir spectral studies. The fabrication of the experimental set up for the preparation of glow discharge polymers is described in the last chapter. A glow discharge polymer film of p-toluidine is prepared and the ir spectrum of the film is studied vis-a-vis that of the monomer film. The characteristic lines of the polymer are identified and the probable polymerisation mechanism is explained.

The original contributions contained in the present work are the following:

1. A new criterion called the "method of equal co-ordinates" for fixing the exact force field in the case of multiple solutions is identified.

2. A linear relation connecting the parameter and mass ratio is developed which can be made use of for the evaluation of force fields, mean amplitudes of vibration and other molecular constants.

3. An approximation method termed "the Hybrid High Low Frequency Separation Method" is developed and applied to some third order problems and all the twelve force constants are evaluated.

4. An easy and elegant method is presented for the determination of the association constant for ternary liquid systems and the 'K' values for a few cresol-ketone systems are evaluated.

5. A glow discharge polymerization unit and a special ir cell are fabricated and the polymer film prepared is identified with the help of ir spectral studies.

Part of these investigations carried out by the author has been published in the following papers.

1. Parameter Representation of Harmonic Force Field. Method of Equal Co-ordinates Ind. J. of Pure & Appl. Phys. 15 49 (1977).

2. Relation Between Force Field, Parameter and Mass Ratio, Curr. Sci. 45 827 (1976).

3. Hybrid High Low Frequency Separation (HLFS) method: Harmonic Force Fields of Methyl Halides, Czech. J. of Phys. (In Press).

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CHAPTER I

INTRODUCTION

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

1. Introduction

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

A molecule may be regarded as a group of atoms bound together by certain forces. Acting between the atoms, these forces tend to keep the molecule in equilibrium. Small oscillations of atoms about their equilibrium positions in the molecule cause the appearance of the so called vibrational infrared and Raman spectra.

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

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

In diatomic molecules, the vibration of the nuclei occurs only along the line connecting two nuclei. In polyatomic molecules however the situation is much more complicated because all the nuclei perform their own harmonic oscillations. It can be shown that any of these extremely complicated vibrations of the molecule may be represented as a superposition of a number of normal vibrations corresponding to the harmonic frequencies.

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

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

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

$$T = 1/2 \sum_{i}^{3N} \dot{q}_i^2 \qquad (1.2)$$

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

$$q_k = \sum_{i} B_{ki} \; Q_i \qquad (1.3)$$

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

$$T = 1/2 \sum_{i} \dot{Q}_i^2 \qquad (1.4)$$

$$V = 1/2 \sum_{i} \lambda_i \; Q_i^2 \qquad (1.5)$$

without any cross products.

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

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

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

$$\begin{vmatrix} b_{11}-\lambda & b_{12} & b_{13} & - & - \\ b_{21} & b_{22}-\lambda & b_{23} & - & - \\ b_{31} & b_{32} & b_{33}-\lambda & - & - \\ - & - & - & - & - \\ - & - & - & - & - \end{vmatrix} = 0 \qquad (1.7)$$

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

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

On solving the secular equation we get in general 3N-6 nonzero real roots, (3N-5 for linear molecules), equal in number to the vibrational degrees of freedom. The zero roots of the secular equation represent the translational and rotational modes of the molecule. In practice using experimentally observed fundamental vibrational frequencies, the secular equation is solved for the force constants and normal modes. The programme of evaluating force constants and normal co-ordinates of a molecule is known as normal co-ordinate analysis.

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

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

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

where f is the force constant matrix. The internal co-ordinates r are transfered into an orthogonal set of symmetry co-ordinates which are linear combinations of the internal co-ordinates and are constructed in such a way that they transform according to the character of the vibrational type of the point group to which they belong. The symmetry co-ordinates are defined by the transformation

$$S = Ur \qquad (1.10)$$

where U is an orthogonal matrix.

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

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

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

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

The corresponding expression for the kinetic energy of the molecule is

$$2T = \tilde{\dot{r}} \, g^{-1} \, \dot{r} \qquad (1.13)$$

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

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

The kinetic energy matrix G^{-1} is determined by the atomic masses and molecular geometry. The method for calculating elements of the G matrix is reported in the literature (7-11). The G_{ij} elements for a non-degenerate species are given by

$$G_{ij} = \sum_{p} \mu_p \; g_p \; \vec{S}_i^{\,t} \cdot \vec{S}_j^{\,t} \qquad (1.15)$$

and for a degenerate species

$$G_{ij} = \frac{1}{d} \sum_{p} \mu_{P} \; g_p \left(\vec{S}_{ia}^{\,t} \cdot \vec{S}_{ja}^{\,t} + \vec{S}_{ib}^{\,t} \cdot \vec{S}_{j}^{\,t} + \ldots \right) \qquad (1.16)$$

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

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

$$\vec{S}_i^{\,t} = \sum_{k} U_{ik} \; \vec{s}_{kt} \qquad (1.17)$$

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

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

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

or

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

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

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

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

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

3. Approximate Force Fields

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

According to the VFF postulated by Bjerrum (12) the restoring forces oppose the changes in valence coordinates like bond lengths and interbond angles. Here also the number of force constants is less than that of the vibrational frequencies. However the interactions between stretching and bending of different bonds in the molecule are not considered. A combination of central and valence type force fields has been postulated by Mecke (14) for XY_2 type molecules. Taking into account Pauling's idea that the stability of a molecule is due to the overlap of the orbitals of the bonded atoms, Wilson and Howard formulated a modified valence force field (MVFF) for XY_3 type molecules (15). In the OVFF introduced by Linnett and Heath (16-18) the electron density in each bond is represented by localized molecular orbitals. In this theory no interactions between bond-stretching and bond-bending co-ordinates are included. But the properties of bonds in a molecule are well related to the inter-bond angles (19, 20). The hybrid bond force field (HBFF), a modification of OVFF based on the correlation of bond strength with bond angle, is successfully applied to ammonia molecule (21).

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

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

4. Approximation Procedures in a GVFF Framework

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

4.1 Parameter Method

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

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

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

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

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

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

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

where Λ is a diagonal matrix of elements $\lambda_i = 4\pi^2 c^2 \omega_i^2$

The force constant matrix F is given by

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

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

$$L = L_o A \qquad (1.25)$$

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

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

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

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

Here V and Γ are respectively the eigen-vector and the eigen-value matrices of G. T is a triangular matrix which can be written in two alternative forms, viz. $T_{ij} = 0$ with $i < j$ or with $i > j$. The former one is preferable if the normal co-ordinates are nearly pure and if the ordering of frequencies is such that $\lambda_1 > \lambda_2 > \cdot \cdot \cdot \cdot \cdot \lambda_n$ (32, 33).

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

(a) Angle parameters

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

Here A_{ij} is an elementary rotation matrix in the ij plane, the iith and jjth elements are cos ϕ_{ij}, the ijth element is - sin ϕ_{ij} and the jith element is sin ϕ_{ij}. All other diagonal elements are unity and the off-diagonal elements are zero.

(b) Antisymmetric parameter matrix

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

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

$$K = 1/2 \begin{bmatrix} 0 & \alpha_{12} & \alpha_{13} & \cdots & \alpha_{1n} \\ -\alpha_{12} & 0 & \alpha_{23} & \cdots & \alpha_{2n} \\ -\alpha_{13} & -\alpha_{23} & 0 & \cdots & \alpha_{3n} \\ -\alpha_{1n} & -\alpha_{2n} & - & \cdots & 0 \end{bmatrix} \qquad (1.30)$$

(c) Exponetial parameter matrix

$$A = e^{K} \qquad (1.31)$$

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

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

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

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

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

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

Equation (1.32) is of basic importance and furnishes a systematic approach to the study of the complete set of mathematically possible solutions. This equation enables one to express the $1/2\, n\,(n+1)$ elements of F_{ij} as a function of $1/2\, n\,(n-1)$ parameters in a vibrational problem of order n. The second order problem is particularly interesting in this respect, since there is only one variable parameter, and one can always look for the variation of the F_{ij} elements with this single parameter. Expressions for the elements F_{11}, F_{12} and F_{22} have been given as a function of a single parameter in such second order cases (47-49). Graphs showing the variation of the force constant elements with respect to an angle parameter have been drawn by Pfeiffer (35) and Strey (47). Similar graphs are presented for some pyramidal XY_3 type molecules in Chapter II.

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

4.2 Iterative Methods

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

$$G_o = \Lambda \exp G_o^{-1} \qquad (1.33)$$

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

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

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

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

$$G_k F_{k-1} L_k = L_k \Lambda_k \qquad (1.34)$$

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

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

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

$$\left[G_K F_{k-1},\ G_k \Delta F_K\right] = 0 \qquad (1.35)$$

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

4.3 Non-iterative Methods

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

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

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

$$F = V \Gamma^{1/2} X \Lambda \tilde{X} \Gamma^{-1/2} \tilde{V}' \qquad (1.37)$$

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

$$\mathrm{tr}\, F^{s} = \sum_{i} \Gamma_i^{-1} \lambda_i^{s} \qquad (1.38)$$

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

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

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

$$\sum_{i=1}^{n} \left|Q_i - S_i\right|_{\min} = n + \mathrm{tr}\, G - 2 \left[\mathrm{tr}\, L\right]_{\max} \tag{1.39}$$

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

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

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

Müller et.al. (66-70) developed the L matrix approximation method, imposing the condition $\alpha_{ij} = 0, \ i < j$. The method is equivalent to Torkington's (71-72) approximation

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

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

According to the approximation method formulated by Reddington and Aljibury (77), the constraints are made directly on the restoring forces acting on a molecule in any displaced position and not on the force constant matrix. The basic assumption of this method rests on considerations of minimum potential energy. The parametrized restroing force F_k is assumed to be parallel to the corresponding internal co-ordinate. It is also assumed that the restoring force exerted by the molecule for each internal co-ordinate is as large as possible. The condition to maximise the restoring forces for all displacements simultaneously is achieved through the virial theorem. The method is found to be suitable for obtaining reliable sets of force constants for species with no redundant symmetry coordinates.

4.4 Pseudo-Exact Methods

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

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

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

5. Exact Determination of Force Constants Using Additional Data

The inadequqcy of the frequency data alone in solving the secular determinant for $\frac{1}{2}$ n (n+1) force constants using 'n' frequencies for a symmetry species constitutes the main problem of normal co-ordinate analysis. In such cases additional experimental data like isotopic frequencies, coriolis coupling constants, mean amplitudes of vibration and centrifugal distortion constants are very useful. The normal co-ordinate transformation matrix L plays an important role in the theory of these constants.

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

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

Here * denotes the case after isotopic substitution.

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

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

The graphical method of locating interactions cannot be extended to higher orders since even in the n = 3 case, one would require a six dimensional parameter space. Török (87) has suggested a simple method for mapping the F matrix by changing the values of ½ (n - 1) (n-2) parameters in some systematic fashion.

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

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

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

$$\zeta = \tilde{A} (L_0)^{-1} C^{\alpha} (\tilde{L}_0)^{-1} A \qquad (1.43)$$

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

$$\zeta^{\alpha} = \tilde{A} \; J \; A \qquad (1.44)$$

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

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

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

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

(1.45)

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

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

Expressions for the mean amplitude of vibration ℓ (X–Y) and ℓ (Y. . . Y) in terms of the elements of the symmetrised mean square amplitude matrix Σ have been tabulated by Cyvin (90) for some molecules. The Σ matrix is related to L matrix and the vibrational frequencies ω_i as (90)

$$L \Delta \tilde{L} = \Sigma \qquad (1.46)$$

where Δ is a diagonal matrix of elements

$$\Delta_i = \frac{h}{8\pi^2 \omega_i} \coth \frac{h\,\omega_i}{2kT} \qquad (1.47)$$

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

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

$$t_{\alpha\beta\gamma\delta} = -2I^{e}_{\alpha\alpha}\; I^{e}_{\beta\beta}\; I^{e}_{\gamma\gamma}\; I^{2}_{\delta\delta}\; \tau_{\alpha\beta\gamma\delta} \qquad (1.48)$$

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

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

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

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

The matrix B is given by

$$B = (L_o)^{-1} T_s \qquad (1.51)$$

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

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CHAPTER II

PARAMETER REPRESENTATION OF HARMONIC FORCE FIELDS OF PYRAMIDAL XY_3 TYPE MOLECULES: METHOD OF EQUAL COORDINATES

The method of determination of force constants using isotopic frequencies in the parameter formalism is applied to ammonia, phosphine and arsine each having three isotopic species. To tackle the problem of multiplicity of intersections in parameter space a criterion called the "principle of equal co-ordinates" is introduced. With the help of this principle the force fields of ammonia phosphine and arsine, have been obtained which are in good agreement with previously reported values.

1. Introduction

In the general valence force field representation, the F matrix associated with a vibrational species of order 'n' contains $1/2$ n (n + 1) elements and their evaluation using the 'n' vibrational frequencies is mathematically impossible. Isotopic frequencies provide convenient additional data, since the changes in the potential energy function and in the geometry of the molecule due to isotopic substitution are assumed to be negligible. Thus the assumption that the force constants are invariant under isotopic substitution is very often employed for an unambiguous solution of the molecular force field. Although Duncan and Mills (1) found that isotopic frequencies are ineffective constraints on force constants, this conclusion was disputed by Chalmer and McKean (2) who showed the usefulness of isotopic shifts in force constant refinements. The applicability of isotopic frequencies in evaluating F elements through force constant displays has been demonstrated by Nibler and Pimentel (3). Török and Pulay (4) have summarised the advantages of the parameter representations in fixing force constants using additional data such as isotopic frequencies, mean amplitudes of vibration and rotation distortion constants. In this Chapter the parameter formalism is used in conjunction with isotopic frequencies (5) for fixing the force fields of pyramidal

XY_3 type molecules. The parameters for the molecule and its isotopic substituent are plotted in a two dimensional parameter space and in the case of multiple intersection the correct one is selected by a self-evident method, termed the principle of equal co-ordinates.

2. The Parameter Representation for n = 2 case

Elements of the force constant matrix are given by the relation

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

where L is the transformation matrix connecting the internal coordinates S and normal coordinates Q. Λ is the diagonal matrix having elements $\lambda_i = 4 \pi c^2 \omega_i^2$ corresponding to the harmonic frequencies ω_i.

A mathematically acceptable L matrix may be written as (combining eq. (1.25) and (1.27))

$$L = TA \qquad (2.1)$$

where A is any orthogonal matrix and

$$T \tilde{T} = G \qquad (2.2)$$

T matrix is taken in the triangular form, with the elements $T_{ij} = 0, \; i < j$. The A matrix for a species of order n can be written using $1/2 \; n \; (n - 1)$ independent parameters c_{ij}.

Thus

$$A = \prod A_{ij} \quad i, j = 1, 2 \ldots n, \quad i < j \tag{2.3}$$

where A_{ij} is a unit matrix except for terms

$$A_{ii} = \frac{1}{\sqrt{1+c^2_{ij}}} = A_{jj} \tag{2.4}$$

$$A_{ij} = \frac{c_{ij}}{\sqrt{1 + c^2_{ij}}} = -A_{ji} \tag{2.5}$$

Thus for $n = 2$, putting $c_{12} = c$

$$A = \begin{bmatrix} \dfrac{1}{\sqrt{1 + c^2}} & \dfrac{c}{\sqrt{1 + c^2}} \\ \dfrac{-c}{\sqrt{1 + c^2}} & \dfrac{1}{\sqrt{1 + c^2}} \end{bmatrix} \tag{2.6}$$

Substituting eqs. (2.6) and (2.1) in eq. (1.24) the F elements can be expressed as functions of the parameter c:

$$F_{11} = (T_{11}{}^{-1})^2 (\lambda_1 + \lambda_2 c^2) + (T_{21}{}^{-1})^2 (\lambda_1 c^2 + \lambda_2)$$

$$\frac{+\ 2\ T_{11}{}^{-1}\ T_{21}{}^{-1}\ (\lambda_2 - \lambda_1)\ c}{1 + c^2} \tag{2.7}$$

$$F_{12} = \frac{T_{11}^{-1}\, T_{22}^{-1}\, (\lambda_2 - \lambda_1)\, c + T_{21}^{-1} T_{22}^{-1} (\lambda_1 c^2 + \lambda_2)}{1 + c^2} \tag{2.8}$$

$$F_{22} = \frac{(T_{22}^{-1})^2\, (\lambda_1\, c^2 + \lambda_2)}{1 + c^2} \tag{2.9}$$

Similar expressions can be written for the isotopic substituent also, but by designating the F_{ij}, λ_k, $T_{ij}{-1}$ and c elements with asterisks as F^*_{ij}, λ^*_k $T^*_{ij}{}^{-1}$ and c* respectively.

For the potential function and the force constants to remain invariant under isotopic substitution the conditions are $F_{11} = F_{11}^*$, $F_{12} = F_{12}^*$ and $F_{22} = F_{22}^*$. These conditions lead to three equations involving two parameters c and c*. Though a solution of these three equations should lead to the evaluation of the two parameters, actual calculations indicate that a single pair of c and c* satisfying all the three equations exactly does not exist for most molecules. Inconsistencies of this sort are quite possible in view of inaccuracies in experimental data. However, parameter studies do not allow even slightest errors in frequencies and other data.

Considering the possible errors in the experimental data, the best possible values of c and c* can be obtained by a graphical method. For different values of c the values of c* are calculated and c - c* curves plotted for each one of eqs. (2.7), (2.8) and (2.9). The equations yield two solutions for c* corresponding to each value of c due to their quadratic nature. In the ideal case, a unique point must exist in the parameter space corresponding to the actual force field of the molecule and the c-c* values of this point must naturally satisfy the eqs. (2.7), (2.8) and (2.9). However because of the quadratic nature of the equations the curves representing the equations intersect at two points, one near the origin (c_A, c^*_A) and the other away from the origin (c_V, c^*_V) yielding two sets of force fields. Since only one force field is physically acceptable for a molecule, the exact force field can be chosen by considering some other experimental data or by invoking some criterion.

3. Equal Coordinates Criterion

In the present work three isotopic species are considered rather than two and an improvement is made over the original approach (5) and is applied to some pyramidal XY_3 type molecules. Parameter curves are plotted in separate two dimensional spaces, taking a pair at a time. With the increase in the number of the isotopic species, a large number of intersections have been obtained. To select the correct point from a multiplicity of inter sections near the origin, a principle called the method of equal coordinates has been applied. This principle may be stated as follows. If A, B, C are isotopic species of the same molecule, the intersections of parameter curves for the pairs A-B and B-C should be such that B is represented by equal co-ordinates in the parameter spaces $c_A - c_B$ and $c_B - c_C$. The acceptable intersections are those for which the common isotope is represeanted by equal co-ordinates in the two parameter spaces.

4. Pyramidal XY_3 Type Molecules

In the present investigation the above technique has been applied to the evaluation of the force fields of ammonia, phosphine and arsine. These molecules belong to the pyramidal XY_3 type having C_{3v} point group symmetry and possess the geometry illustrated in the Fig.(2.1). There are two species of normal vibrations which are classified into $2a_1 + 2e$. The following symmetry co-ordinates (6) are used in the analysis of the vibrations.

a_1 species:

$$s_1 = \frac{1}{\sqrt{3}} (\Delta r_1 + \Delta r_2 + \Delta r_3)$$

$$s_2 = \frac{r}{\sqrt{3}} (\Delta\alpha_{12} + \Delta\alpha_{23} + \Delta\alpha_{13}) \qquad (2.10)$$

e species:

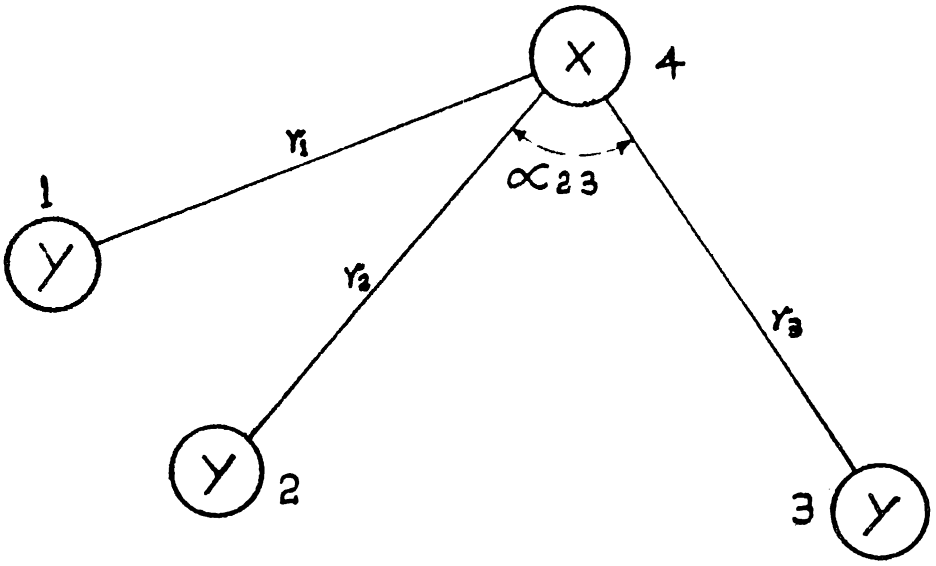

FIG. 2.1

PYRAMIDAL XY_3 MOLECULAR MODEL
INTERNAL CO-ORDINATES

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

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

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

$$S_{4b} = \frac{r}{\sqrt{2}} (\Delta \alpha_{13} - \Delta \alpha_{12}) \qquad (2.11)$$

where r represents the equilibrium distance X-Y. Δr_1, Δr_2 and Δr_3 are changes in bond lengths and $\Delta\alpha_{12}$, $\Delta\alpha_{23}$ and $\Delta\alpha_{13}$ are changes in bond angles.

The G matrix elements corresponding to this symmetry co-ordinates are given below.

a_1 species:

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

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

$$G_{22} = 2 \left(\frac{1+2\cos\alpha}{1+\cos\alpha} \right) \left[\mu_y + 2\mu_x (1 - \cos\alpha) \right] \qquad (2.12)$$

e species:

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

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

$$G_{44} = \frac{1}{(1 + \cos\alpha)} (2 + \cos\alpha) \left[\mu_y + (1 - \cos\alpha)^2 \mu_x \right] \qquad (2.13)$$

The F matrix elements are listed as follows:

a_1 species

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

$$F_{12} = 2 f_r + f'_{r\alpha} \qquad (2.14)$$

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

e species

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

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

$$F_{44} = f_\alpha - f_{\alpha\alpha} \qquad (2.15)$$

$f_{r\alpha}$ denotes the interaction between Δr and $\Delta\alpha$ having a common bond and $f'_{r\alpha}$ is the interaction between Δr and $\Delta\alpha$ having no common bond.

The structural parameters and vibrational frequencies of all the three molecules and their deuterated substituents have been taken from reference (7, 8) while the harmonic frequencies for the tritium substituents are estimated using the anharmonicity factors reported by McKean and Schatz (9). All the calculations were done on a digital computer using a suitable programme.

For all isotopic pairs a wide range in parameter space ($-10 \leq c \leq 10$) has been scanned for intersections of parameter curves. The value of the parameter c is systematically varied, from -10 to -1 at steps of 0.5, from -1 to $+1$ at steps of 0.01 and from $+1$ to $+10$ at steps of 0.5. Figures 2.2 to 2.37 show the parameter curves obtained for these molecules and their isotopic substituents. These graphs are drawn in such a manner that for a pair of isotopic species A and B, the parameter c for A is plotted along the x-axis and that for B along y-axis. Coordinates corresponding to the interesections of c-c* curves are sought. The region near the origin has been plotted separately using a magnified scale to enable clear and exact identification of the intersections. Graphs for the full range of c as well as for the magnified region near the origin are shown side by side for each pair of isotopic species, for the a_1 and e species. Details regarding the intersections of the parameter curves are presented in Table 2.1. For each intersection, the parameter values are given and the corresponding intersecting curves are identified.

5. Results and Discussions

5.1 Ammonia - For the a_1 species of ammonia taking the NH_3 - ND_3 pair, (Fig. 2.3) two very close intersections have been obtained for two pairs of roots (F_{11}, F_{22} and F_{11},

F_{12}). The arithmetic mean of the corresponding force constants compares well with previously reported values (10). However, since the various intersections for the species are not in accord with the equal coordinates criterion, the force constants reported herein cannot be taken as the final set. Another curious feature is that there is no intersection for the ND_3 - NT_3 (Fig.2.7) pair near the origin while the only intersection obtained for the range that has been scanned gives an inverse assignment of frequencies (Fig. 2.6).

The parameter curves for the e-species of NH_3 and ND_3 pair intersect at four points near the origin and form three islands (Fig.2.9). A similar multiplicity of intersections without island formation is noticed for NH_3-NT_3 (Fig. 2.11) and consequently, we cannot fix the e-species force field by considerations based on island formation. For NH_3 - ND_3 and NH_3 - NT_3 (Figs. 2.9 and 2.11) the intersections near the origin are (-0.01, - 0.026) and (-0.016, -0.05) respectively so that the equal co-ordinates criterion may be applied to NH_3. However, if we take NT_3 as a common isotopic species in the NH_3 - NT_3 and ND_3 - NT_3 pairs (Figs. 2.11 and 2.13) the values of the parameter for NT_3 are (-0.026 and -0.04) which are far apart and not acceptable according to the equal co-ordinates principle. It is also noted that the F_{34} values calculated from these intersections carry opposite signs (Table 2.2). For these reasons the intersections for the ND_3-NT_3 pair are rejected in favour of the intersections obtained for the other two pairs. The average set of force constants obtained from these intersections is taken as the true set and is in agreement with earlier values (8). The breakdown of the equal-co-ordinates principle for the a_1 species, makes one feel that while the structural data are correct the a_1 species frequencies are probably in error.

Phosphine - A unique intersection of all the parameter curves for the a_1 species of PH_3 - PD_3 and PD_3 - PT_3 exists near the orign (Figs. 2.15 and 2.19). But the PH_3 - PD_3 intersection alone gives a satisfactory force field (10). Likewise, for PH_3- PT_3 intersection, (Fig.2.17) only two of the parameter curves intersect in pairs near the origin and fails to produce a reasonable force field.

For the e species, one notices unique intersections for PH_3 - PD_3 and PD_3 - PT_3 (Figs. 2.21 & 2.25) but only the former yields a force field in agreement with previous values (10). The PH_3 - PT_3 intersection (Fig.2 .23) may be rejected because it is a binary one. It is a curious feature of all these intersections that they do not conform to the equal co-ordinates criterion. This may be due to possible inaccuracies in experimental data regarding the tritium substituent. It may be noted that the method of equal coordinates is warranted only when the number of isotopic species is greater than two and no unique intersections exist.

Arsine - In the case of the a_1 species of AsH_3 - AsD_3, two close intersections are encountered near the origin (Fig.2.27). The average value of the AsH_3 parameter corresponding to these points is comparable to the value obtained from the pair AsH_3 - AsT_3 (Fig. 2.29) so that the equal co-ordinates principle is involved. The resulting set of force constants agrees well with previously reported values (10).

A more precise application of the method of equal co-ordinates is to the intersections for the e species of the AsH_3 - AsD_3, AsH_3-AsT_3 and AsD_3 - AsT_3 pairs (Figs. 2.33, 2.35, 2.37). This yields a force field in agreement with that of previous workers (10). Though for all these pairs there is another intersection which is nearer to the origin, it does not produce a satisfactory force field nor does it satisfy the above criterion.

From the above discussion we have seen that when the number of isotopic species exceeds two there is a multiplicity of intersections. But in a given parameter space, these intersections lie in a small region. As the parameter for the true force field should be inside this range, the size of the range may be taken as a measure of the uncertainty in fixing the true co-ordinate. With the help of more than two parameter spaces, the extent of uncertainty can be reduced. The minimum value of the uncertainty obtained from an analysis of the graphs corresponds to the smallest range common to all the parameter spaces. This is also in agreement with the method of equal co-ordinates. The mean of the values for the extreme points of the common range along with the extent of the uncertainties is taken as the true parameter. All points of intersection whether unique or not, outside the corresponding common range are taken as spurious ones and are automatically eliminated.

Acceptable values of the parameters for the various molecular species, arrived at using the methods explained above, together with the force constants are given in Table 2.2. The two sets of force constants corresponding to the two solutions are capable of reproducing the vibrational frequencies of the corresponding isotopic species, but only that set obtained from the intersections near the origin has any physical significance. With the predominance of the bending mode the second set turns out to be unphysical. The final set of actual force constants is reported in Table 2.3 and they compare well with values taken from the literature.

The equal coordinates criterion renders the parameter method a powerful calculational tool for the harmonic force field. Also it may be invoked to test the reliability of experimental data when more than two isotopic species are present. This procedure is very sensitive to inaccuracies in experimental data. It may, therefore, be employed as a check on the reliability of measured frequencies.

Fig.2.2 to 2.37 ϵ-ϵ^* parameter curves for different isotopic pairs. In all these figures for a (A-B) pair, parameter ϵ for the isotopic species A is plotted along the X-axis and that for B along the Y-axis.

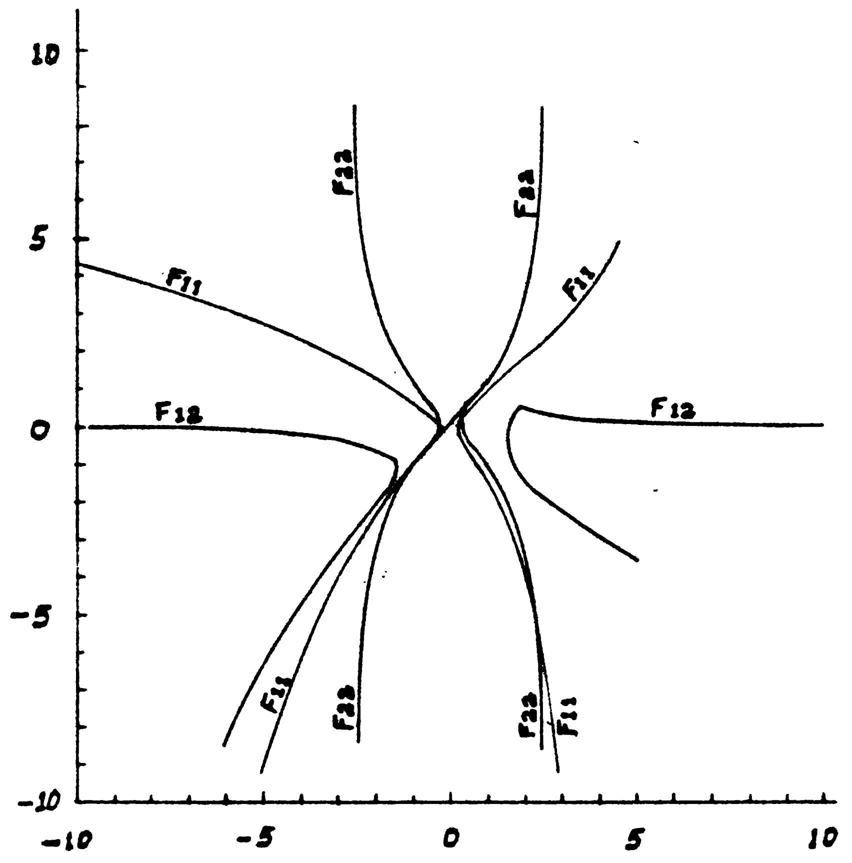

FIG. 2.2

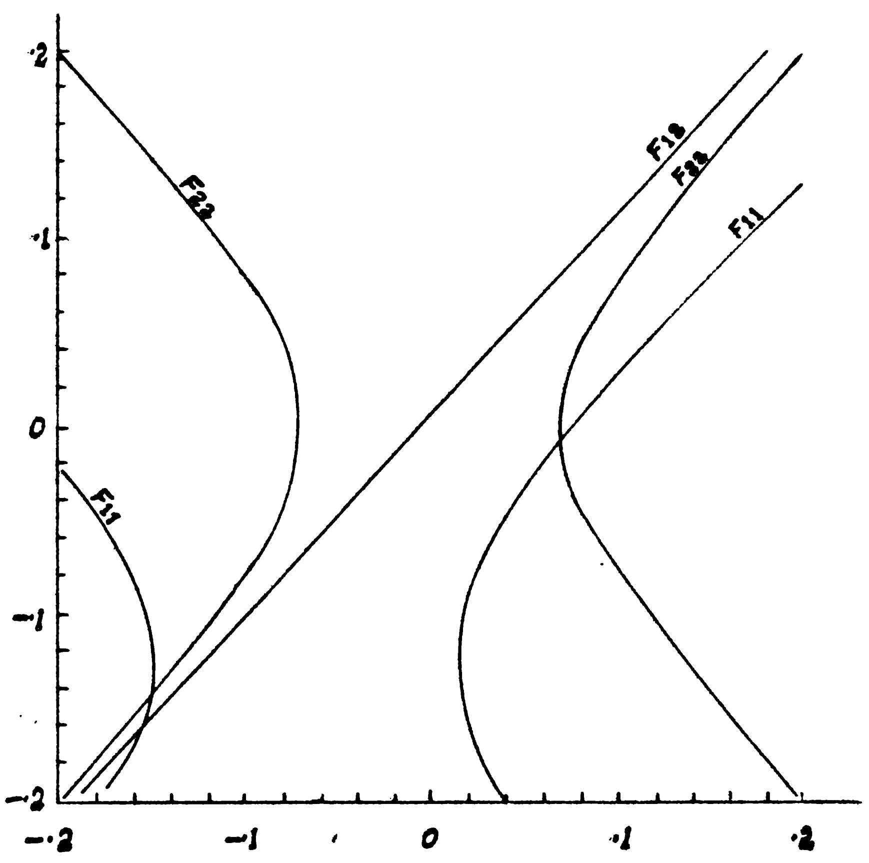

FIG. 2.3

NH_3-ND_3-4

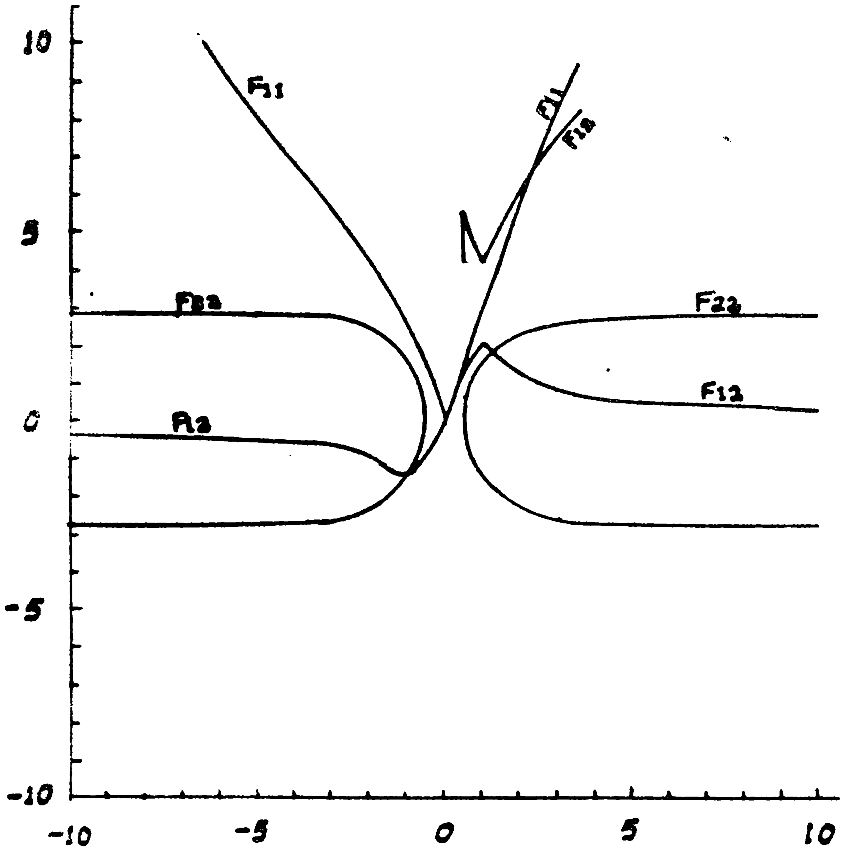

FIG.2.4

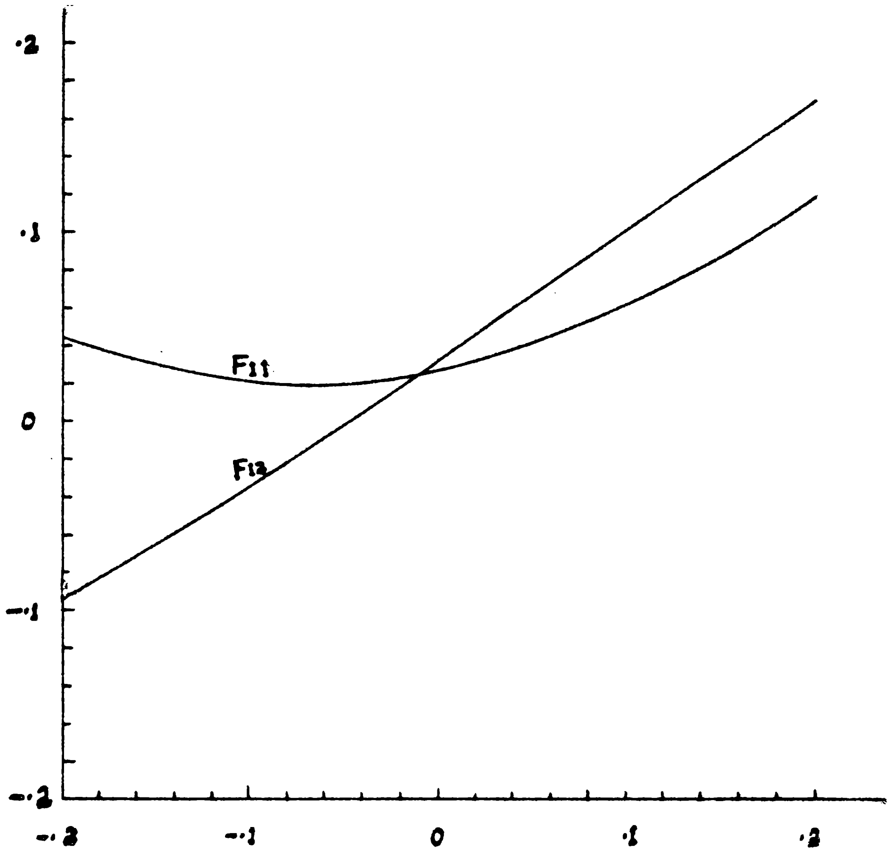

FIG.2.5

NH_3-NT_3-a_1

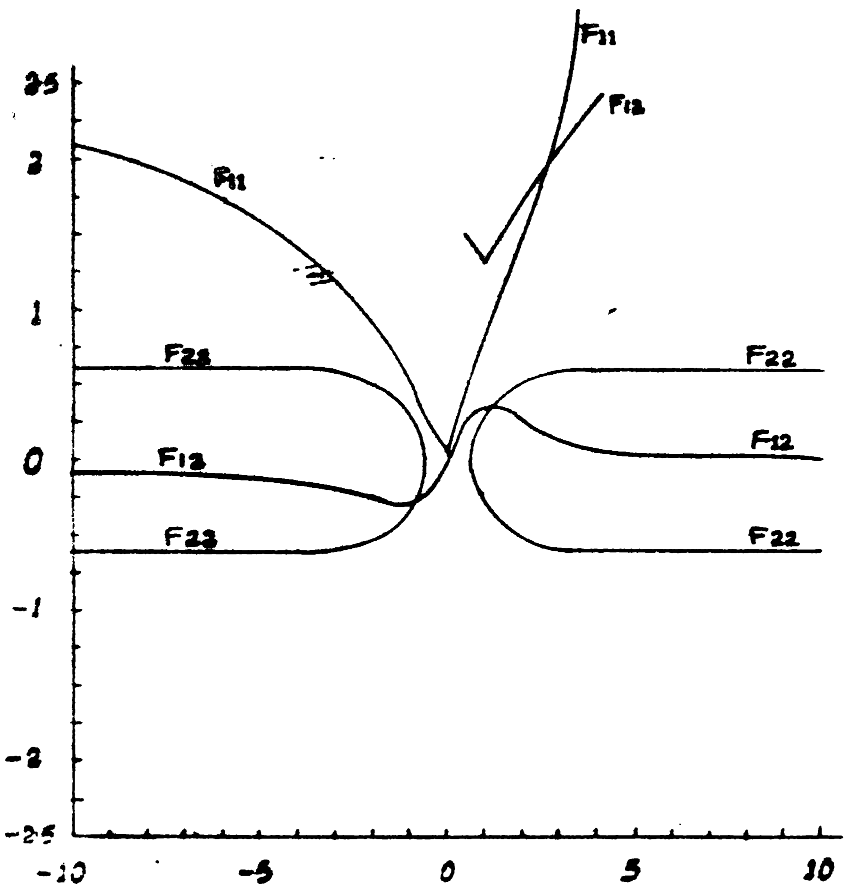

FIG. 2.6

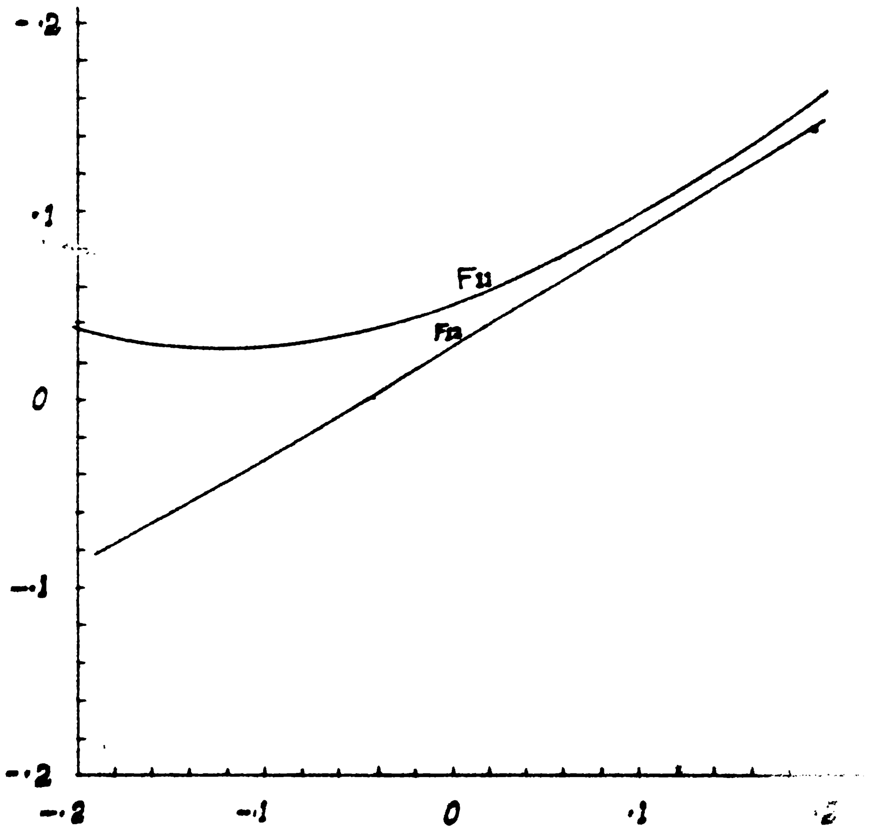

FIG. 2.7

$ND_3 - NT_3 - Q_1$

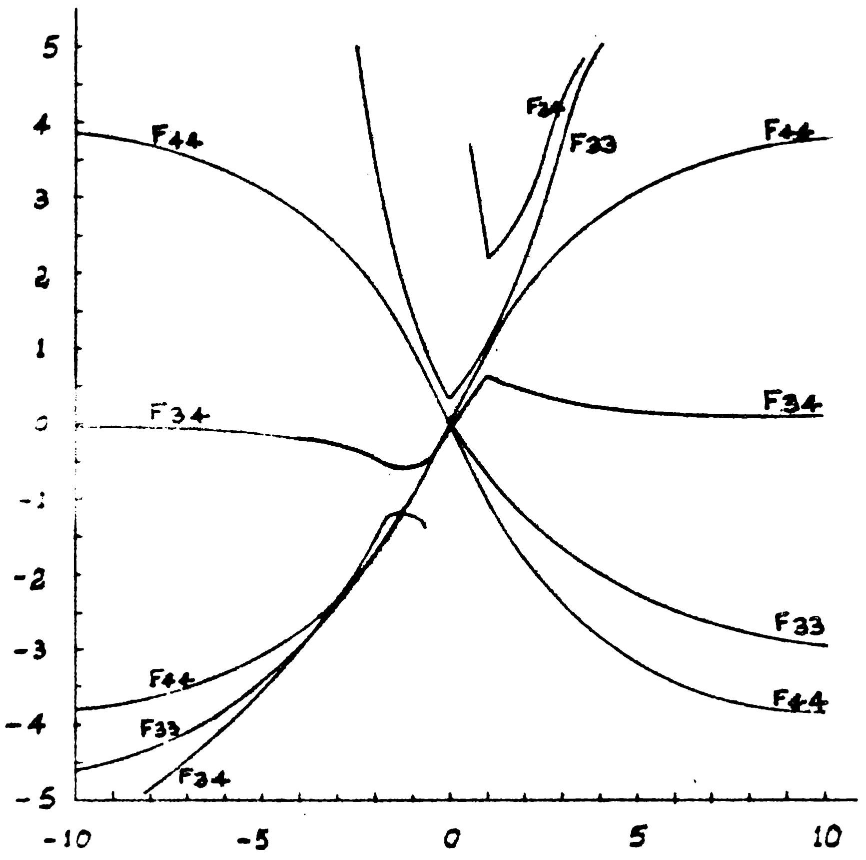

FIG. 2.8

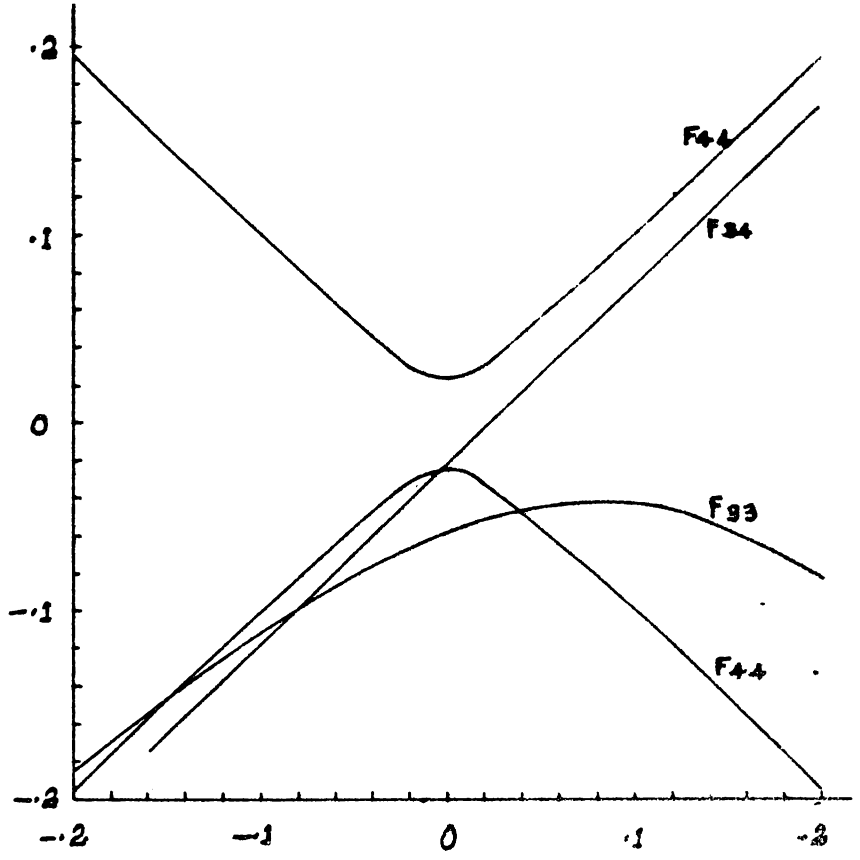

FIG. 2.9

$NH_3 - ND_3 - e$.

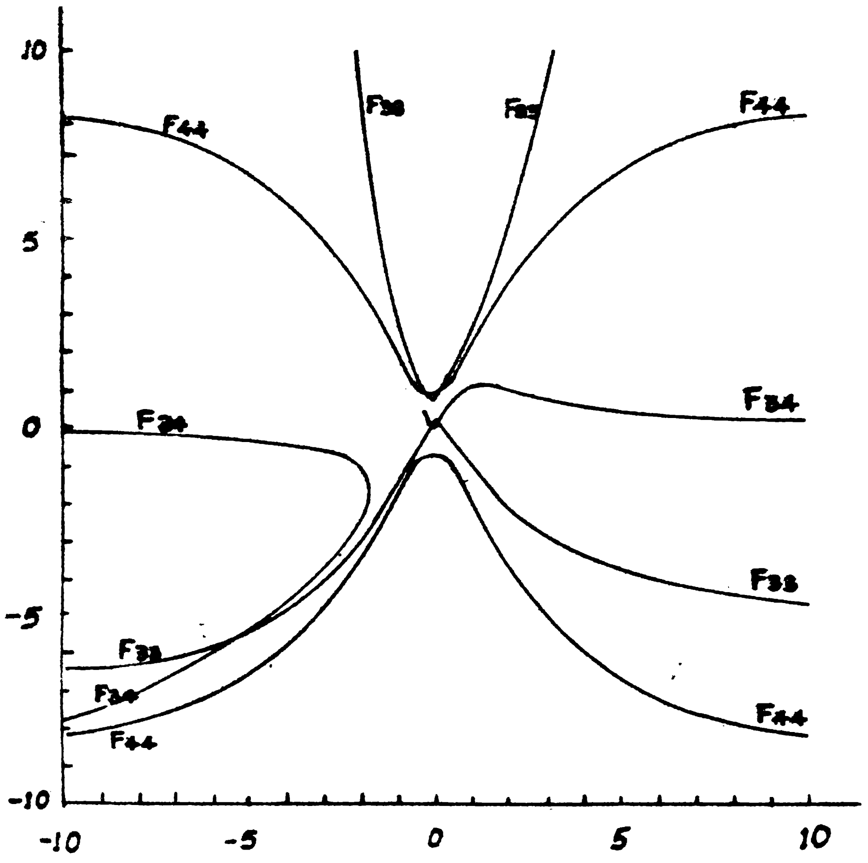

Fig. 2.10

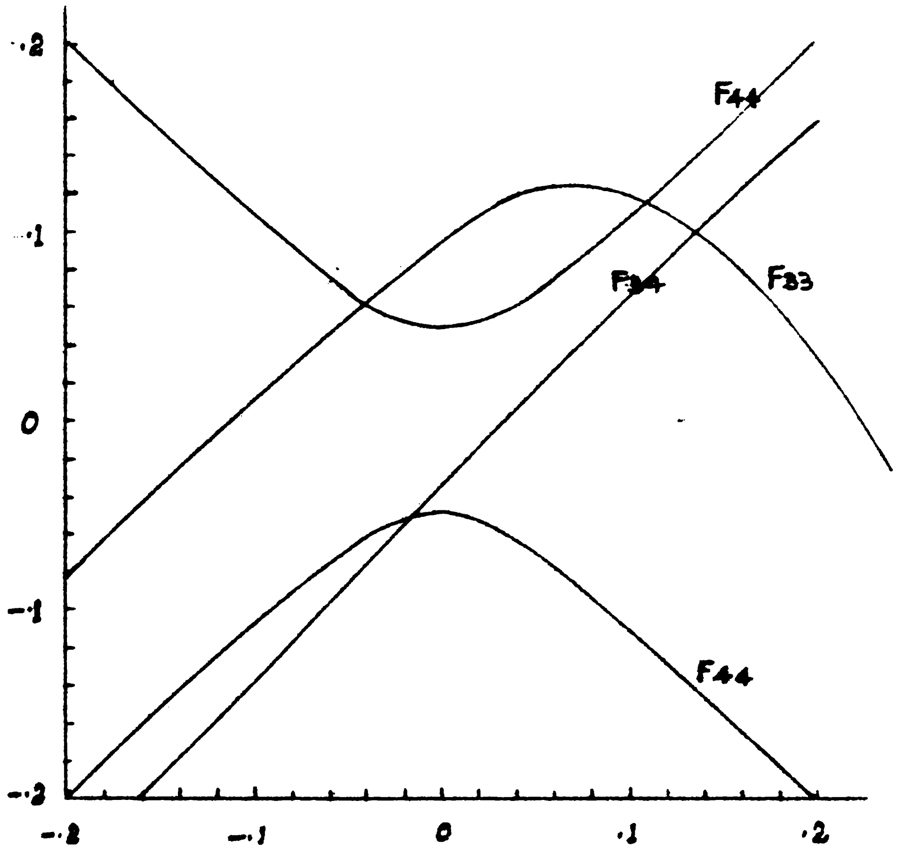

Fig. 2.11

$NH_3 - NT_3 - e$

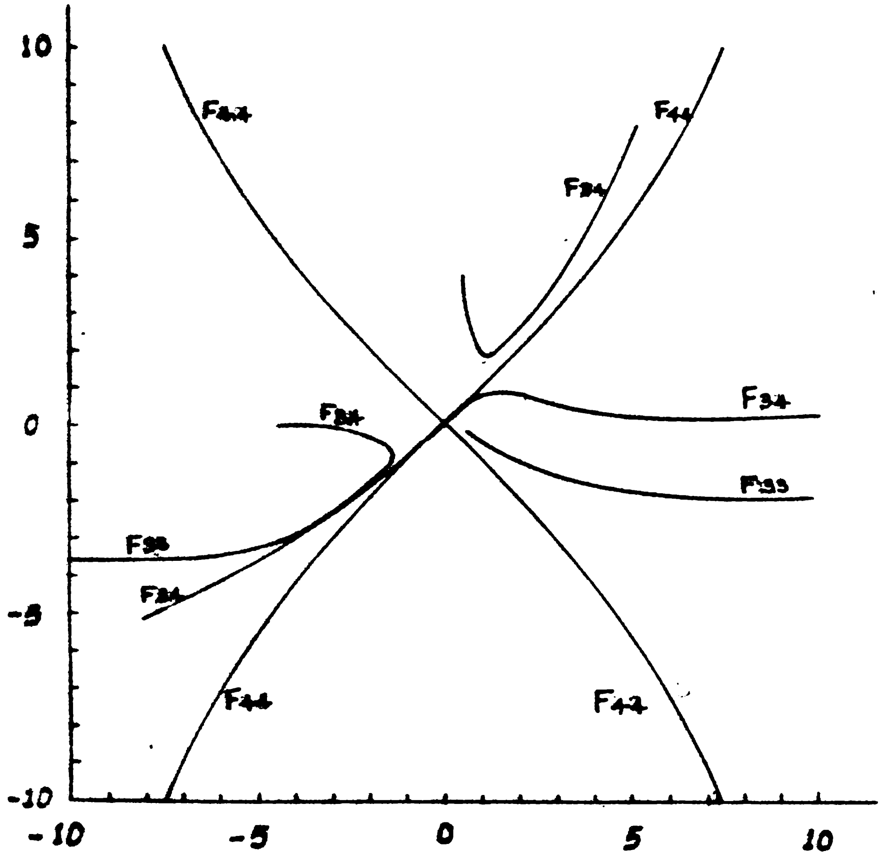

FIG. 2.12

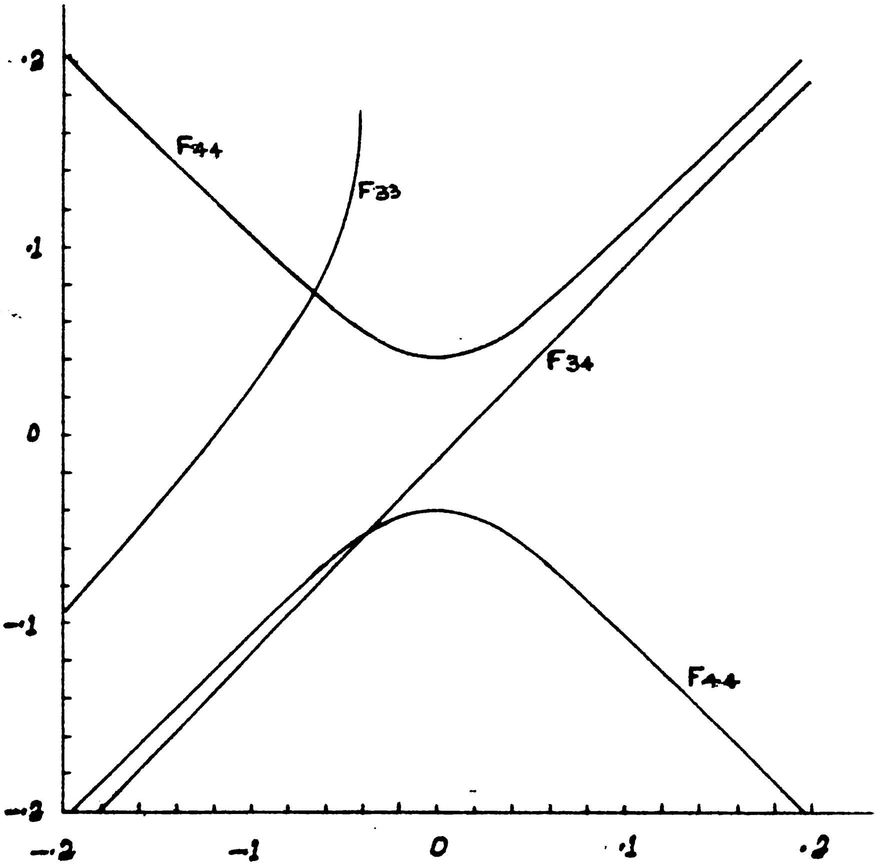

FIG. 2.13

ND_3-NT_3-e

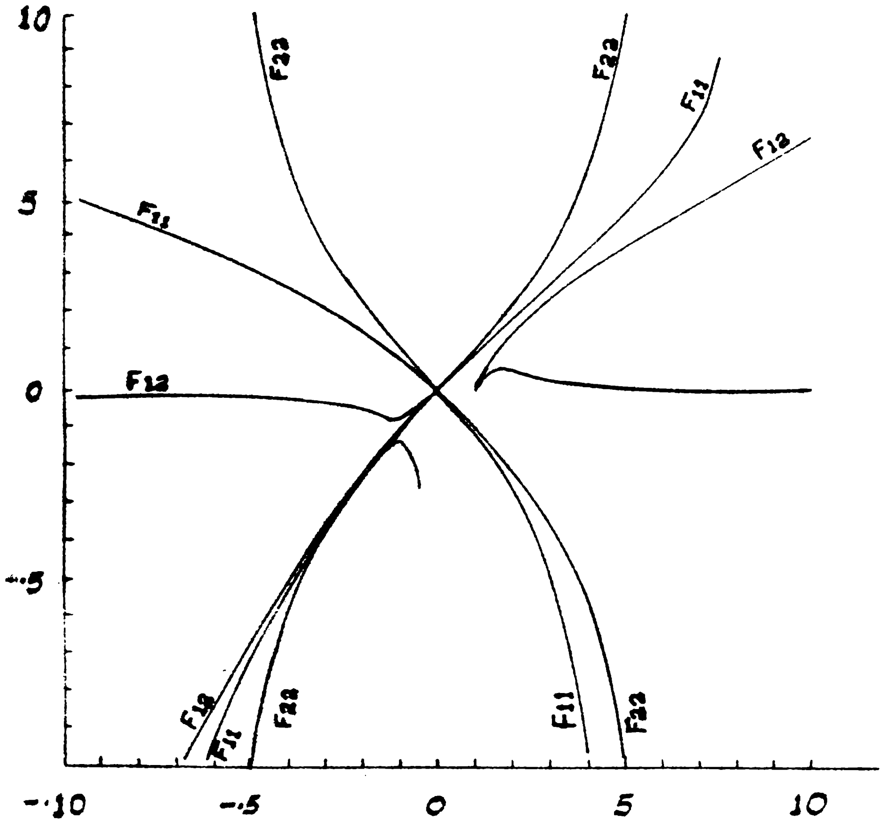

Fig.2.14

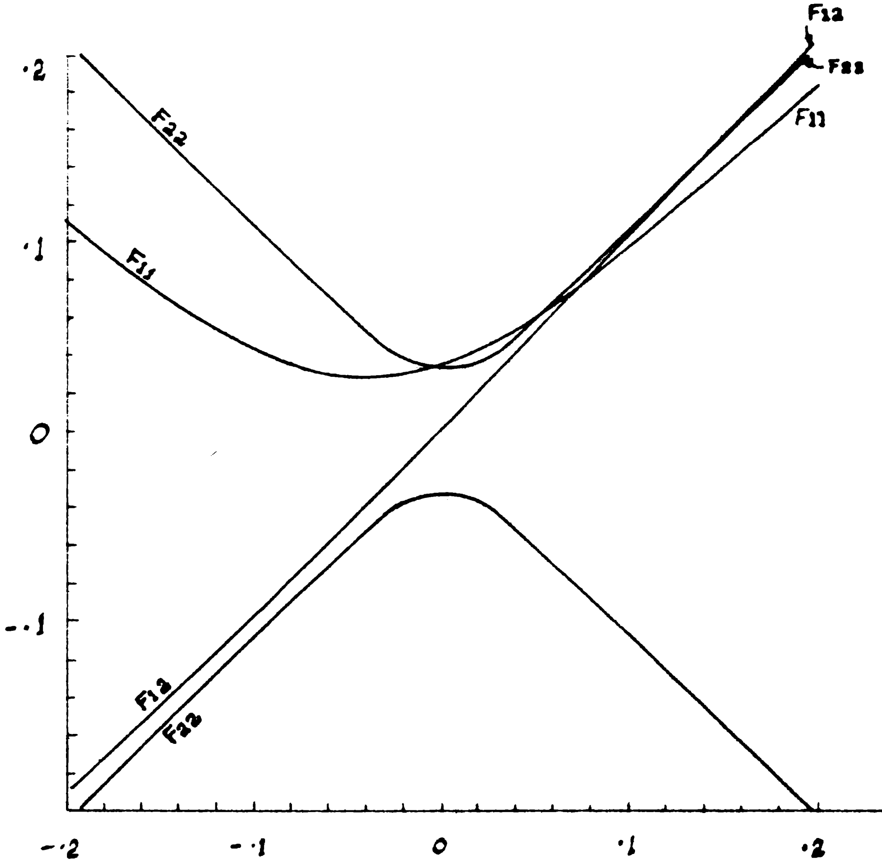

Fig.2.15

PH_3-PD_3 - a_1

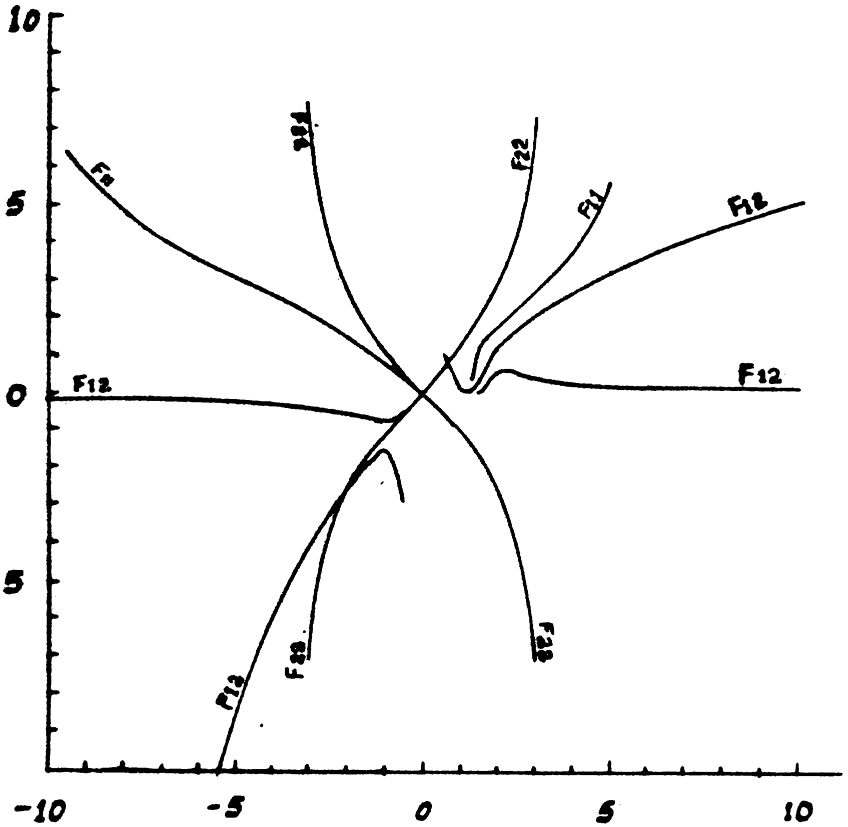

FIG.2.16

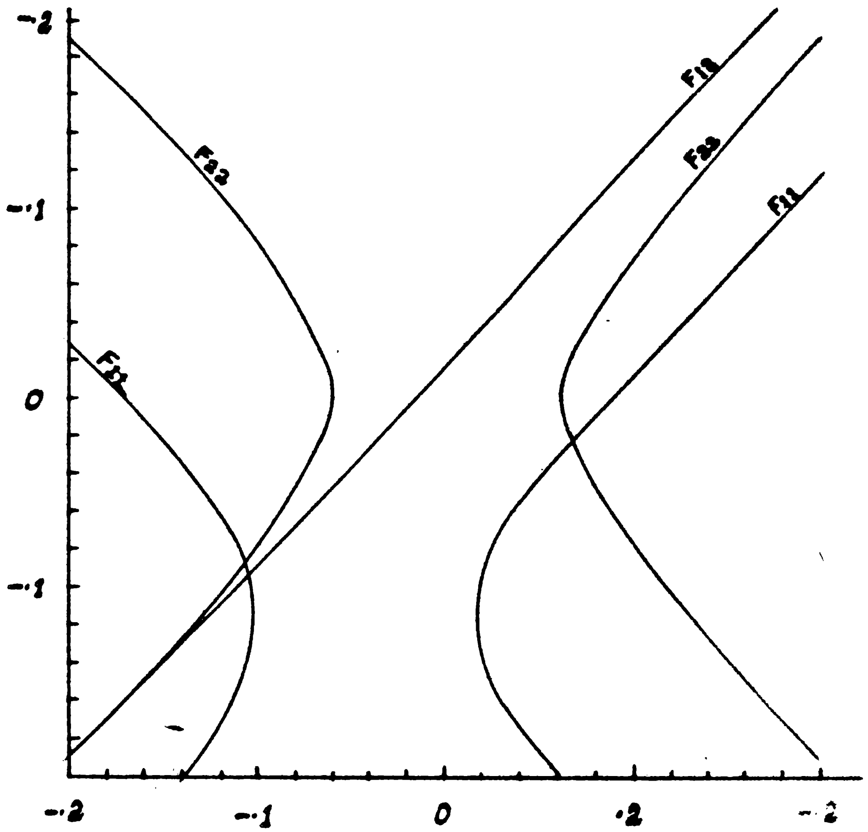

FIG.2.17

PH$_3$- PT$_3$-a$_1$

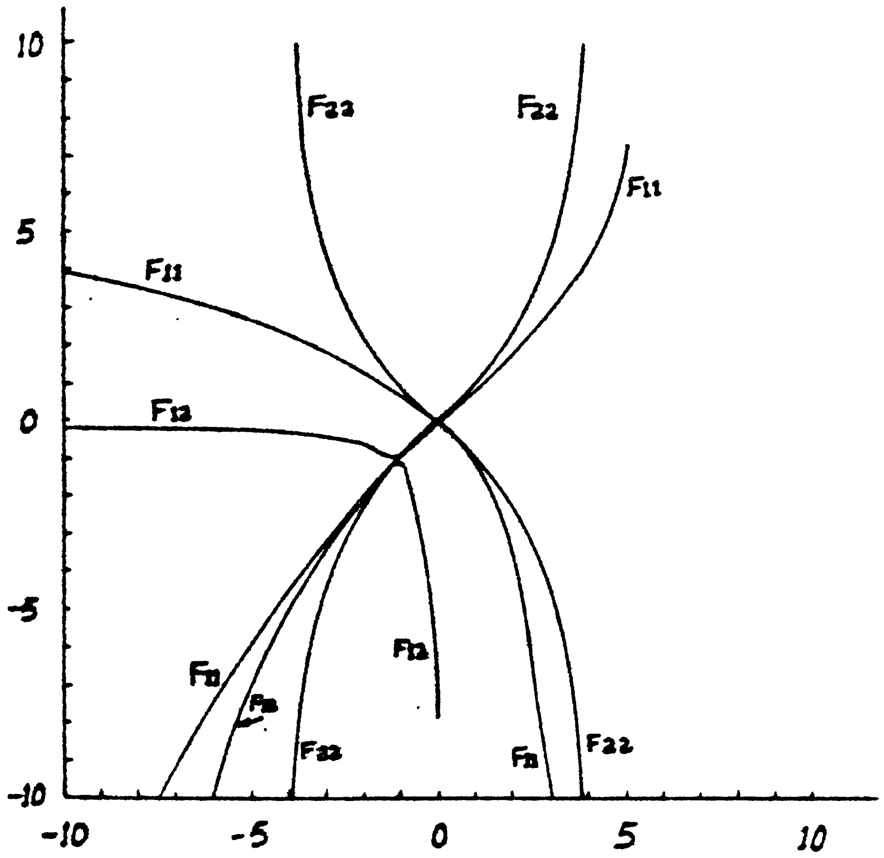

FIG.2.18

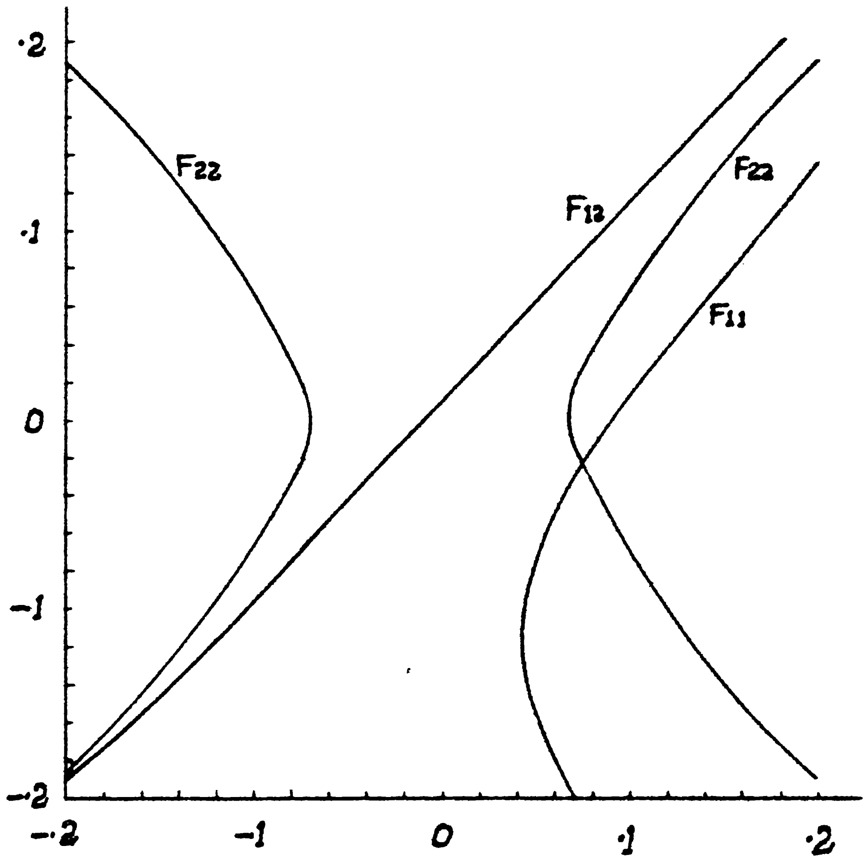

FIG.2.19

PD3-PT3-a1

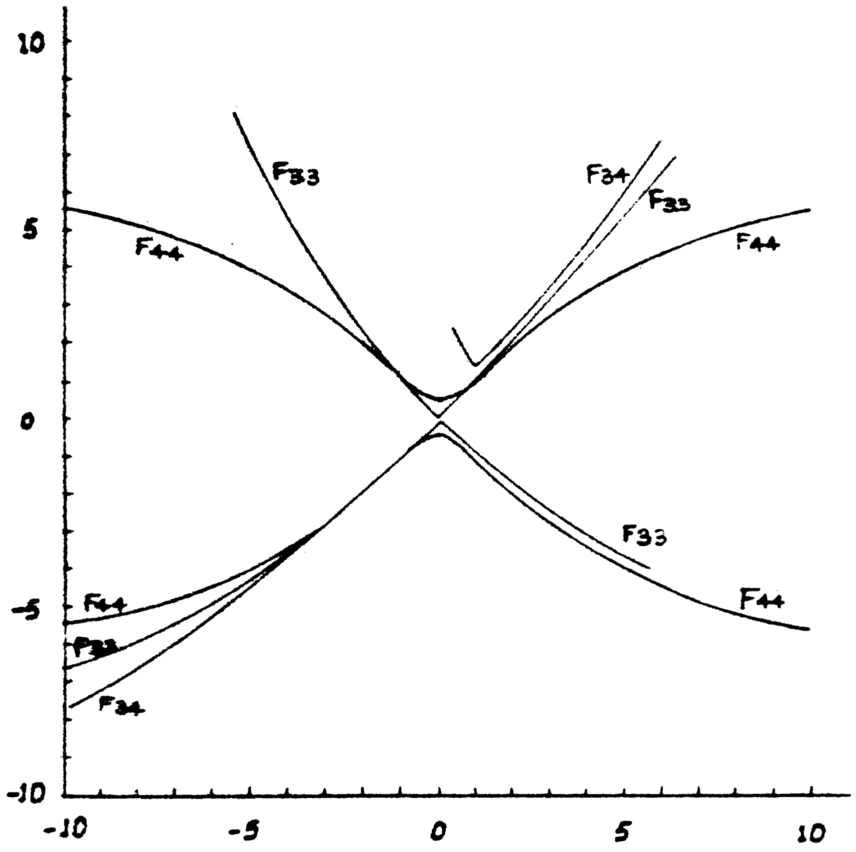

FIG. 2.20

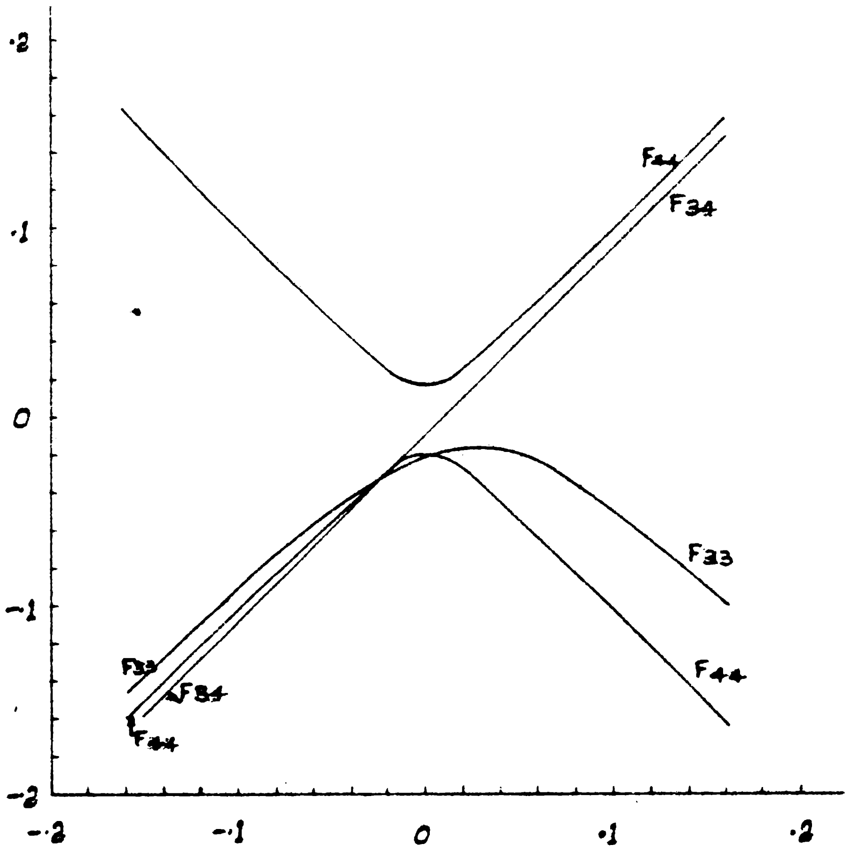

FIG. 2.21

$PH_3 - PD_3 - e$

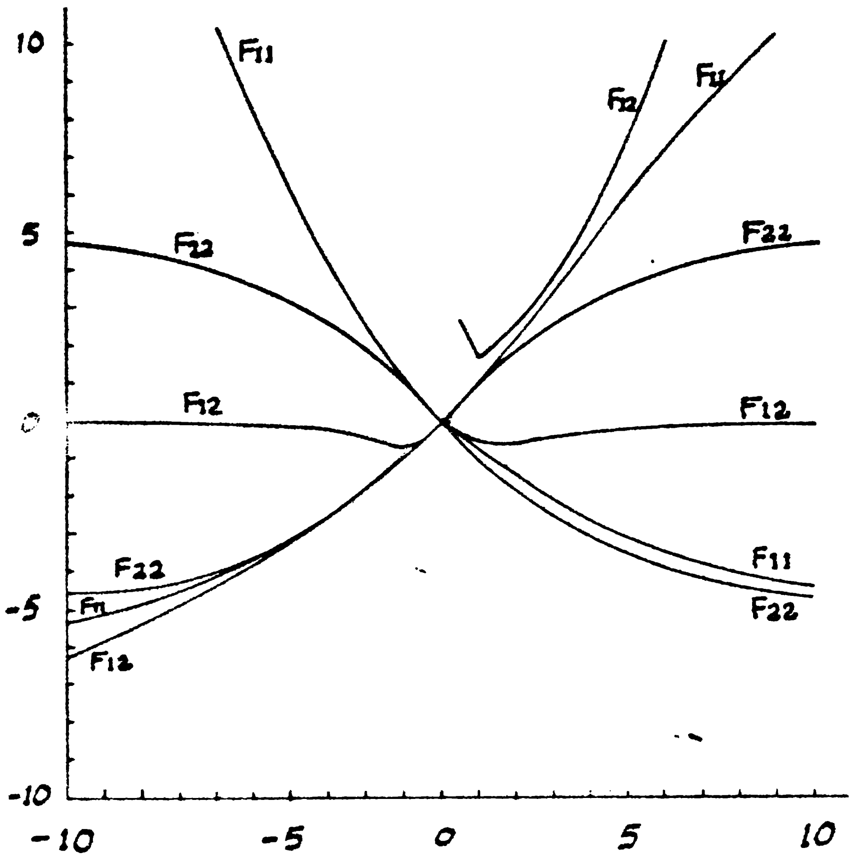

Fig. 2.22

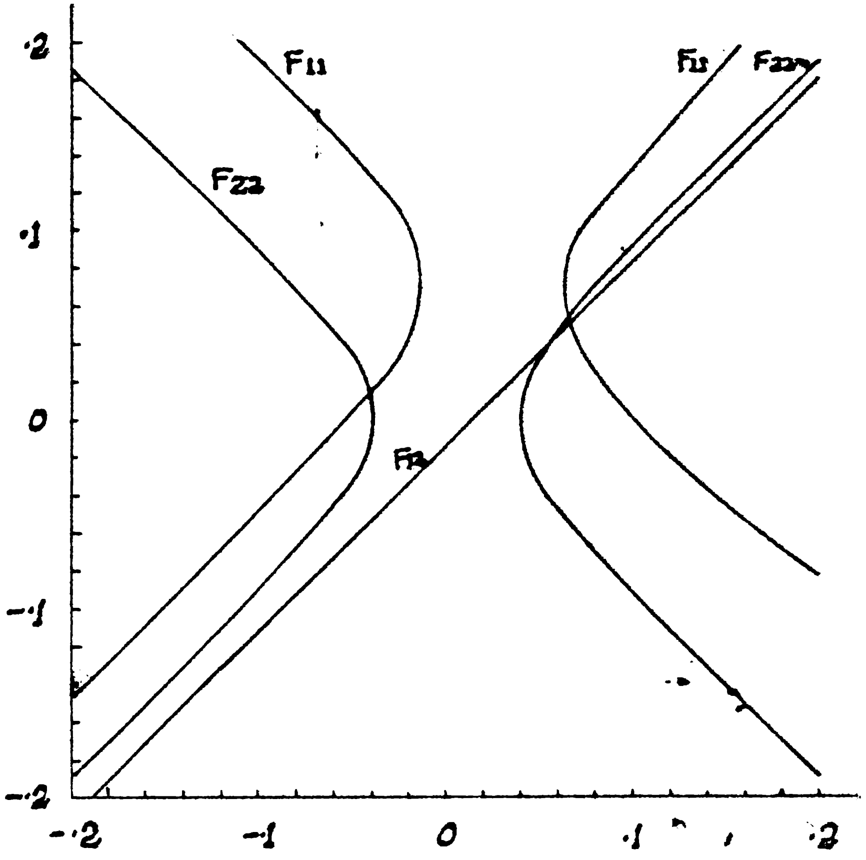

Fig. 2.23

PH_3 - PT_3-e

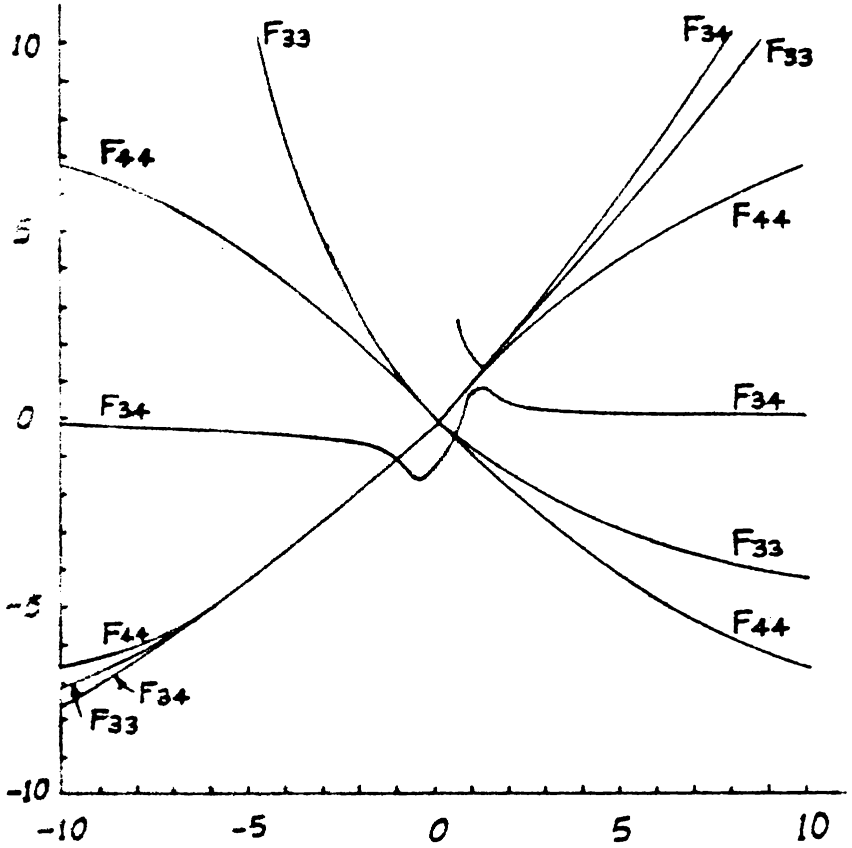

FIG. 2.24

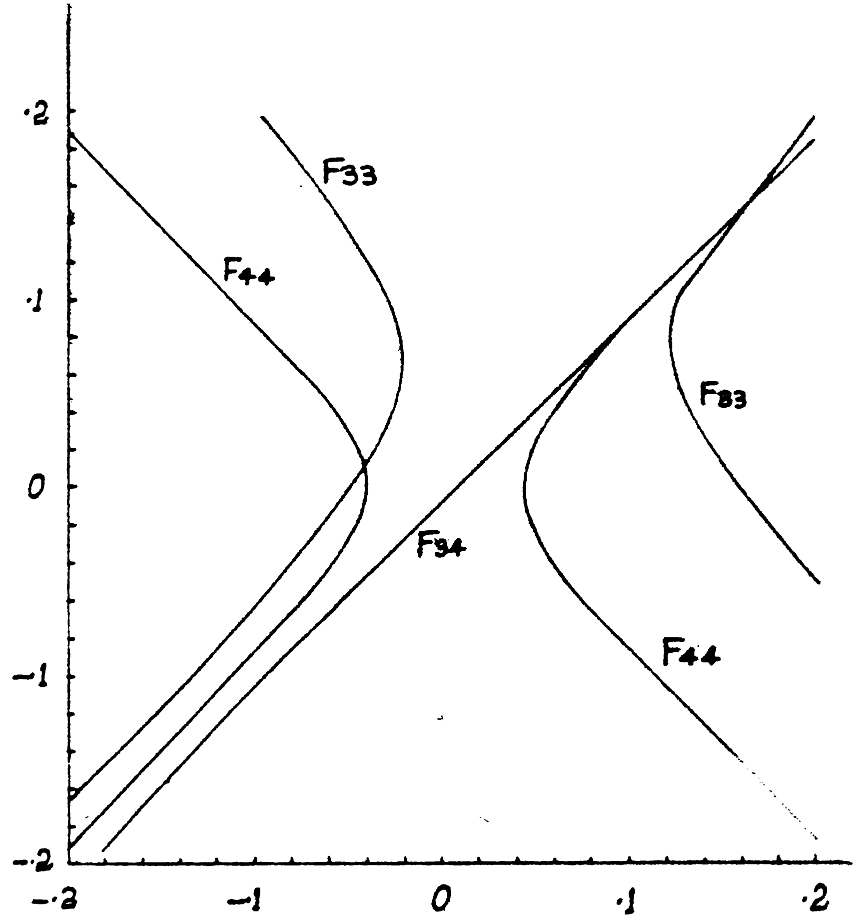

FIG. 2.25

PD$_3$-PT$_3$-e

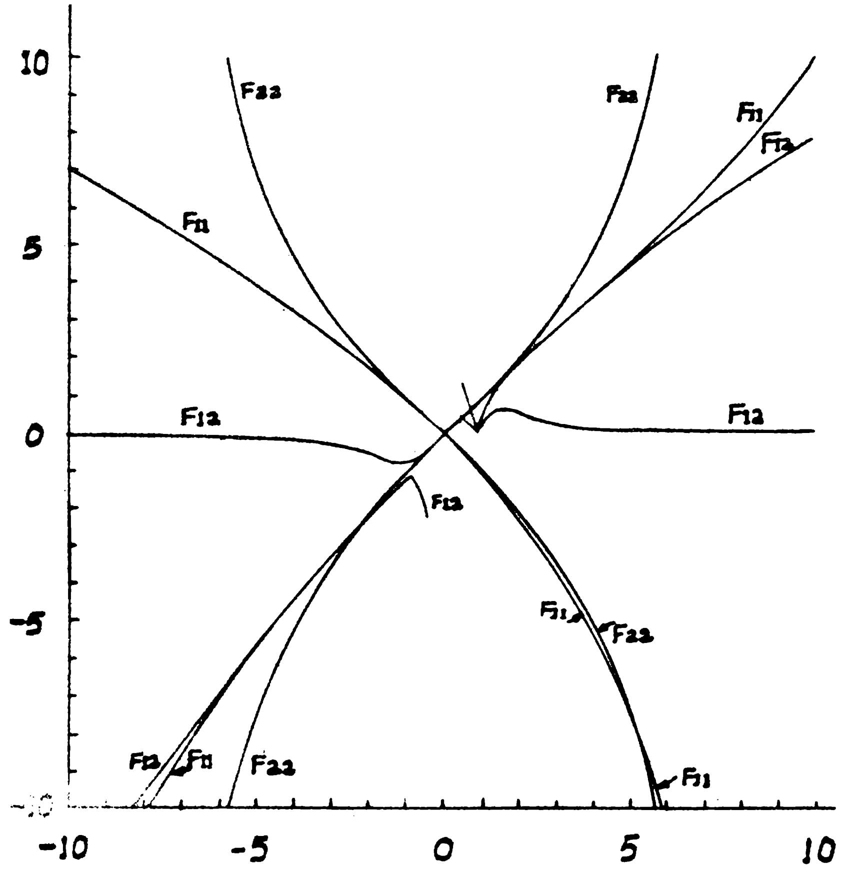

FIG. 2.26

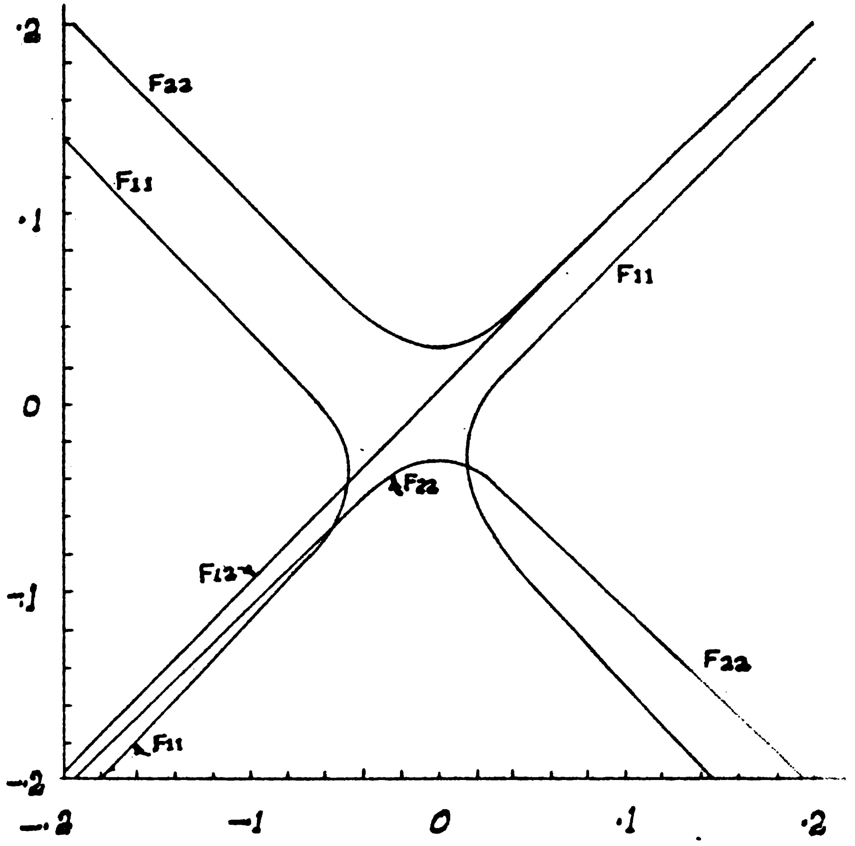

FIG. 2.27

$AsH_3 - AsD_3 - a_1$

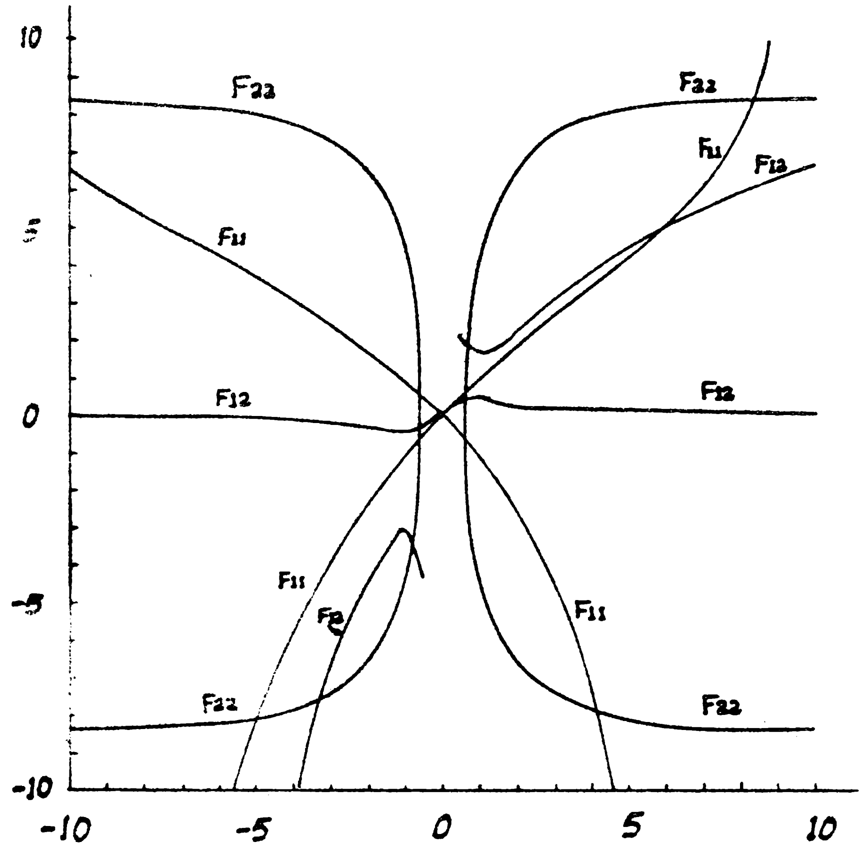

FIG. 2.28

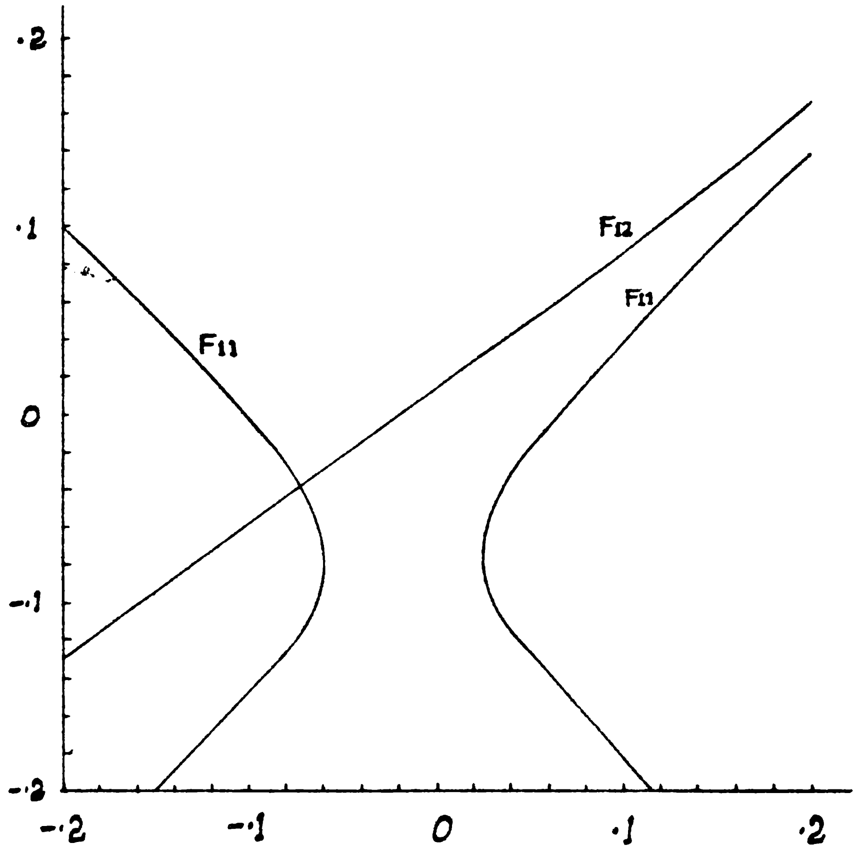

FIG. 2.29

AsH_3 - AsT_3 - a_1

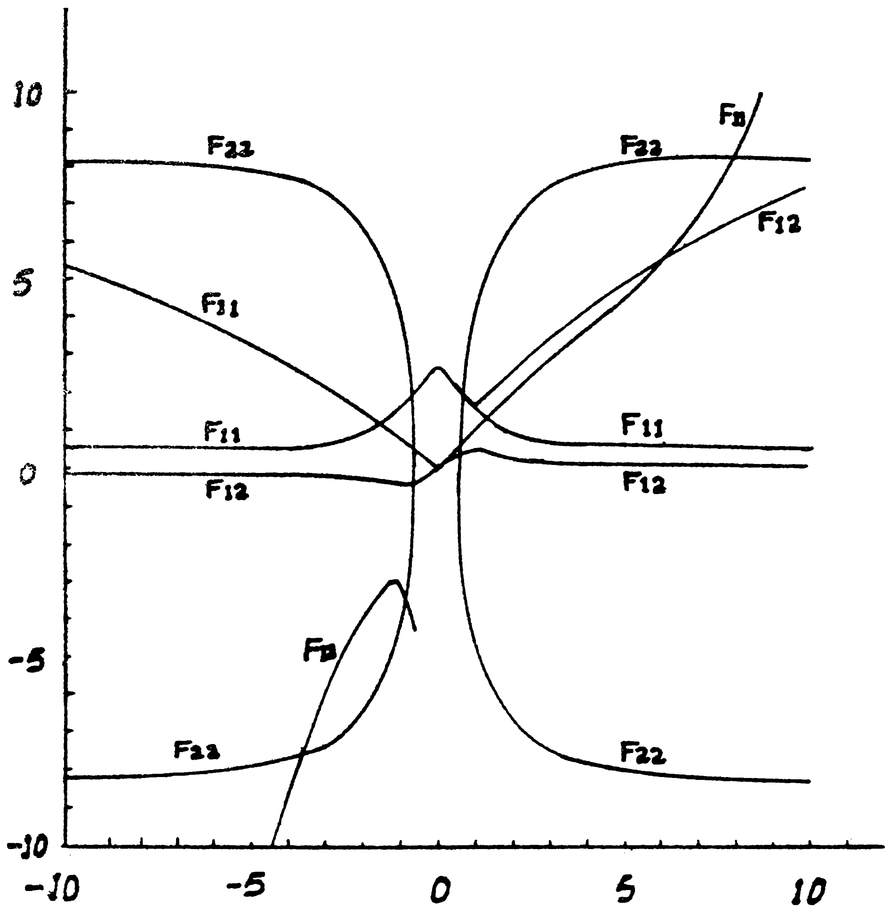

FIG.2.30

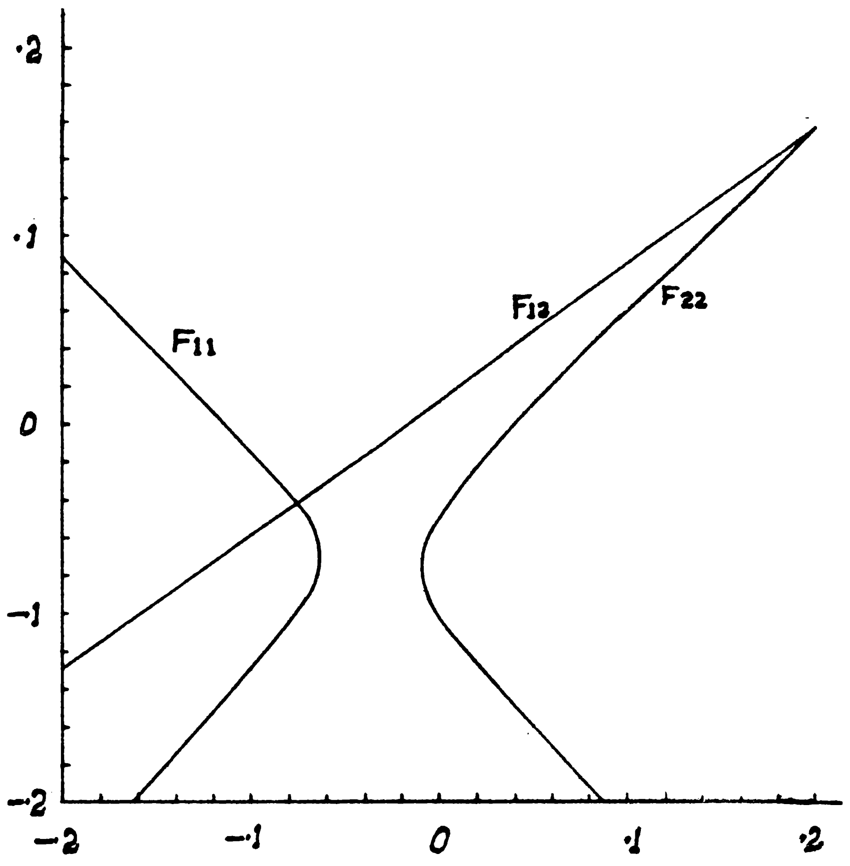

FIG.2.31

$AsD_3 - AsT_3 - a_1$

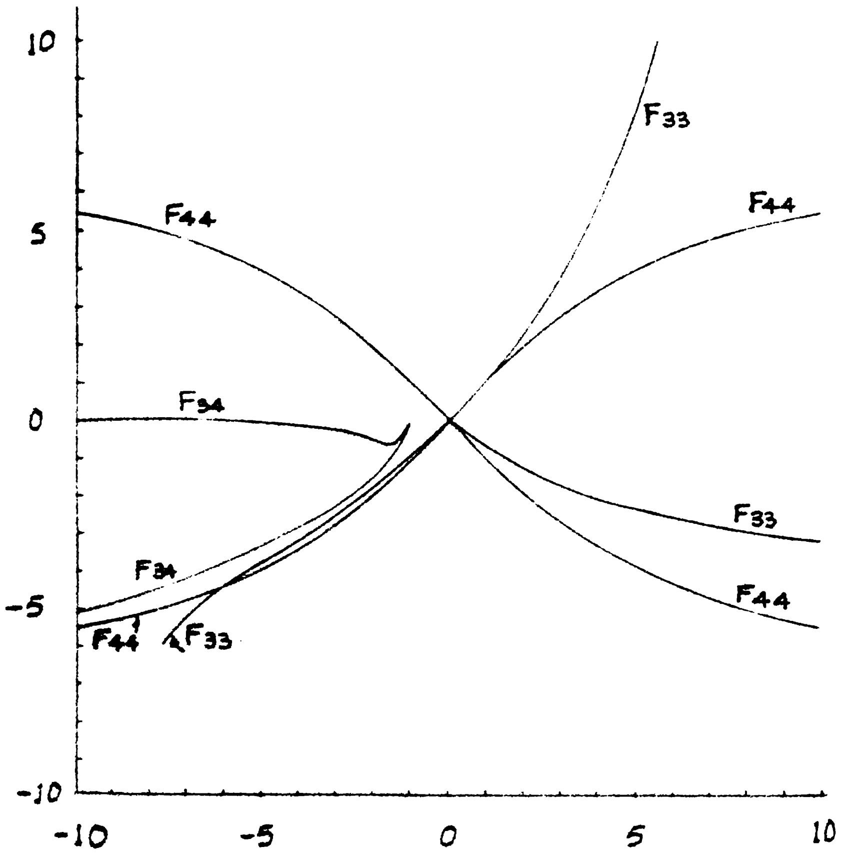

FIG.2.32

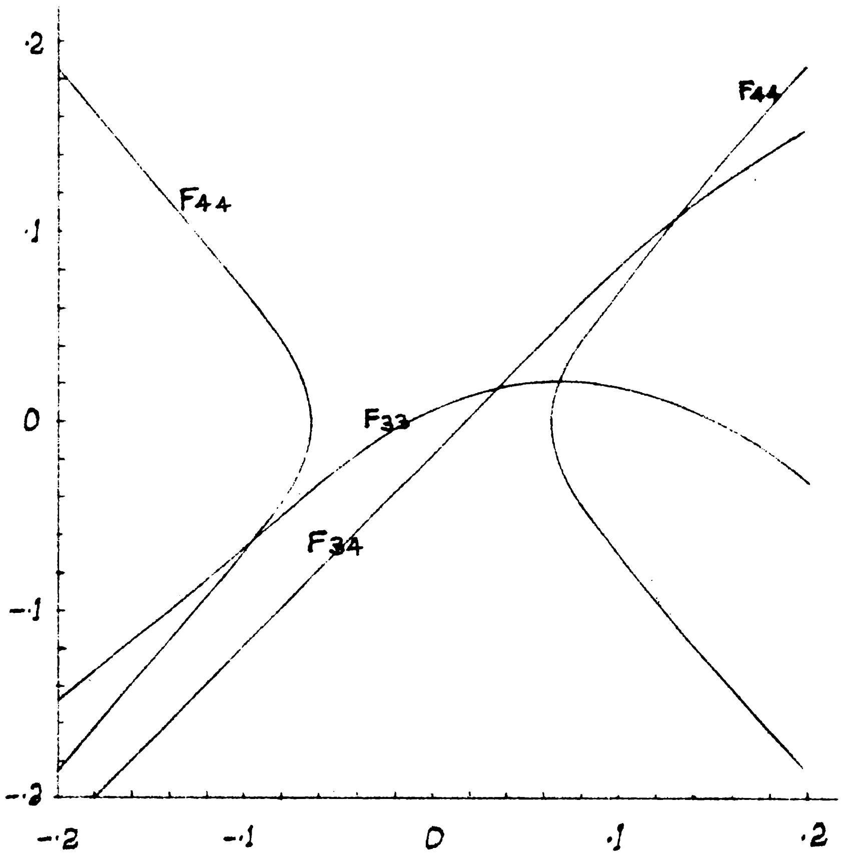

FIG.2.33

$AsH_3 - AsD_3 - e$

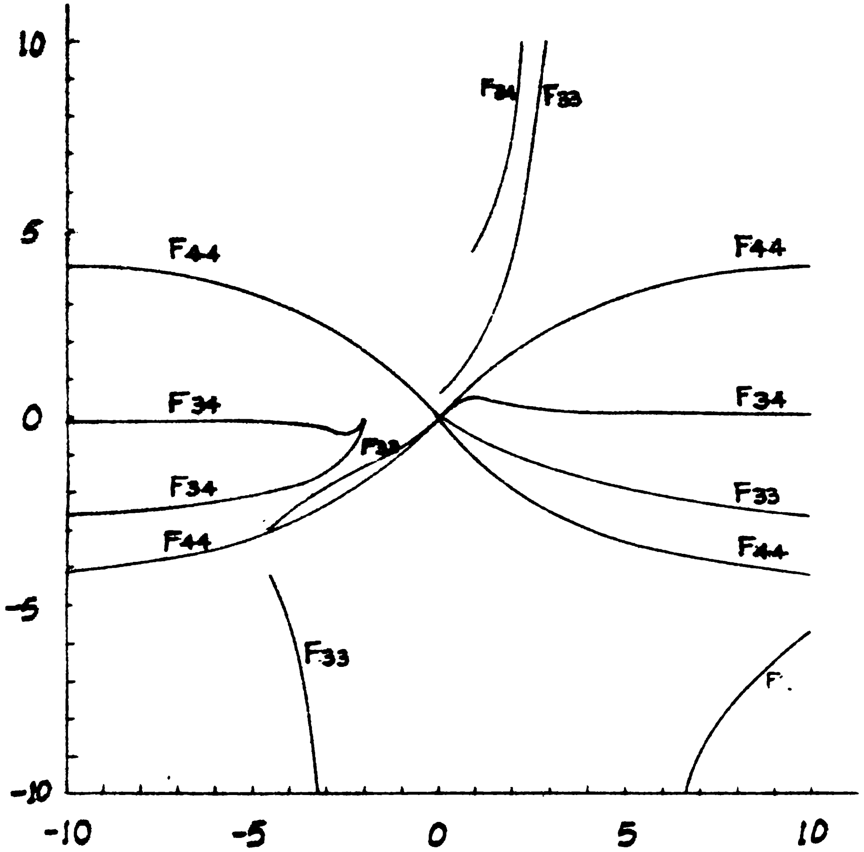

FIG.2.34

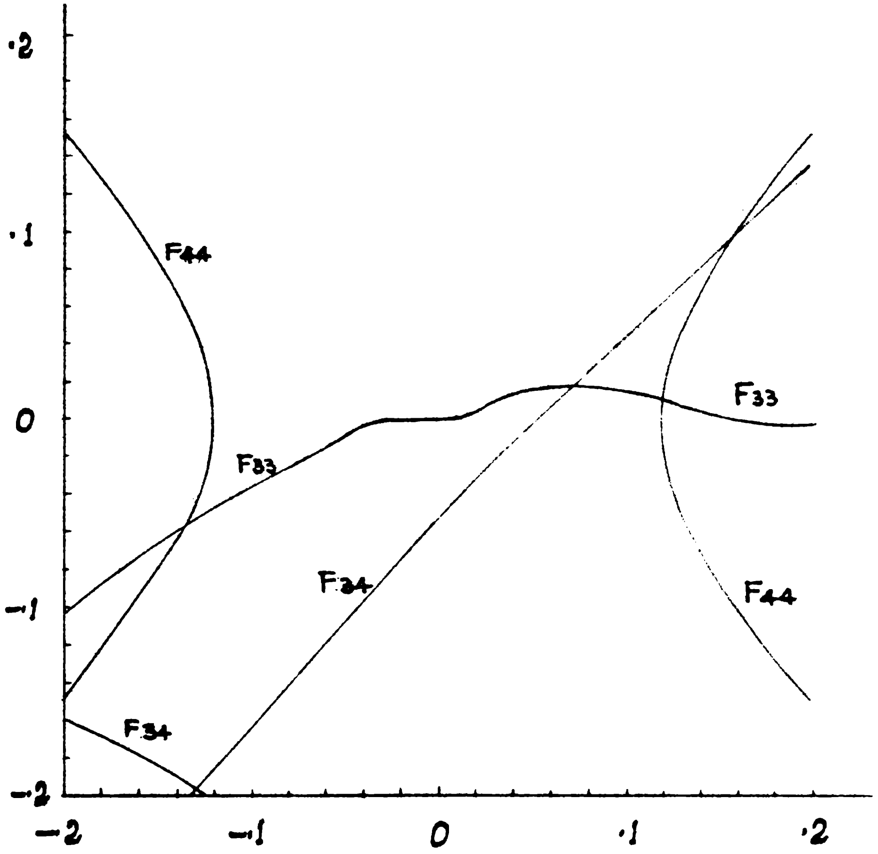

FIG.2.35

AsH_3-AsT_3-e

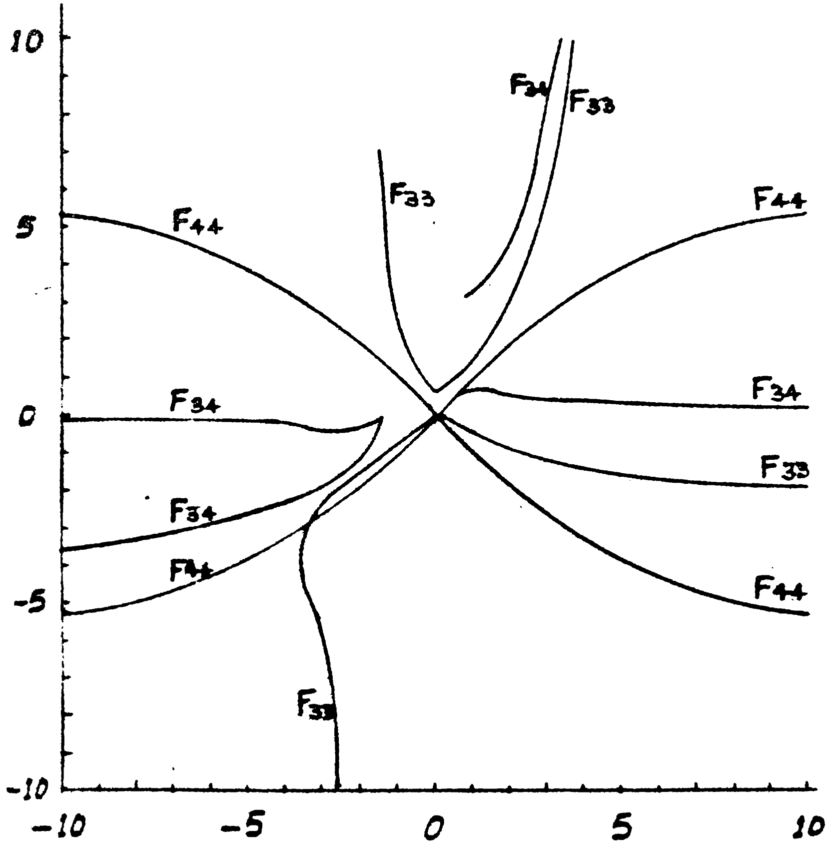

FIG. 2.36

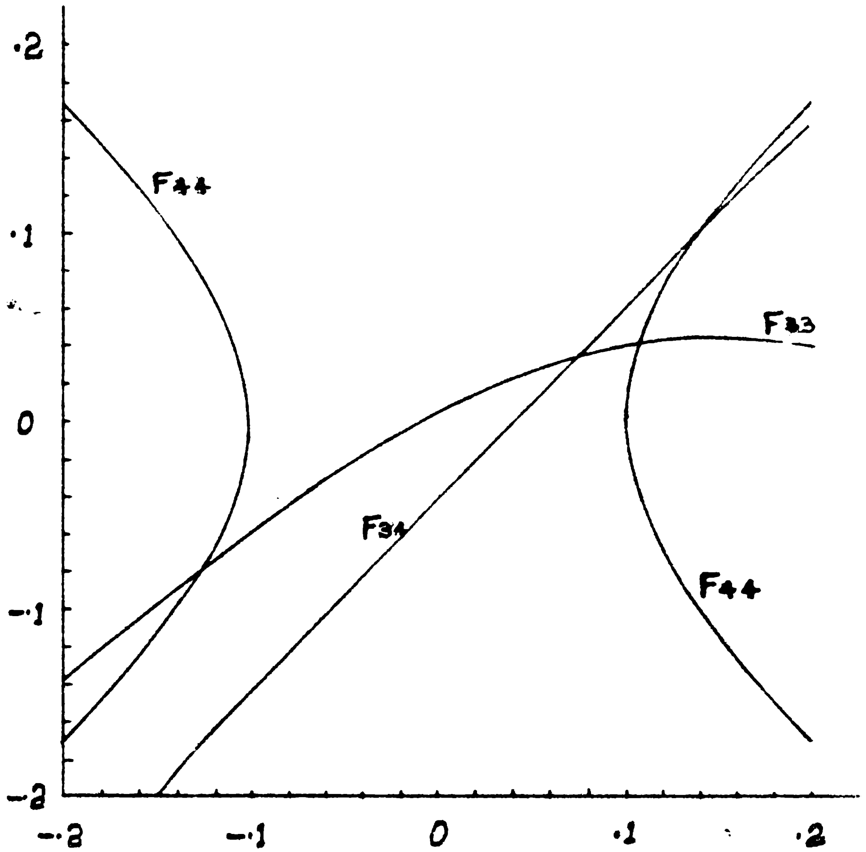

FIG. 2.37

AsD$_3$-AsT$_3$ · e

TABLE 2.1

DETAILS OF INTERSECTIONS OF C - C* CURVES

Molecular Species	Isotopic pair	Parameter values corresponding to intersections					
		near the origin			away from the origin		
		C_A		C_A^*	C_v		C_v^*
		- 0.152	(F_{11}, F_{22})	- 0.144			
	NH_3-ND_3	- 0.158	(F_{11}, F_{12})	- 0.164	2.4	(F_{22}, F_{11})	- 5.7
		- 0.07	(F_{11}, F_{22})	- 0.01			
a_1	NH_3 - NT_3	- 0.014	(F_{11}, F_{12})	0.024	2.5	$(F_{11}, F_{12}$	1.68
	ND_3- NT_3	-	-	-	2.5	(F_{11}, F_{12})	1.65
	NH_3-ND_3	0.01	(F_{34}, F_{44})	- 0.026			
		- 0.15	(F_{33}, F_{44})	- 0.15	- 3	(F_{33}, F_{34}, F_{44})	-2.35
		- 0.086	(F_{33}, F_{44})	- 0.1			
		0.04	(F_{33}, F_{34})	- 0.046			
e		- 0.016	(F_{34}, F_{44})	- 0.05			
	NH_3 - NT_3	0.04	(F_{33}, F_{44})	- 0.06	-4.8	$(F12, F_{11})$	-2.6
		0.1	(F_{33}, F_{34})	0.114			
		0.136	(F_{33}, F_{34})	0.098			

Table 2.1 (contd.)

Molecular Species	Isotopic pair	Parameter values corresponding to intersections near the origin C_A		C_A^e	away from the origin C_v		C_v^e
a	ND_3-NT_3	- 0.04	(F_{34}, F_{44})	- 0.056	-3.5	(F_{12} F_{11})	- 2.7
		- 0.064	(F_{33}, F_{44})	0.078			
	PH_3-PD_3	- 0.06	(F_{11}, F_{12}, F_{22})	0.07	-3	(F_{11}, F_{12}, F_{22})	-3.6
a_1	PH_3-PT_3	-0.15	(F_{22} , F_{12})	-0.14			
		- 0.11	(F_{11} , F_{22})	-0.08			
		-0 .1	(F_{11} , F_{12})	-0.1	-1.5	(F_{11}, F_{12}, F_{22})	-1.8
		0.07	(F_{11} , F_{22})	-0.02			
	PD_3-PT_3	-0.3	(F_{11}, F_{12}, F_{22})	-0.3	-1.7	(F_{11}, F_{12}, F_{22})	-1.6
		+0.08	(F_{11} , F_{22})	-0.03			
	PH_3-PD_3	-0.03	(F_{33}, F_{34}, F_{44})	-0.036	3	(F_{33}, F_{34}, F_{44})	2.7
		0.004	(F_{33}, F_{44})	-0.02		([illegible], [illegible], F_{44})	-3.3
a	PH_3-PT_3	0.08	(F_{34} , F_{44})	0.07			
		0.06	(F_{33} , F_{34})	0.06	-4	(F_{33}, F_{34}, F_{44})	- 3.2
		0.07	(F_{33}, F_{44})	0.05			
	PD_3 - PT_3	0.15	(F_{33}, F_{34}, F_{44})	0.14	-5	(F_{33}, F_{34}, F_{44})	-4.3
		-0.05	(F_{44} , F_{33})	0.01			

Molecular species	Isotopic pair	Parameter values corresponding to intersections near the origin			away from the origin		
		C_A		C_A^*	C_v		C_v^*
a_1	$A_SH_3-A_SD_3$	- 0.05	(F_{11}, F_{12})	-0.046			
		-0.06	$F_{11}, F_{22})$	-0.066	- 2.5	(F_{11}, F_{12}, F_{22})	-2.7
		0.15	$(F_{22}, F_{12}$	0.18			
	$A_SH_3-A_ST_3$	- 0.07	(F_{11}, F_{12})	-0.04	5.5	(F_{11}, F_{12})	4.6
		0.28	F_{11}, F_{12}	0.22			
	$A_SD_3-A_ST_3$	- 0.08	(F_{11}, F_{22})	- 0.05	5.3	(F_{11}, F_{12})	4.6
		0.08	(F_{11}, F_{12})	0.03			
		0.12	(F_{11}, F_{22})	0.04			
		0.16	(F_{12}, F_{22})	0.12			
e	$A_SH_3-A_SD_3$	- 0.06	(F_{33}, F_{44})	-0.05			
		0.04	(F_{33}, F_{34})	0.01	2.6	(F_{44}, F_{34})	2.4
		0.07	(F_{33}, F_{44})	0.02			
		0.15	(F_{34}, F_{44})	0.13			
	$A_SH_3-A_ST_3$	- 0.13	(F_{33}, F_{44})	-0.06			
		0.07	(F_{33}, F_{34})	0.01			
		0.12	(F_{33}, F_{34})	0.04			
		0.15	(F_{34}, F_{44})	0.14			
	$A_SD_3-A_ST_3$	0.13	(F_{33}, F_{44})	0.09			
		0.08	(F_{33}, F_{34})	0.04	- 3.5	(F_{33}, F_{44})	- 3
		0.12	(F_{33}, F_{44})	0.04			
		0.15	(F_{34}, F_{44})	0.16			

TABLE 2.2

SELECTED PARAMETER VALUES AND CORRESPONDING FORCE CONSTANTS

Molecular pair	Molecular Species	F_{ij}	Actual set using $C_A F_{ij}$ in mdyn/A°		Virtual set using $C_V F_{ij}$ in mdyn/A°	
			Molecule	Isotope	Molecule	Isotope
NH_3- ND_3			$C_A = -0.155$	$C_A^* = -0.144$	$C_V = 2.4$	$C_V^* = -5.7$
	a_1	F_{11}	7.073	7.0669	1.2771	1.2607
		F_{12}	0.8899	0.8566	-1.6272	-1.562
		F_{22}	0.5601	0.5673	4.5526	2.661
			$C_A = -0.01$	$C_A^* = -0.026$	$C_V = -3$	$C_V^* = -2.5$
	e	F_{33}	6.9481	7.017	1.8854	1.911
		F_{34}	-0.0409	-0.0448	0.7419	0.7453
		F_{44}	0.6609	0.6608	2.7267	2.7169
NH_3-NT_3			$C_A = -0.014$	$C_A^* = 0.024$	$C_V = 2.5$	$C_V^* = 1.68$
	a_1	F_{11}	7.095	7.2818	1.8261	1.2497
		F_{12}	0.091	0.1144	-2.2881	-1.5496
		F_{22}	0.4474	1.4388	4.6007	9.923
			$C_A = -0.016$	$C_A^* = -0.05$	$C_V = -4.8$	$C_V^* = -2.6$
	e	F_{33}	6.9384	6.6997	1.6533	1.6571
		F_{34}	-0.0058	-0.016	0.3734	0.3879
		F_{44}	0.6616	0.6612	2.8608	2.757

Table 2.2 (Contd.)

Molecular pair	Molecular species	F_{ij}	Actual set using C_A		Virtual set using C_V	
			Molecule	Isotope	Molecule	Isotope
ND_3-NT_3					$C_V = 2.5$	$C_V^* = 1.65$
		F_{11}			1.1236	1.2957
	a_1	F_{12}			-1.1445	-1.5994
		F_{22}			4.0799	9.8488
			$C_A = -0.014$	$C_A^* = -0.056$	$C_V = -3.5$	$C_V^* = -2.7$
	e	F_{33}	6.9903	6.6755	1.7628	1.6355
		F_{34}	0.005	0.0048	0.6093	0.3483
		F_{44}	0.663	0.6627	2.783	2.777
PH_3-PD_3			$C_A = 0.06$	$C_A^* = 0.07$	$C_V = -3$	$C_V^* = -3.6$
	a_1	F_{11}	3.4332	3.4337	0.9902	0.9888
		F_{12}	-0.1018	-0.1014	0.7057	0.7038
		F_{22}	0.3300	0.3381	1.6636	1.6362
			$C_A = -0.03$	$C_A^* = -0.036$	$C_V = -3$	$C_V^* = -2.7$
		F_{33}	3.2718	3.2893	0.9785	0.9821
	e	F_{34}	0.0395	0.0385	0.4763	0.4821
		F_{44}	0.3764	0.3765	1.4888	1.4883

Table 2.2 (Contd.)

Molecular pair	Molecular species	F_{ij}	Actual set using C_A		Virtual set using C_V	
			Molecule	Isotope	Molecule	Isotope
			$C_A = -0.15$	$C_A^* = -0.14$	$C_V = -1.5$	$C_V^* = -1.8$
PH_3-PT_3	a_1	F_{11}	3.4307	3.452	1.6149	1.6306
		F_{12}	0.3189	0.3213	1.0157	1.0349
		F_{22}	0.3569	0.3564	1.3339	1.3475
			$C_A = 0.08$	$C_A^* = 0.07$	$C_V = -4$	$C_V^* = -3.2$
		F_{33}	3.2718	3.2768	0.8482	0.8797
	e	F_{34}	-0.1538	-0.1632	0.3138	0.3574
		F_{44}	0.3832	0.3834	1.5666	1.5428
			$C_A = -0.3$	$C_A^* \neq -0.3$	$C_V = -1.7$	$C_V^* = -1.6$
		F_{11}	3.3738	3.3694	1.5924	1.7856
PD_3-PT_3	a_1	F_{12}	0.6011	0.5981	1.032	1.0718
		F_{22}	0.4399	0.4407	1.3739	1.2875
			$C_A = 0.15$	$C_A = 0.14$	$C_V = -5$	$C_V^* = -4.3$
		F_{33}	3.2642	3.2643	0.8343	0.8058
	e	F_{34}	-0.2903	-0.2836	0.2836	0.2376
		F_{44}	0.4027	0.4018	1.565	1.591

Table 2.2 (Contd.)

			$C_A = -0.055$	$C_A^* = -0.055$	$C_V = 2.5$	$C_V^* = 2.7$
$A_SH_3 - A_SD_3$	a_1	F_{11}	2.8581	2.8579	0.9029	0.8944
		F_{12}	0.0978	0.1099	0.6017	0.5968
		F_{22}	0.2873	0.2863	1.2998	1.3003
			$C_A = 0.15$	$C_A^* = 0.13$	$C_V = 2.6$	$C_V^* = 2.4$
	e	F_{33}	2.9008	2.9484	1.0229	1.2268
		F_{34}	-0.2714	0.2747	-0.6776	-0.8447
		F_{44}	0.3231	0.3224	1.2931	1.295
			$C_A = -0.07$	$C_A^* = -0.04$	$C = 5.3$	$C^* = 4.6$
$A_S H_3 - A_S T_3$	a_1	F_{11}	2.855	2.8546	0.6699	0.6189
		F_{12}	0.1223	0.1305	-0.2638	-0.2646
		F_{22}	0.2895	0.5533	1.4219	2.6377
			$C_A = 0.15$	$C_A^* = 0.14$		
	e	F_{33}	2.9008	3.029		
		F_{34}	-0.2714	-0.3542		
		F_{44}	0.3287	0.3372		
			$C_A = -0.08$	$C_A^* = -0.05$	$C_V = 6$	$C_V^* = 5.5$
$A_S D_3 - A_ST_3$	a_1	F_{11}	2.8547	2.8559	0.6045	0.5999
		F_{12}	0.1443	0.1528	-0.2306	-0.1921
		F_{22}	0.2899	0.5553	1.4305	2.6639
			$C_A = 0.15$	$C_A^* = 0.16$	$C_V = -3.5$	$C_V^* = -3$
	e	F_{33}	2.949	2.9667	0.6506	0.6522
		F_{34}	-0.3068	-0.3873	0.1493	-0.0441
		F_{44}	0.3287	0.3439	1.3794	1.3766

TABLE 2.3

FORCE CONSTANTS OF AMMONIA, PHOSPHINE AND ARSINE

Molecule	Species	Force constants in mdyn/Å: Present result	Force constants in mdyn/Å: Previous result	Ref for force constants
Ammonia	F_{11}	7.0666 ± 0.0031	7.075	
	F_{12}	0.8617 ± 0.0547	0.780	10
	F_{22}	0.5633 ± 0.0133	0.543	
	F_{33}	6.8584 ± 0.1587	6.963	
	F_{34}	-0.0109 ± 0.0058	0.000	
	F_{44}	0.6612 ± 0.0004	0.666	8
Phosphine	F_{11}	3.4335 ± 0.0003	3.438	
	F_{12}	-0.1016 ± 0.0002	-0.108	
	F_{22}	0.3341 ± 0.0041	0.335	
	F_{33}	3.2806 ± 0.0088	3.274	
	F_{34}	0.0390 ± 0.0005	0.0460	11
	F_{44}	0.3764 ± 0.0001	0.378	
Arsine	F_{11}	2.8568 ± 0.0022	2.8550	
	F_{12}	0.1099 ± 0.0207	0.1420	11
	F_{22}	0.2872 ± 0.0022	0.2890	
	F_{33}	2.9892 ± 0.0403	2.6070	
	F_{34}	-0.3294 ± 0.0580	-0.5610	
	F_{44}	0.3332 ± 0.0108	0.4520	

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CHAPTER III

The variation of the parameter determining the force field has been studied as a function of the mass-ratio m_y/m_x in several XY_2 and XY_4 type molecules and a linear relation has been found to exist between the two. Force fields, coriolis constants and mean amplitudes of vibration of a number of molecules belonging to these types have been determined with the aid of the parameter-mass ratio plots.

RELATION BETWEEN FORCE FIELD PARAMETER AND MASS RATIO: XY_2 AND XY_4 TYPE MOLECULES

1. Introduction

From the preceeding chapters it is clear that the fundamental problem of intra-molecular mechanics is the determination of the normal transformation matrix L which may be written as

$$L = TA \tag{2.1}$$

where A is an orthogonal matrix. The L matrix is normalised to the inverse kinetic energy matrix G in the sense

$$L\tilde{L} = G \tag{2.2}$$

From studies conducted on isotopic species (1) it is clear that the parameter c is mass-dependent, but the true functional form of this dependence cannot be obtained from the theory of molecular vibrations. Muller and collaborators (2) have investigated the variation of the ratio L_{12}/L_{21} with a mass coupling parameter T defined as

$$T = \frac{G_{12}}{|G|^{1/2}} \tag{3.1}$$

which turns out to be a function of masses and geometry of the molecule and have noted certain regularities. The influence of atomic masses on coriolis constants and their limiting values has been studied by Cyvin et.al (3-7) for several molecular models, viz. tetrahedral XY_4, planar symmetrical XY_3, octahedral XY_6 and planar symmetrical X_2Y_4. In these works, limiting values for certain coriolis constants are evaluated when the atomic mass ratio m_y/m_x approaches infinity and zero respectively. Expressions for some of the limiting values are given in terms of force constants in the mentioned work. The mass dependence of coriolis constants, mean amplitudes of vibration and other molecular constants have been investigated by several authors (8-10). For the evaluation of force constants using bond polarizability theory usually there exists multiple solutions and it is found that these multiple solutions depend on the nature of the mass coupling or the mass ratio m_x/m_y (11).

In this chapter, the variation of the parameter c with the mass ratio m_y/m_x (ρ) has been studied for some bent XY_2 and tetrahedral XY_4 type molecules. It is found that there exists a linear relationship between the parameter and mass ratio. Using parameter-mass ratio plots, the force constants of XY_2 and XY_4 type molecules and coriolis constants and mean amplitudes of vibration of XY_4 type molecules are predicted and compared with standard values taken from the literature.

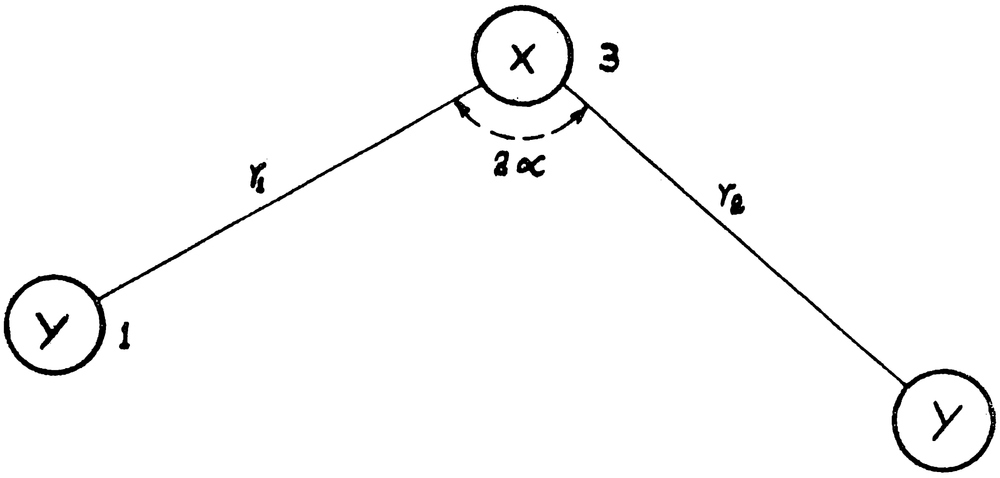

FIG. 3.1

XY_2 (C_{2v}) MOLECULAR GEOMETRY

2. Bent XY_2 Type Molecules

Bent symmetric XY_2 type molecules belong to the C_{2v} point group having a molecular geometry as shown in Fig.3.1 The three possible fundamental modes of vibration are classified as $2a_1 + b_1$. The corresponding symmetry co-ordinates (12) are

a_1 species:

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

$$S_2 = r\Delta\alpha \tag{3.2}$$

b_1 species

$$S_3 = \frac{1}{\sqrt{2}} (\Delta r_1 - \Delta r_2) \tag{3.3}$$

where Δr_1 and Δr_2 refer to changes in the $X - Y_1$ and $X - Y_2$ bond lengths and $\Delta\alpha$ to change in the interbond angle $Y\hat{X}Y$.

The G matrix elements corresponding to these symmetry co-ordinates are given below.

a_1 species:

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

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

$$G_{22} = 2[\mu_y + \mu_x (1 - \cos\alpha) \tag{3.4}$$

b_1 species:

$$G_{33} = \mu_y + \mu_x (1 - \cos\alpha) \tag{3.5}$$

The F matrix elements referred to the above set of symmetry coordinates are listed as follows.

a_1 species:

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

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

$F_{22} = f_\alpha$ (3.6)

b_1 species:

$F_{33} = f_r - f_{rr}$ (3.7)

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

3. Tetrahedral XY_4 Type Molecules

Tetrahedral XY_4 type molecules belong to the point group T_d. The internal co-ordinates and the geometry of the molecule are as shown in Fig. 3.2. According to the irreducible representations of the point group T_d, the normal vibrations are classified as a_1, e and f_2. Of these f_2 alone is of second order. Let r be the equilibrium X-Y distance and α_{12} the angle between the bonds r1 and r2. A set of symmetry co-ordinates transforming according to the irreducible representations of the T_d point group are listed below (12).

a_1 species

$$S_1 = 1/2\ (\Delta r_1 + \Delta r_2 + \Delta r_3 + \Delta r_4) \qquad (3.8)$$

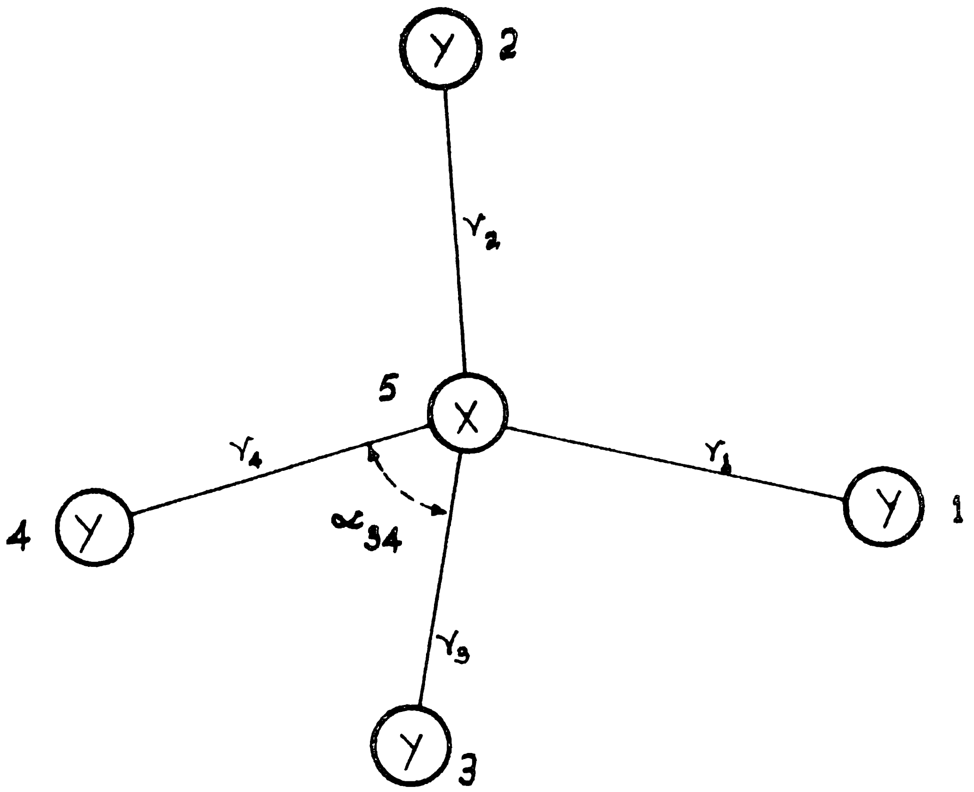

FIG. 3.2

TETRAHEDRAL XY4 MODEL : MOLECULAR GEOMETRY e species:

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

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

(3.9)

f_2 species:

$$S_{3a} = ½ (\Delta r_1 - \Delta r_2 + \Delta r_3 - \Delta r_4)$$

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

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

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

$$S_{3c} = ½ (\Delta r_2 + \Delta r_3 - \Delta r_1 - \Delta r_4)$$

$$S_{4c} = \frac{r}{\sqrt{2}} (\Delta\alpha_{14} - \Delta\alpha_{23}) \tag{3.10}$$

where Δr and $\Delta\alpha$ are the changes in bond lengths and bond angles.

The G matrix elements corresponding to these symmetry co-ordinates are

a_1 species:

$$G_{11} = \mu_y \tag{3.11}$$

e species:

$$G_{22} = 3\mu_y \tag{3.12}$$

f_2 species:

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

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

$$G_{44} = \frac{16}{3}\mu_x + 2\mu_y \qquad (3.13)$$

The symmetry F elements are given by

a_1 species:

$$F_{11} = f_r + 3\,f_{rr} \qquad (3.14)$$

e species:

$$F_{22} = (\,f_{\alpha} - 2\,f_{\alpha\alpha} + f'_{\alpha\alpha}\,) \qquad (3.15)$$

f_2 species:

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

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

$$F_{44} = (\,f_{\alpha} - f'_{\alpha\alpha}) \qquad (3.16)$$

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

4. Force fields

The a_1 species force fields of XY_2 type molecules and f_2 species force fields of XY_4 type molecules are studied here. The a_1 and f_2 species of vibrations of these molecules are of second order and hence they can be expressed as quadratic functions of the parameter c (Eqs. 2.7 - 2.9). The parameter c has been evaluated from exact force fields employing the procedure discussed in Chapter II. Plots of parameter c versus mass ratio ρ have been drawn and are found to be linear (Fig. 3.3). Values of c as well as ρ are collected in Table 3.1 References for exact force fields and harmonic frequencies of respective molecules are also given in Table 3.1. With the help of the parameter mass-ratio graphs, the force fields of a few molecules have been predicted. It can be seen from Tables 3.2 and 3.3 that these predicted force fields agree very well with those reported in literature.

5. Coriolis Constants

As described in the introductory chapter the coriolis constants can be calculated by the method put forward by Meal and Pole (13):

$$\zeta^{\alpha} = L^{-1} C^{\alpha} (\tilde{L})^{-1} \qquad \left[\text{Eq. (1.42)}\right]$$

The C^{α} matrices can be calculated from the geometry and atomic masses of the molecule. Substituting for L matrix in the parametric formalism eq. 1.42 can be written as:

$$\zeta^{\alpha} = (TA)^{-1} C^{\alpha} (\tilde{A}\tilde{T})^{-1} \qquad (3.17)$$

or

$$\mathcal{J}^{\alpha} = \tilde{A}\ J\ A \qquad [\text{Eq. } (1.44)]$$

where $J = T^{-1}\ C^{\alpha}\ (\tilde{T})^{-1}$ (3.18)

with T matrix in the triangular form.

The C^{α} matrix for the $f_2 \times f_2$ type coriolis coupling in the tetrahedral XY_4 model (14) is given by

$$C_{33} = \frac{4}{3}\mu_x$$

$$C_{34} = \frac{8}{3}\mu_x + \mu_y$$

$$C_{44} = \frac{16}{3}\mu_x + \mu_y \qquad (3.18)$$

Substituting for the C^{α} matrix in eq. (3.17) the elements of the J matrix are obtained.

$$J_{33} = \frac{C_{33}}{T_{33}^{2}}$$

$$J_{34} = -\frac{C_{33}\ T_{43}}{T_{33}^{2}\ T_{44}} + \frac{C_{34}}{T_{33}\ T_{44}}$$

$$J_{44} = \frac{C_{33}T_{43}^{2}}{T_{33}^{2}T_{44}^{2}} - \frac{2\ C_{34}\ T_{43}}{T_{33}\ T_{44}^{2}} + \frac{C_{44}}{T_{44}^{2}}$$

(3.19)

The diagonal elements of the $\mathcal{J}^{\alpha}$ matrix are given by the following expressions

$$\mathcal{J}_{33} = \frac{1}{1 + c^{2}}\left[J_{33} - 2c\ J_{34} + c^{2}\ J_{44}\right]$$

$$\mathcal{J}_{44} = \frac{1}{1 + c^{2}}\left[J_{44} + 2c\ J_{34} + c^{2}\ J_{33}\right]$$

(3.20)

where c denotes the force field parameter. The $\mathcal{T}_{33}$ and $\mathcal{T}_{44}$ values are calculated for some molecules taking the c values from the c versus ρ plot. As can be seen from Table 3.4 the calculated $\mathcal{T}$ values agree well with the experimental values.

6. Mean amplitudes of Vibration

The mean amplitudes of vibration l (X - Y) and l (Y---Y) can be expressed in terms of the symmetrized mean square amplitude matrix Σ (14). where Σ is given by

$$\Sigma = L \Delta \tilde{L} \qquad \left[\text{Eq. } (1.46)\right]$$

and

$$\Delta_i = \frac{h}{8\pi^2 \omega_i} \coth \frac{h\omega_i}{2KT} \qquad \left[\text{Eq. } (1.47)\right]$$

For a second order vibrational species the elements of the Σ matrix (15) can be expressed in terms of parameter c using eq. (1.25) and (1.27) in (1.46).

The Σ matrix elements are

$$\Sigma_{11} = \frac{T_{11}^2 \Delta_2 c^2}{1 + c^2} + \frac{T_{11}^2 \Delta_1}{1 + c^2}$$

$$\Sigma_{12} = \frac{T_{11} T_{21} \Delta_2 c^2}{1 + c^2} + \frac{T_{11} T_{22} (\Delta_2 - \Delta_1) c}{1 + c^2} + \frac{T_{11} T_{21} \Delta_1}{1 + c^2}$$

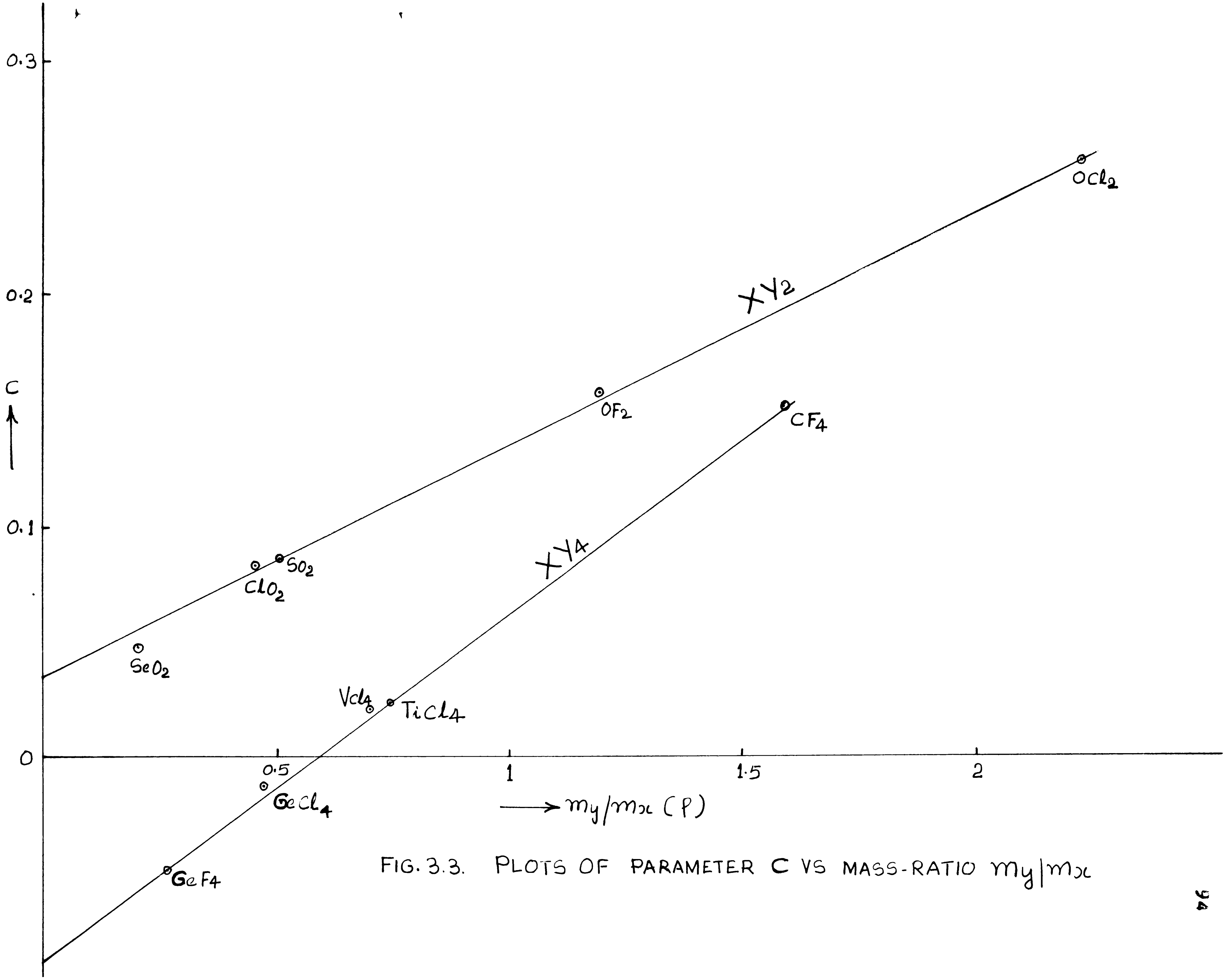

FIG. 3.3. PLOTS OF PARAMETER C VS MASS-RATIO m_y/m_x

$$\Sigma_{22} = \frac{(T_{22}^2 \Delta_1 + T_{21}^2 \Delta_2)\, c^2}{1 = c^2} + \frac{2\, T_{21}\, T_{22}\, (\Delta_2 - \Delta_1)\, c}{1 + c^2} + \frac{T_{21}^2 \Delta_1 + T_{22}^2 \Delta_2}{1 + c^2} \tag{3.21}$$

Using the above Σ elements the mean square amplitudes for the XY_4 system can be written as

$$l\,(X - Y)^2 = \frac{1}{4} \Sigma(a_1) + \frac{3}{4} \Sigma_{11}(f_2) \tag{3.22}$$

$$l\,(Y---Y)^2 = \frac{2}{3} \Sigma(a_1) + \frac{1}{9} \Sigma(e) + \frac{2}{3} \Sigma_{11}(f_2) - \frac{2}{3} \Sigma_{12}(f_2) + \frac{1}{6} \Sigma_{22}(f_2) \tag{3.23}$$

with the aid of eq. (3.22) the bonded mean amplitudes of vibration $l\,(x-y)$ for some XY_4 molecules are calculated and compared with the literature values (Table 3.5).

7. Discussion

From the results given above it is clear that this is a simple and straightforward method for the approximate evaluation of force constants and other molecular constants. It is found that separate straight lines connecting parameter c and mass ratio ρ are obtained for XY_2 and XY_4 molecules. Hence for an XY_n system ($n = 2, 4$)

the relation between parameter c and mass ratio can be expressed as

$$c = k\rho + l \tag{3.24}$$

The slope k and intercept l are characteristic of the molecular system XY_n. The values of the constants k and l for the bent XY_2 molecular model are found to be 0.1 and 0.034 respectively. For the tetrahedral XY_4 system, however $k = 0.144$ and $l = -0.085$. Such relationships will be of value in the elimination of spurious force fields and also the correct assignment of frequencies and other molecular constants.

TABLE 3.1

VALUES OF MASS RATIO AND PARAMETER

Molecular type	Molecule	Mass ratio ρ	Parameter e	Reference for exact force fields
XY_2	SeO_2	0.203	0.046	16
	$Cl\ O_2$	0.451	0.082	17
	$S\ O_2$	0.499	0.084	18
	$O\ F_2$	1.188	1.156	19
	$O\ Cl2$	2.216	0.256	20
XY_4	$Ge\ F_4$	0.262	-0.048	21
	$Ge\ Cl_4$	0.469	-0.013	21
	$V\ Cl_4$	0.696	0.02	21
	$Ti\ Cl4$	0.74	0.022	21
	$C\ F_4$	1.582	0.15	21

TABLE 3.2

FORCE FIELDS OF XY_2 TYPE MOLECULES

Molecule	Force Fields*(A_1) mdyn/A°		Reference
	Present work	Previous result	
NO_2	12.375 0.390 1.188	12.309 0.592 1.100	22
Cl_2S	2.586 -0.021 0.295	2.58 0. 0.294	23
MgF_2	2.236 -0.02 0.1465	2.321 0.03 0.141	24
SrF_2	5.0398 -0.063 0.362	5.329 0.174 0.44	25
CaF_2	2.364 0.014 0.085	2.48 0.05 0.08	26

* The three values of the force constants reported corresponds to F_{11}, F_{12} and F_{22}.

TABLE 3.3

FORCE FIELDS OF XY_4 TYPE MOLECULES

Molecule	Force Fields * (f_2) mdyn/A°		Reference
	Present work	Previous result	
SiF_4	6.592	6.406 ± 0.37	21
	0.345	0.291 ± 0.15	
	0.435	0.438 ± 0.01	
$SiCl_4$	2.744	2.96 ± 0.09	21
	0.109	0.14 ± 0.03	
	0.242	0.236 ± 0.005	
$SnCl_4$	2.53	2.688 ± 0.08	21
	0.121	0.22 ± 0.1	
	0.122	0.118 ± 0.01	
RuO_4	6.699	6.49 ± 0.05	21
	0.369	0.07 ± 0.05	
	0.390	0.381 ± 0.05	
OsO_4	7.903	8.11 ± 0.08	21
	0.358	0.1 ± 0.1	
	0.441	0.47 ± 0.01	

*The three values of the force constants corresponds to F_{33}, F_{34} and F_{44}.

TABLE 3.4

CORIOLIS CONSTANTS OF XY_4 TYPE MOLECULES

Molecule	ζ_3		ζ_4		Reference
	Present work	Previous result	Present work	Previous result	
SiF_4	0.4486	0.56	0.0527	0.09	27
$SnCl_4$	0.344	0.26 ± 0.05	0.1558	0.22 ± 0.05	28
$GeCl_4$	0.4145	0.396 ± 0.05	0.0824	0.104 ± 0.05	29
RuO_4	0.2666	0.18 ± 0.05	0.2314	0.32 ± 0.03	28
OsO_4	0.21173	0.093	0.2885	U.407	28

TABLE 3.5

MEAN AMPLITUDES OF VIBRATION OF XY_4 TYPE MOLECULES

Molecule	Mean amplitudes of Vibration (l(X-Y)A°		Reference
	Present work	Previous result	
$SnCl_4$	0.0459	0.046	29
$SiCl_4$	0.0465	0.0479 ± 0.0016	30
$GeCl_4$	0.0504	0.047 ± 0.003	31
$Si\ F_4$	0.0382	0.0394	32
$Ru\ O_4$	0.0366	0.0372	33
$Os\ O_4$	0.0346	0.036 ± 0.002	34

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CHAPTER IV

HYBRID HIGH LOW FREQUENCY SEPARATION (HLFS) METHOD: HARMONIC FORCE FIELDS OF METHYL HALIDES (XY_3Z)

A parameter formulation of Wilson's High low Frequency Separation (HLFS) Method is given in conjunction with isotopic frequencies in a third order vibrational problem. A new approximation scheme called the "Hybrid HLFS Method" is proposed which is superior to pure HLFS method in the sense that it enables the evaluation of all the twelve force constants. This, however, furnishes two sets of force fields out of which one is seen to be in better agreement with that obtained using various additional data.

1. Introduction

The normal coordinate analysis of molecules with three or more vibrations in a single species has attracted the attention of several authors in the recent past (1-6). As mentioned earlier the evaluation of $1/2$ n(n+1) ~~(n+1)~~ elements of the force constant matrix F using n vibrational frequencies in the general valence representation is a cumbersome exercise. Even with the knowledge of additional experimental data a satisfactory solution of the force field is often difficult in many cases. So one is usually forced to adopt some approximation method force normal coordinate analysis. Pesudo-exact force constants for some third order vibrational problems have been evaluated by Muller and Rai (4) and also by Ananthakrishnan (5), using coriolis coupling constants. Recently Ramaswamy et al (6) have proposed a method for the determination of angle parameters of some XYZ type molecules utilizing isotopic frequencies. Along with isotopic frequencies Schmidt and Muller (3) have applied high-low frequency separation (HLFS) method for a few molecules.

In the present work a parameter formulation of the HLFS method (7-9) mentioned in the Introduction Chapter is given in conjunction with isotopic frequencies in a third order vibrational problem. The original n=3 problem involves a set of three parameters. Corresponding to high frequency separation, for example, only one of the parameters (the one associated with the second order determinant) is different from zero but the other two parameters are constrained at the zero value. In order to rectify this defect of the HLFS method, a new approximation scheme called "Hybrid HLFS Method" is proposed which is superior to pure HLFS method in the sense that it leads to a complete knowledge of all the three parameters. The use of isotopic frequencies enhances the reliability of HLFS method and the method developed in an earlier paper (10) is followed to harness the isotopic frequency data in evaluating the HLFS parameters. This method is applied to the vibrations of methyl halides and the force constants obtained here are in excellent agreement with the exact values reported earlier using additional experimental data such as isotopic shifts, coriolis coupling constants and centrifugal distortion constants (10).

2. HLFS Method in the Parameter Formalism

In Wilson's FG matrix method the F and G matrices satisfy the trace relation

$$\mathrm{tr}\ GF = \sum_{i} \lambda_{i} \qquad (4.1)$$

where $\lambda i = 4 \pi c^2 (\omega_i)^2$, ω_i being the harmonic frequency in cm^{-1}. For a pair of isotopic species labelled A, B let us introduce the matrix differences (9)

$$\Delta G^{AB} = G^{A} - G^{B} \qquad (4.2)$$

and

$$\Delta \lambda_{i}^{AB} = \lambda_{i}^{A} - \lambda_{i}^{B} \qquad (4.3)$$

Consider a vibrational species of order three so that eq. (4.1) gives

$$\begin{aligned} \Delta G_{11}^{AB} F_{11} + \Delta G_{22}^{AB} F_{22} + \Delta G_{33}^{AB} F_{33} + 2\Delta G_{12}^{AB} F_{12} \\ + 2\Delta G_{13}^{AB} F_{13} + 2\Delta G_{23}^{AB} F_{23} \\ = \Delta\lambda_{1}^{AB} + \Delta\lambda_{2}^{AB} + \Delta\lambda_{3}^{AB} \end{aligned} \qquad (4.4)$$

"Approximate separation of high and low frequencies" HLFS developed by Crawford and Edsall (6) and Wilson et. al (7,8) enables one to reduce the order of secular determinant describing the vibrations of molecules by factoring out the vibrations corresponding to higher or the lower frequencies. The secular equation

$$\left| GF - \lambda E \right| = 0 \qquad (4.5)$$

can be written also in the form

$$\left| F - G^{-1}\lambda \right| = 0 \qquad (4.6)$$

The factoring of the higher frequency vibrations (HFS) is accomplished by dropping the corresponding rows and columns of G^{-1} and F and then by solving the truncated secular determinant using eq. (4.6). On the other hand, if one uses eq. (4.5), this reduction of the secular determinant is equivalent to using a reduced G° matrix whose elements are given by the equation

$$G^{\circ}_{tt'} = G_{tt'} - \sum_{ss'} G_{ts} X_{ss'} G_{s't'} \tag{4.7}$$

where s covers the co-ordinates S_s to be held rigid, while the elements $X_{ss'}$ satisfy the equation

$$\sum_{s'} X_{ss'} G_{s's''} = \delta_{ss''} \tag{4.8}$$

The factoring of the lower frequency vibration (LFS) is achieved simply by dropping the corresponding rows and columns of G and F and by solving the reduced secular determinant using eq. (4.5)

A third order secular determinant $|GF - \lambda E|$ can be factored into a second order determinant and a first order one by the above seperation method. For a third order vibrational species the elements of the reduced G matrix are given by

HFS

$$G^{\circ}_{11} = G_{11}$$

$$G^{\circ}_{12} = 0$$

$$G^{\circ}_{13} = 0$$

$$G^{\circ}_{22} = G_{22} - \frac{G_{12}^{2}}{G_{11}}$$

$$G^{\circ}_{23} = G_{23} - \frac{G_{12}\, G_{13}}{G_{11}}$$

$$G^*_{33} = G_{33} - \frac{G^2_{13}}{G_{11}} \qquad (4.9)$$

LFS

$$G^*_{11} = G_{11}$$

$$G^*_{12} = G_{12}$$

$$G^*_{13} = 0$$

$$G^*_{22} = G_{22}$$

$$G^*_{23} = 0$$

$$G^*_{33} = G_{33} \qquad (4.10)$$

With the highest frequency separated to give a first order determinant and the remaining frequencies to yield a second order one eq.(4.4) breaks up into

$$\Delta G^{AB}_{11} F_{11} = \Delta \lambda^{AB}_{1} \qquad (4.11)$$

$$\Delta G^{*AB}_{22} F_{22} + \Delta G^{*AB}_{33} F_{33} + 2\Delta G^{*AB}_{23} F_{23} = \Delta\lambda^{AB}_{2} + \Delta\lambda^{AB}_{3}$$

(4.12)

where G^*_{22}, G^*_{33} and G^*_{23} are elements of the reduced G^* matrix (eq.4.7)

In low frequency separation the corresponding relations are

$$\Delta G_{33}^{AB} F_{33} = \Delta \lambda_3^{AB} \qquad (4.13)$$

$$\left.\begin{aligned} \Delta G_{11}^{AB} F_{11} + \Delta G_{22}^{AB} F_{22} + \\ 2 \Delta G_{12} F_{12} \end{aligned}\right\} = \Delta \lambda_1^{AB} + \Delta \lambda_2^{AB} \qquad (4.14)$$

The F elements in eqs. (4.12) and (4.14) can be expressed in terms of the parameter c using eqs. (2.7) to (2.9).

$$\begin{aligned} c^2 \Big\{ & \Delta G_{22}^{\bullet AB} \left[(T_{22}^{-1})^2 \lambda_3 + (T_{23}^{-1})^2 \lambda_2 \right] + 2 \Delta G_{23}^{\bullet AB} T_{23}^{-1} T_{33}^{-1} \lambda_2 \\ & + \Delta G_{33}^{\bullet AB} (T_{33}^{-1})^2 \lambda_2 - (\Delta \lambda_2^{AB} + \Delta \lambda_3^{AB}) \Big\} \\ & + c \left[2 (\lambda_3 - \lambda_2) (\Delta G_{22}^{\bullet AB} T_{22}^{-1} T_{23}^{-1} + \Delta G_{23}^{\bullet AB} T_{22}^{-1} T_{33}^{-1}) \right] \\ & + \Delta G_{22}^{\bullet AB} \left[(T_{22}^{-1})^2 \lambda_2 + (T_{23}^{-1})^2 \lambda_3 \right] + 2 \Delta G_{23}^{\bullet AB} T_{23}^{-1} T_{33}^{-1} \lambda_3 \\ & + \Delta G_{33}^{\bullet AB} (T_{33}^{-1})^2 \lambda_3 - (\Delta \lambda_2^{AB} + \Delta \lambda_3^{AB}) = 0 \end{aligned} \qquad (4.15)$$

$$\begin{aligned} c^2 \Big\{ & \Delta G_{11}^{AB} \left[(T_{11}^{-1})^2 \lambda_2 + (T_{21}^{-1})^2 \lambda_1 \right] + 2 \Delta G_{12}^{AB} T_{21}^{-1} T_{22}^{-1} \lambda_1 \\ & + \Delta G_{22}^{AB} (T_{22}^{-1})^2 \lambda_1 - (\Delta \lambda_1^{AB} + \Delta \lambda_2^{AB}) \Big\} \\ & + c \left[2 (\lambda_2 - \lambda_1) (\Delta G_{11}^{AB} T_{11}^{-1} T_{22}^{-1} + \Delta G_{12}^{AB} T_{11}^{-1} T_{22}^{-1}) \right] + \end{aligned}$$

$$+\ \Delta G^{AB}_{11}\left[(T^{-1}_{11})^{2}\ \lambda_1 + (T^{-1}_{21})^{2}\ \lambda_2\right] + 2\Delta G^{AB}_{12}\ T^{-1}_{21}\ T^{-1}_{22}\ \lambda_2$$

$$+\ \Delta G^{AB}_{22}\ (T^{-1}_{22})^{2}\ \lambda_2 - \left(\Delta\lambda_1^{AB} + \Delta\lambda_2^{AB}\right) = 0 \qquad (4.16)$$

Solving these equations two parameters c_1 and c_2 are obtained corresponding to high frequency separation and low frequency separation.

3. Hybrid HLFS Method

It is clear that in the pure HLFS method a three parameter problem is reduced to a two parameter one. Thus for example when the highest frequency is separated, the mixing occurs between the two lower frequencies, and this is represented by a non-zero angle of rotation in the plane of the corresponding symmetry coordinates. The complete A matrix is parametrised in terms of three angle parameters (Eulerian angles) and can be generated by taking the product of three rotation matrices each referring to a two dimensional rotation. Let A_H and A_L be the approximate A matrices corresponding to high frequency separation and low frequency separation respectively, that are obtained by the use of isotopic data. We assume that the complete A matrix is approximated by taking the product of A_H and A_L. This approach is called the "Hybrid HLFS method". Since the commutator $[A_H, A_L] \neq 0$, this gives two distinct solutions for the A matrix. Denoting the product $A_H\ A_L$ and $A_L\ A_H$ by A_{HL} and A_{LH} respectively, these matrices are written as

$$A_{HL}= \begin{bmatrix} \frac{1}{\sqrt{1+c_2^2}} & \frac{c_2}{\sqrt{1+c_2^2}} & 0 \\ \frac{-c_2}{\sqrt{1+c_1^2}\ \sqrt{1+c_2^2}} & \frac{1}{\sqrt{1+c_1^2}\ \sqrt{1+c_2^2}} & \frac{c_1}{\sqrt{1+c_1^2}} \\ \frac{c_1c_2}{\sqrt{1+c_1^2}\ \sqrt{1+c_2^2}} & \frac{-c_1}{\sqrt{1+c_1^2}\ \sqrt{1+c_2^2}} & \frac{1}{\sqrt{1+c_1^2}} \end{bmatrix} \qquad (4.17)$$

$$A_{LH}= \begin{bmatrix} \frac{1}{\sqrt{1+c_2^2}} & \frac{c_2}{\sqrt{1+c_1^2}\ \sqrt{1+c_2^2}} & \frac{c_1c_2}{\sqrt{1+c_1^2}\ \sqrt{1+c_2^2}} \\ \frac{-c_2}{\sqrt{1+c_2^2}} & \frac{1}{\sqrt{1+c_1^2}\ \sqrt{1+c_2^2}} & \frac{c_1}{\sqrt{1+c_1^2}\ \sqrt{1+c_2^2}} \\ 0 & \frac{-c_1}{\sqrt{1+c_1^2}} & \frac{1}{\sqrt{1+c_1^2}} \end{bmatrix} \qquad (4.18)$$

Equating A_{HL} or A_{LH} to a matrix parametrized in terms of Eulerian angles $\alpha,\ \beta,\ \gamma$ we deduce the following relations

$$\sin\beta = \begin{cases} \dfrac{-c_1\ c_2}{\sqrt{1+c_1^2}\ \sqrt{1+c_2^2}} \\ 0 \end{cases} \qquad (4.19)$$

$$\sin\alpha\cos\beta = \begin{cases} \dfrac{c_2}{\sqrt{1+c_1^2}\ \sqrt{1+c_2^2}} \\ \dfrac{c_2}{\sqrt{1+c_1^2}} \end{cases} \qquad (4.20)$$

$$\cos\beta\ \sin\gamma = \begin{cases} \dfrac{c_1}{\sqrt{1+c_1^2}\ \sqrt{1+c_2^2}} \\ \dfrac{c_1}{\sqrt{1+c_1^2}} \end{cases} \qquad (4.21)$$

The third order F matrix elements are listed below:

$$\begin{aligned} F_{11} = {} & \lambda_1 \left(A_{11}T_{11}^{-1} + A_{21}T_{21}^{-1} + A_{31}T_{31}^{-1}\right)^2 \\ & + \lambda_2 \left(A_{12}T_{11}^{-1} + A_{22}T_{21}^{-1} + A_{32}T_{31}^{-1}\right)^2 \\ & + \lambda_3 \left(A_{13}T_{11}^{-1} + A_{23}T_{21}^{-1} + A_{33}T_{31}-1\right)^2 \end{aligned}$$

$$F_{22} = \lambda_1 (A_{21}T_{22}^{-1} + A_{31}T_{32}^{-1})^2 + \lambda_2(A_{22}T_{22}^{-1} + A_{32}T_{32}^{-1})^2$$

$$+ \lambda_3(A_{23}T_{22}^{-1} + A_{33}T_{32}^{-1})^2$$

$$F_{33} = (T_{33}^{-1})^2(\lambda_1 A_{31}^2 + \lambda_2 A_{32}^2 + \lambda_3 A_{33}^2)$$

$$F_{12} = T_{11}^{-1} T_{22}^{-1} (\lambda_1 A_{11}A_{21} + \lambda_2 A_{12}A_{22} + \lambda_3 A_{13}A_{23})$$

$$+ T_{11}^{1} T_{32}^{-1} (\lambda_1 A_{11}A_{31} + \lambda_2 A_{12}A_{32} + \lambda_3 A_{13}A_{33})$$

$$+ T_{21}^{-1} T_{22}^{-1} (\lambda_1 A_{21}^2 + \lambda_2 A_{22}^2 + \lambda_3 A_{23}^2)$$

$$+ (T_{21}^{-1}T_{32} + T_{22}^{-1}T_{31}^{-1})(\lambda_1 A_{21}A_{31} + \lambda_2 A_{22}A_{32}$$

$$+ \lambda_3 A_{23}A_{33}$$

$$+ T_{31}^{-1}T_{32}^{-1} (\lambda_1 A_{31}^2 + \lambda_2 A_{32}^2 + \lambda_3 A_{33}^2)$$

$$F_{13} = T_{11}^{-1} T_{33}^{-1} (\lambda_1 A_{11}A_{31} + \lambda_2 A_{12}A_{32} + \lambda_3 A_{13}A_{33})$$

$$+ T_{21}^{-1}T_{33}^{-1} (\lambda_1 A_{21}A_{31} + \lambda_2 A_{22}A_{32} + \lambda_3 A_{23}A_{33})$$

$$+ T_{31}^{-1}T_{33}^{-1}(\lambda_1 A_{31}^2 + \lambda_2 A_{32}^2 + \lambda_3 A_{33}^2)$$

$$F_{23} = T_{22}^{-1}T_{33}^{-1} (\lambda_1 A_{21}A_{31} + \lambda_2 A_{22}A_{32} + \lambda_3 A_{23}A_{33})$$

$$+ T_{32}^{-1}T_{33}^{-1} (\lambda_1 A_{31}^2 + \lambda_2 A_{32}^2 + \lambda_3 A_{33}^2)$$

(4.22)

where

$A_{11} = \cos\alpha \cos\beta$

$A_{12} = \sin\alpha \cos\gamma - \sin\gamma \cos\alpha \sin\beta$

$A_{13} = \sin\alpha \sin\gamma + \cos\alpha \sin\beta \cos\gamma$

$A_{21} = -\sin\alpha \cos\beta$

$A_{22} = \cos\alpha \cos\gamma + \sin\alpha \sin\beta \sin\gamma$

$A_{23} = \cos\alpha \sin\gamma - \sin\alpha \sin\beta \cos\gamma$

$A_{31} = -\sin\beta$

$A_{32} = -\cos\beta \sin\gamma$

$A_{33} = \cos\beta \cos\gamma$

and $T_{ij}^{-1} = (T^{-1})_{ij}$.

4. Methyl Halides

Methyl halides belong to the XY_3Z type having C_{3v} point group symmetry and possess the molecular geometry as shown in Fig. (4.1). There are three vibrations each in a_1 and e species. The symmetry co-ordinates employed for the calculation are given below (11)

a_1 species:

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

$$S_{2a} = \frac{r}{\sqrt{6}} (\Delta\alpha_1 + \Delta\alpha_2 + \Delta\alpha_3 - \Delta\beta_1 - \Delta\beta_2 - \Delta\beta_3)$$

$$S_{2b} = \frac{1}{\sqrt{6}} (\Delta\alpha_1 + \Delta\alpha_2 + \Delta\alpha_3 + \Delta\beta_1 + \Delta\beta_2 + \Delta\beta_3)$$

$$S_3 = R.$$

(4.23)

The redundancy in the symmetry co-ordinates S_{2a} and S_{2b} may be removed by the orthonormal transformation

$$S_2 = p.\, S_{2a} - Q.\, S_{2b} \qquad (4.24)$$

where

$$P = (1+K)/(2+2K^2)^{1/2}$$

$$Q = (1-K)/(2+2K^2)^{1/2}$$

and

$$K = \frac{-\, 3 \sin\beta \cos\beta}{\sin\alpha}$$

e species:

$$S_{4x} = \frac{1}{\sqrt{6}} (2\Delta r_1 - \Delta r_2 - \Delta r_3)$$

$$S_{4y} = \frac{1}{2} (\Delta r_2 - \Delta r_3)$$

$$S_{5x} = \frac{1}{\sqrt{6}} (2\Delta\alpha_1 - \Delta\alpha_2 - \Delta\alpha_3)$$

$$S_{5y} = \frac{1}{\sqrt{2}} (\Delta\alpha_2 - \Delta\alpha_3)$$

$$S_{6x} = \frac{1}{\sqrt{6}} (2\Delta\beta_1 - \Delta\beta_2 - \Delta\beta_3)$$

$$S_{6y} = \frac{1}{\sqrt{2}} (\Delta\beta_2 - \Delta\beta_3) \qquad (4.25)$$

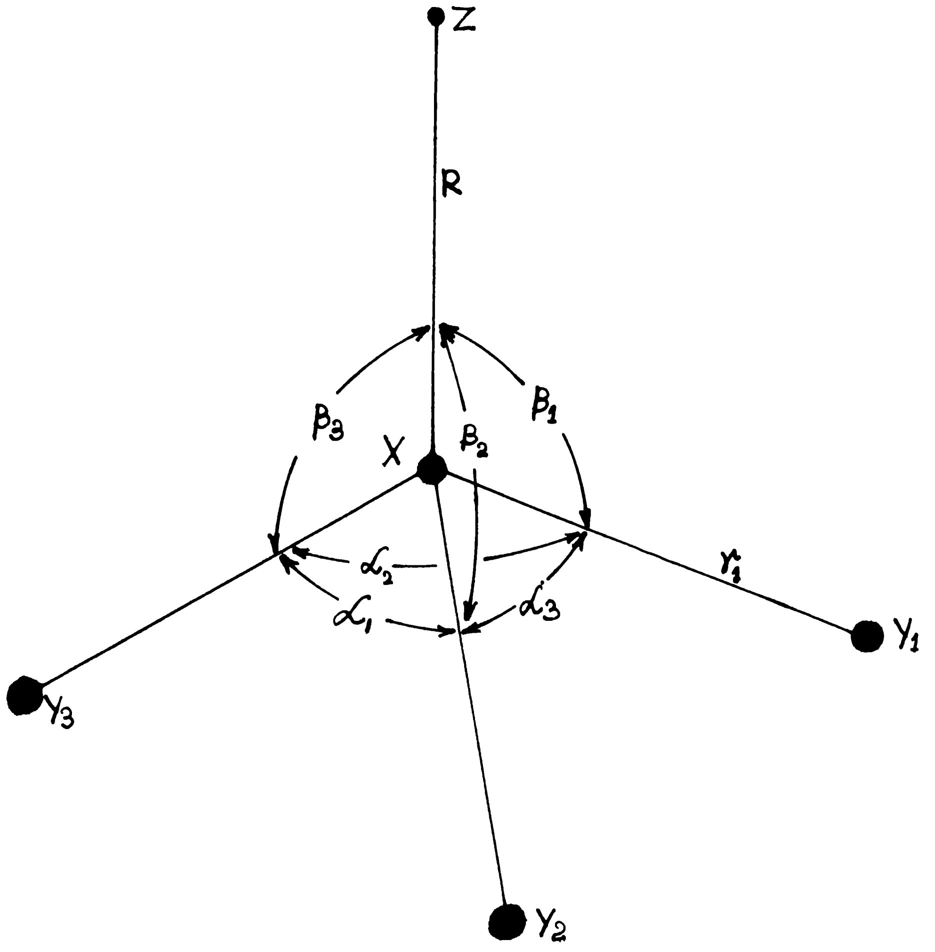

FIG. 4.1 XY_3Z (C_{3v}) MOLECULAR GEOMETRY

where r and R represent the equilibrium distance X-Y and X-Y respectively. Δr_1, Δr_2 and Δr_3 are the changes in bond lengths and $\Delta\alpha_1$, $\Delta\alpha_2$, $\Delta\alpha_3$, $\Delta\beta_1$, $\Delta\beta_2$ and $\Delta\beta_3$ are the changes in bond angles $Y\hat{X}Y$ and $Y\hat{X}Z$.

The G matrix elements corresponding to these symmetry co-ordinates are

a_1 species:

$$G_{11} = \mu_y + 3\mu_x \cos^2\beta$$

$$G_{12} = \frac{3\mu_x\sqrt{K^2+1}}{\sin\beta\cos\beta}$$

$$G_{13} = \sqrt{3}\,\mu_x \cos\beta$$

$$G_{22} = (K^2+1)\,(\mu_y + 3\mu_x \sin^2\beta\ )$$

$$G_{23} = \sqrt{3}\,\mu_x\,\sqrt{K^2+1}\quad\sin\beta$$

$$G_{33} = \mu_x + \mu_z \tag{4.26}$$

e species:

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

$$G_{45} \quad \frac{\mu_x\,(1-\cos\alpha)}{\sin\alpha}$$

$$G_{46} = \frac{3\,\mu_x\,\sin\beta\,(\cos\beta - L)}{2}$$

$$G_{55} = \mu_y\left(3 - \frac{K^2}{2}\right) + \frac{\mu_x (1 - \cos\alpha)^3}{\sin^2\alpha}$$

$$G_{56} = \frac{K}{2}\left[\frac{\mu_y - 3\mu_x (\cos\beta - L)(1 - \cos\alpha)}{\cos\beta}\right]$$

$$G_{66} = \mu_y + \frac{3\mu_x (\cos\beta - L)^2 + 3\mu_z L^2}{2}$$

(4.27)

$$L = \frac{r}{R} \quad \text{and} \quad K = \frac{-3 \sin\beta \cos\beta}{\sin\alpha}$$

The elements of the F matrix are

a_1 species:

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

$$F_{12} = \frac{1}{\sqrt{2}} (2 f_{r\alpha} - f_{r\beta} + f'_{r\alpha} - f'_{r\beta})$$

$$F_{13} = \sqrt{3} \quad f_{rR}$$

$$F_{22} = \frac{1}{2} (f_\alpha + f_\beta + 2 f_{\alpha\alpha} + 2 f_{\beta\beta} - 2f'_{\alpha\beta})$$

$$- 4 f_{\alpha\beta})$$

$$F_{23} = \frac{3}{\sqrt{6}} (f_{R\alpha} - f_{R\beta})$$

$$F_{33} = f_R$$

(4.28)

e species:

$$F_{44} = f_r - f_{rr}$$

$$F_{45} = f'_{r\alpha} - f_{r\alpha}$$

$$F_{46} = f_{r\beta} - f'_{r\beta}$$

$$F_{55} = f_{\alpha} - f_{\alpha\alpha}$$

$$F_{56} = f'_{\alpha\beta} - f_{\alpha\beta}$$

$$F_{66} = f_{\beta} - f_{\beta\beta} \qquad (4.29)$$

5. Results and Discussion

All the twelve force constants F_{ij} (i, j = 1, 2 . . . 6) of methyl chloride, bromide and iodide have been calculated using the above method. The harmonic frequencies used for the calculation are taken from ref.(12). The force fields are calculated first by the pure HLFS method (Table 4.1). But by this method the interaction force constants F_{13} and F_{46} cannot be calculated. Hence the force fields are evaluated once again by the modified "Hybrid HLFS method". Force constants corresponding to A_{HL} and A_{LH} matrices are calculated and tabulated in Table (4.2). Even though the two sets of force field obtained by this method agree well with the exact values, F_{13} and F_{46} values corresponding to the A_{LH} matrix compare better with the standard values.

The success of Hybrid HLFS method depends to a large extent on the accuracy of the data on isotopic shifts employed in the computation. Eventhough this method can be formulated excluding this additional information an infinite multiplicity of solutions would present themselves, and hence it would be difficult to choose the right solution for the force field.

TABLE 4.1

HARMONIC FORCE FIELDS OF METHYL HALIDES BY HLFS METHOD

CH_3Cl - CD_3Cl

Vibrational species	HLFS PARAMETERS		Force Constants in mdyn/A°		
	HFS c_1	LFS c_2		By HFS	By LFS
a_1	0.1704	-0.0294	F_{11}	5.453	5.5177
			F_{12}	-	0.1727
			F_{13}	-	-
			F_{22}	0.5816	0.5085
			F_{23}	-0.584	--
			F_{33}	3.5808	--
e	-0.1677	0.0826	F_{44}	5.3604	5.4261
			F_{45}	-	-0.2888
			F_{46}	-	-
			F_{55}	0.4658	0.4771
			F56	-0.0063	-
			F_{66}	0.6114	0.5623

contd...

TABLE 4.1 (Contd.)

CH_3Br - CD_3Br

Vibrational species	HLFS Parameters		Force constants in mdyn/A°		
	HFS c_1	LFS c_2		By HFS	By LFS
a_1	0.129	-0.0806	F_{11}	5.5122	5.4476
			F_{12}	-	0.2905
			F_{13}	-	-
			F_{22}	0.5296	0.49
			F_{23}	-0.4963	-
			F_{33}	2.938	-
e	-0.0259	0.0564	F_{44}	5.4209	5.4409
			F_{45}	-	-0.2204
			F_{46}	-	-
			F_{55}	0.472	0.464
			F_{56}	-0.0075	-
			F_{66}	0.5456	0.5175

Contd. ..

TABLE 4.1 (Contd.)

CH_3I - CD_3I

Vibrational species	HLFS Parameters			Force constants in mdyn/A°	
	HFS c_1	LFS c_2		By HFS	By LFS
a_1	0.1031	-0.0824	F_{11}	5.5115	5.5729
			F_{12}	-	0.2964
			F_{13}	-	-
			F_{22}	0.4949	0.4556
			F_{23}	-0.383	-
			F_{33}	2.393	-
e	-0.1428	0.067	F_{44}	5.418	5.4605
			F_{45}	-	- 0.2524
			F_{46}	-	-
			F_{55}	0.442	0.4575
			F_{56}	0.0114	-
			F_{66}	0.4881	0.4554

TABLE 4.2

HARMONIC FORCE FIELDS OF METHYL HALIDES BY "HYBRID HLFS METHOD"

CH_3Cl- CD_3Cl

Vibrational species	Hybrid HLFS Parameters			Force constants in mdyn/A^0			
		From A_{LH}	From A_{HL}		From A_{LH}	From A_{HL}	Lit. Value*
a_1	α	-1°40'	-1°38'	F_{11}	5.5052	5.5052	5.492
	β	0	17'	F_{12}	0.1136	0.1199	0.071
	γ	9°40'	9°40'	F_{13}	0.1105	0.0273	0.062
				F_{22}	0.5681	0.5684	0.54
				F_{23}	-0.5857	-0.5875	-0.489
				F_{33}	3.6292	3.6292	3.499
e	α	4°43'	4°39'	F_{44}	5.3877	5.3813	5.364
				F_{45}	-0.2763	-0.2669	-0.121
	β	0	47'	F_{46}	0.0636	0.0169	0.056
	γ	-9°31'	-9°29'	F_{55}	0.4637	0.4629	0.461
				F_{56}	-0.006	-0.003	-0.017
				F_{66}	0.6107	0.6117	0.61

contd. ..

TABLE 4.2 contd...

HARMONIC FORCE FIELDS OF METHYL HALIDES BY "HYBRID HLFS METHOD"

CH_3Br - CD_3Br

Vibrational species	Hybrid HLFS Parameters			Force constants in mdyn/A^0			
		From A_{LH}	From A_{HL}		From A_{LH}	From$_{AHL}$	Lit. value
a_1	α	-4°36'	- 4°36'	F_{11}	5.5424	5.5281	5.534
				F_{12}	0.2697	0.2843	0.107
	β	0	35'	F_{13}	0.1083	-0.086	0.039
	γ	7°21'	7°20'	F_{22}	0.5418	0.54	0.512
				F_{23}	-0.4946	-0.5056	-0.436
				F_{33}	2.9957	3.0029	2.938
e	α	3°14'	3°13'	F_{44}	5.4465	5.4448	5.436
				F_{45}	-0.2287	-0.2282	-0.135
	β	0	5'	F_{46}	0.0543	0.0467	0.074
	γ	-1°30'	-1°30'	F_{55}	0.4668	0.4647	0.454
				F_{56}	-0.049	-0.0488	-0.016
				F_{66}	0.5346	0.5346	0.545

Contd.

TABLE 4.2 (Contd.)

CH_3I - CD_3I

Vibrational species	NLFS Parameters			Force Constants in mdyn/A		
	From A_{LH}	From A_{HL}		From A_{LH}	From A_{HL}	Lit. Value*
a_1	α -4°43'	-4°41'	F_{11}	5.5384	5.5364	5.53
	β 0	30'	F_{12}	0.1813	0.295	0.155
			F_{13}	0.086	-0.08	-0.006
	γ 5°53'	5°52'	F_{22}	0.5014	0.5029	0.479
			F_{23}	-0.3989	-0.4086	-0.383
			F_{33}	2.4058	2.411	2.393
e			F_{44}	5.467	5.45	5.45
	α 3°50'	3°48'	F_{45}	-0.2448	-0.2406	-0.131
	β 0 γ -8°8'	33' -8°7'	F_{46}	0.0461	-0.0008	0.118
			F_{55}	0.4428	0.4427	0.447
			F_{56}	0.01	0.013	-0.009
			F_{66}	0.478	0.4785	0.474

* From Reference 12.

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CHAPTER V

EQUILIBRIUM CONSTANTS FOR HYDROGEN BOND FORMATION OF KETONES WITH P-CRESOL

A simple method in which the donor concentration is kept constant and acceptor concentration is varied is identified for the evaluation of equilibrium constant for complex formation in the ketone-p-cresol systems. When the acceptor concentration is changed, the intensity of the bonded OH band increases and that of the free OH decreases. The concentration at which these intensities are extremum is noted. The concentration of the donor is taken as the concentration of the complex formed. On the basis of this assumption equilibrium constants are evaluated for a few ketone-p-cresol systems in the carbontetrachloride medium.

1. Introduction

The phenomenon of hydrogen bonding is of such fundamental importance in Chemistry, Physics and Biology that during the past two decades an enormous volume of work has been done in different fields of study to understand this phenomena completely. The monogrpah by Pimentel and Mc.Cellan(1) and reviews by Cannon, (2) Coulson (3) and the papers presented at the International meeting on hydrogen bonding at Lubyana (4) cover almost the entire work done in spectroscopy and other fields of research.

2. Hydrogen Bond

A hydrogen bond exists between a functional group A-H and an atom or a group of atoms B in the same or different molecule when (a) there is evidence of bond formation or association (b) there is evidence that this new bond linking A-H and B specifically involves the hydrogen atom already bonded to A. Infrared and Raman studies provide the most commonly used tool for the detection of a hydrogen (H) bond, since the vibrational spectra are significantly disturbed by H bond formation. The hydrogen bond produces the following spectral changes in the vibrational spectra: (1) The A-H stretching mode ν_s and its harmonics are shifted to lower frequencies and the RAH bending mode ν_b is shifted to higher frequency. (2) The mode ν_s and its harmonics are broadened (3). The integrated intensity of the fundamental ν_s are temperature, concentration and solvent dependent. H bond formation has dramatically obvious and unusual affects on the infrared (IR) and Raman spectra. The most prominent of the spectral changes occur in the region of ν_s near 3500 cm^{-1} (3μ). These changes have attained the status of qualitative criteria for H bond formation and quantative indices of the H bond energy and of the other physical properties. Hence, we shall examine the behaviour of ν_s in detail.

Spectatcular reduction in the IR and Raman intensity of the band due to association will take place with a temperature rise of 10-20°C. The IR spectra of benzyl alcohol in CCl_4, presented by Coggeshall and Saier (5) , offer a striking and typical example. This sensitivity of the IR and Raman spectra for both gases and liquids was one of the earliest observations of the spectral uniqueness of H bonding system (6-9). It has been used so frequently to verify the presence of H bonded species that many workers consider it to be the primary criterion of H bonding (10-13). The drastic spectral changes caused by temperature changes are caused also by variation of the concentration of a H bonding substance in an inert solvent. The similarity is evident in the works of Coggeshall and Saier (5.14). where spectra of benzyl alcohol at several concentrations are presented together with the spectra at fixed concentration but at several temperature. The narrow band at 2.77 μ due to O-H group not participating in H bond dominates the lower frequency absorption in the most dilute solutions. At high concentrations, the broad band centered near 3.00 μ due to H bonded polymers is by far the more intense one. This extreme sensitivity of ν_s to temperature and concentration changes leads us to the following conclusions:

(a) H bonding systems involve monomeric and usually several polymeric species in rapid equilibrium.

(b) each polymer has a characteristic ν_s and the higher the polymer the lower is ν_s.

(c) each polymer has a characteristic absorption coefficient A at ν_s and the higher the polymer the higher is A.

(d) since A may increase on bond formation, a small shift of equilibrium produces a magnified spectral change.

The solvent is another variable with extreme influence on the IR and Raman spectra of H bonding substances. The changes indicate environmental influence on the distribution of monomeric and polymeric species. Every spectral characteristic of the bond, the structure and its spacing, the frequency, the band width and the integrated intensity, is sensitive to the solvent (15,16).

The recognition of the spectral influence of H bonding stimulated investigation of the effect of diluents in pure H bonding liquids and then the systematic study of binary mixtures (17-20). The extensive examinations carried out by Gordy and his co-workers were particularly important in establishing the generality of H bonding effect and determining what chemical substances have H bonding properties (21-26).

3. Equilibrium constant

Since a H bond is formed in an equilibrium reaction, the thermodynamic equations are applicable. Reliable values of thermodynamic functions of H bonds are derived from the equilibrium constant K, and its variation with temperature. The experimental techniques vary only in the approach to finding the concentration or pressure values needed to determine K. The basic relation for K is

$$K = \frac{\text{activity of product}}{\text{activity of reactants}} = \frac{[A-H\ .\ .\ .\ B]}{[A\ H]\qquad[B]} \qquad (5.1)$$

In eq. (5.1) it is common to use concentration or pressure and to adjust the experimental conditions such that these quantities are nearly equal to activity and fugacity, so that no appreciable error is involved.

The most widely used experimental methods for the determination of K are Infrared (IR), Ultra Violet (UV) and pressure volume temperature (PVT) methods. In the IR method, the concentration of the associated and non-H bonded species are determined from the intensities of both the monomeric and associated γ_s band as a function of concentration and temperature. An usual assumption made in calculating K is that no polymeric species absorb at the monomeric frequency. It is necessary to use a concentration range sufficiently low that only monomer and one polymer (usually taken to be dimer) are the important species, a condition difficult to meet in some cases. Another assumption is that the absorption coefficient does not change with temperature. Despite these necessary simplifications and the major experimental difficulty of making reliable infrared intensity measurements, the IR method probably is the most commonly used method for measuring K in solution.

The equilibrium constant can be evaluated from the infrared data using either Nash method (27) or Brown and Kubota's equation (28). For systems in which the following equilibria exist,

$$A + B \rightleftharpoons AB \qquad K_{11} = \frac{[AB]}{[A]\ [B]} \qquad (5.2)$$

$$AB + B \rightleftharpoons AB_2 \qquad K_{12} = \frac{[AB_2]}{[AB]\ [B]} \qquad (5.3)$$

Brown and Kubota have shown that

$$[A\ B] = p\ (1 + 2\ K_{12}\ b) \qquad (5.4)$$

$$[AB_2] = (p - [AB]\ )\ /2 \qquad (5.5)$$

where p is the total concentration of B that has entered into complex formation and b is the equilibrium concentration of B. The equilibrium constants K_{11} and K_{12} for the 1 : 1 and 1 : 2 complexes can be determined by graphical methods (29).

The equilibrium constants for the 1 : 1 complexes can also be determined by the Nash method. This method utilizes the relation

$$Y = K (K - \mathcal{L}) - K \qquad (5.6)$$

where Y is the reciprocal of the concentration of B monomer at equilibrium and

$$X = \frac{1}{1 - A/Ao} \qquad (5.7)$$

A_e and A are the absobances of A species at a given frequency in the absence and in the presence of B respectively. The quantity $\mathcal{L}$ is equal to K ($\varepsilon c/\varepsilon e$), where εc and εe are the molar absorptivities of complexed and free A species respectively. The intercept of the plot of Y against X is the negative value of the equilibrium constant for the 1 : 1 complex.

In UV spectral study, in general the same procedure and assumptions are used as in the IR method. Because there is smaller separation of monomer and polymer bands UV techniques usually cannot be applied in cases where multiple species exist. For solutions of compounds with appropriate chromophoric groups in monomeric and a single H bonded species the UV method ranks with the IR method in utility.

In the PVT method the pressure of a known volume and weight of gas is measured over a temperature range. In this method it is common to assume that only one polymeric species occurs, normally the dimer. More can be assumed, but the addition of adjustable constants tends to make the interpretation ambiguous. The PVT method is a reasonably good one, particularly when the assumption of a single polymeric form is valid.

4. Hydrogen Bond Formation of Ketone-P-Cresol Systems-Solvent Effect

Intermolecular hydrogen bonds between alcohols or phenols and various types of carbonyl groups have been extensively studied and information is now available on the way $\Delta\nu$ and ΔH vary with the nature of the proton acceptor and to a lesser extent on the effects of changes in the donor alcohol. The effect of different solvents on the frequency and intensity of the carbonyl absorption in ketones has been studied using both Raman and IR spectra. However the specific factors which determine these effects are little understood. Attempts to relate the frequency shifts to the bulk dielectric effects have been only partly successful (30-32). Bellamy and Williams proposed that the specific interactions with the solvents are responsible for the major frequency shifts (33). Caldow and Thompson calculated the individual contribution of the dielectric and specific interaction effects (34). However no direct check on the validity of these results is available.

Later Whetsel and Kagarise (29) have made an extensive investigation of the specific interactions on the carbonyl frequencies using the mixed solvent techniques. The equilibrium constant K for 1 : 1 and 1 : 2 ketone p-cresol complexes are determined using Brown and Kubota's equation (28) and also by Nash method (27). In Brown and Kubota's equation (5.2) and (5.3), A represents the ketone and B represents p-cresol in the monomeric form. Values of b and p required for the solution of eq.(5.2) and (5.3) were determined from the absorption in the hydroxyl region using the method of Widom et.al (35). Values of p and b were determined for a series of solutions in which the ketone concentration was constant and the p-cresol concentration varied up to about 0.09 M. An assumed value for K_{12} was used to calculate $[AB]$ and $[AB_2]$ for the individual solutions from eqs. (5.2) and (5.3). Following the same procedure, the equilibrium constants of ketone-p-cresol systems have been evaluated by several authors (36, 37). In all these investigations the acceptor (ketone) concentration was kept constant and the donor (p-cresol) concentration was varied at regular steps, for the evaluation of equilibrium constant

Eventhough some of the investigations cited above are done carefully and accurately and the results obtained are of fundamental importance it was felt that a reinvestigation of some of the systems is desirable for the following reasons. In the case of compounds capable of forming inter and intramolecular complexes, it has been shown that a competition between these two types of complex formation takes place (14, 38-40). Hence it is desirable to investigate such systems by changing the concentration of the acceptor keeping the donor concentration at a constant low value. A very low concentration of the donor excludes the possibility of any self-association problem. Different authors used different inert media. Use of same inert solvent for all the systems enhances the validity of a comparative study. In all the systems studied here carbontetrachloride is used as the buffer medium. In this report the results of the study of the same donor viz p-cresol in a series of ketones is presented.

Different methods mentioned above for the determination of association constant are very tedious eventhough they give accurate results. In a study like this the main difficulty is in the determination of the concentration of the complex formed and it is natural to resort to integrated intensity for this purpose. If we keep the concentration of the donor at a fixed low value and if the acceptor concentration is increased then a stage will come when all the donor molecules are used up for complex formation. Increasing the concentration of the acceptor beyond this value will not have any effect on the band due to the bonded species. Thus it is not too far away from truth if we take the concentration of the donor as that of the complex. Making use of this idea, the formula for equilibrium constant K for a ternany system involving a proton donor, a proton acceptor and a solvent may be written as

$$K = \frac{C_x}{(C_p^{\circ} - C_x)(C_a^{\circ} - C_x)} \qquad (5.8)$$

where C_p°, C_a° and C_x are the concentration of total proton donor, total proton acceptor, and hydrogen bond complex respectively. C_x the concentration of the hydrogen bond complex is determined by the use of molecular extinction coefficient ϵ for the bonded OH bond, where

$$\epsilon = \frac{\text{absorbance}}{(\text{cell thickness in cms}) \times (\text{conc in mole/lit})} \qquad (5.9)$$

A similar expression was uded by H.Tsubomura (41) for the evaluation of K of hydrogen bonding systems in phenols.

The donor concentration is kept constant and as the acceptor concentration is increased the intensity of the bonded OH band increases and reaches a maximum while the intensity of the free OH band decreases and reaches a minimum. Once this maximum and minimum are attained, even if the acceptor concentration is increased, the intensity of the bands remain unaltered. This can be seen from the Figs. (5.2),(5.4) and (5.6). This shows that almost all of the donor molecules are hydrogen bonded leaving no free molecule for the acceptor to act upon. Therefore, if one assumes $C_x = C^{\circ}_p$ in such solutions the error is only a minimum. is calculated using (5.9) in which absorbance is the maximum absorbance value of the bonded band and concentration is the concentration of the donor. After the peak molecular extinction coefficient ϵ_{max} is calculated in this way, the concentrations of the bonded p-cresol in solutions in which the acceptor is very dilute are calculated by the formula

$$C_x = a^{\circ}_{max} / \epsilon_{max} \qquad (5.10)$$

where a°_{max} is the absorbance at the peak per unit thickness of the solution. (Figs. 5.1, 5.3 and 5.5). Using the C_x values thus obtained, equilibrium constants are calculated from eq. (5.8).

5. Experimental Part

A Beckman IR.20 spectrophotometer with double beam operation is used for infrared measurements. Beckman

Fig. 5.1 to 5.6. Free and bonded O-H bands of P-cresol in mixtures of C cl_4 and different ketones.

Fig. 5.1 & 5.2. P-cresol in Acetone.

Fig. 5.1(a) P-cresol conc. o.o4 M (b) 0.06 M, (c) 0.08 M.
5.2(a) P-cresol conc. 0.4 M (b) 0.8 M (c) 1 M.

Fig. 5.3 and 5.4 P-cresol in Ethyl Methyl ketone.
5.3 (a) P-cresol conc. 0.06 M (b) 0.08 M (c) 0.1 M.
5.4 (a) P-cresol conc. 0.6 M (b) 0.8 M (c) 1 M.

Fig. 5.5 & 5.6 P cresol in Diethyl ketone.
5.5 (a) P cresol conc. 0.02 M, (b) 0.04 M, (c) 0.06 M.
5.6 (a) P cresol conc 0.2 M (b) 0.5 M, 0.6 M.

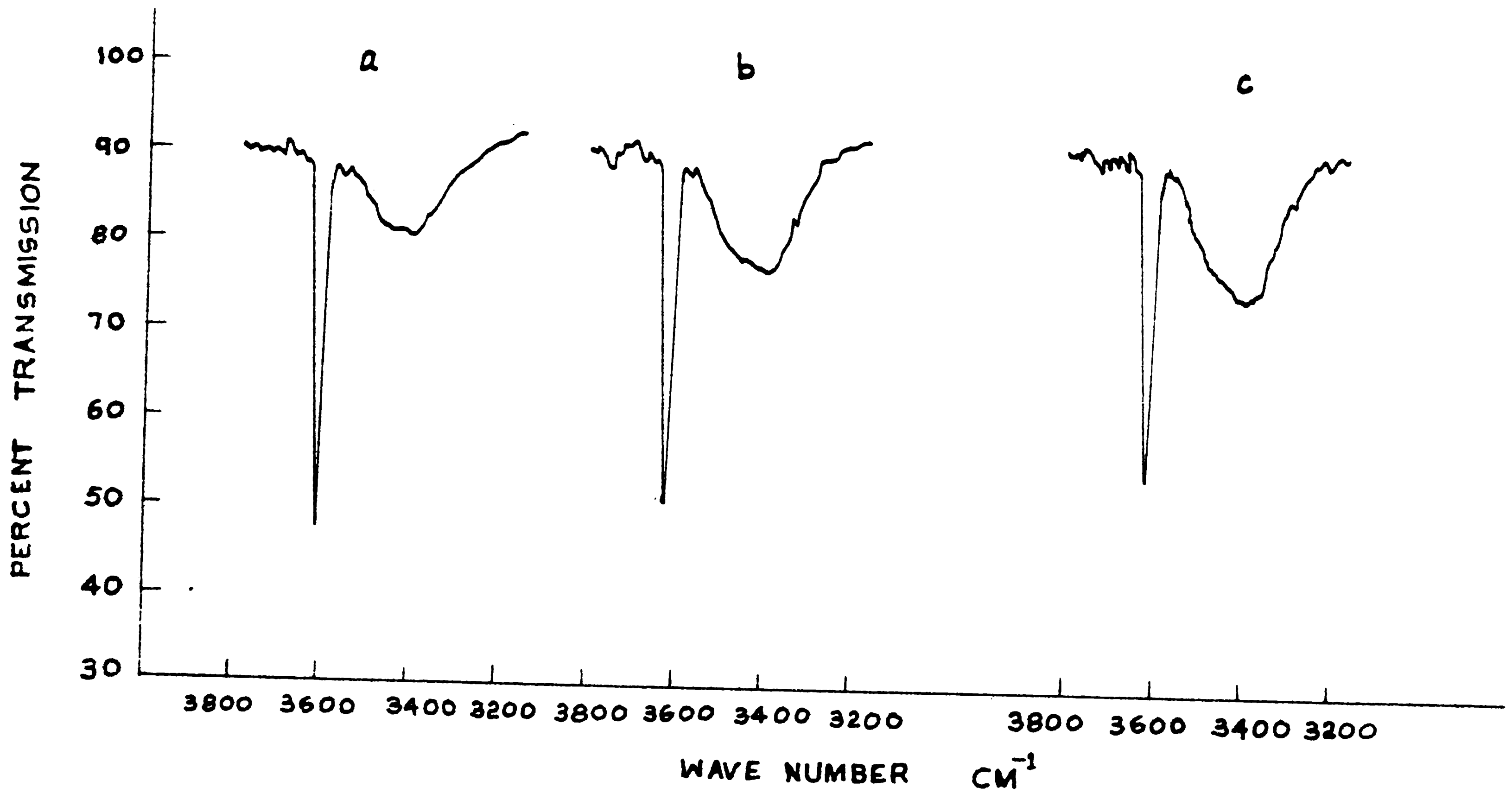
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FIG. 5.1

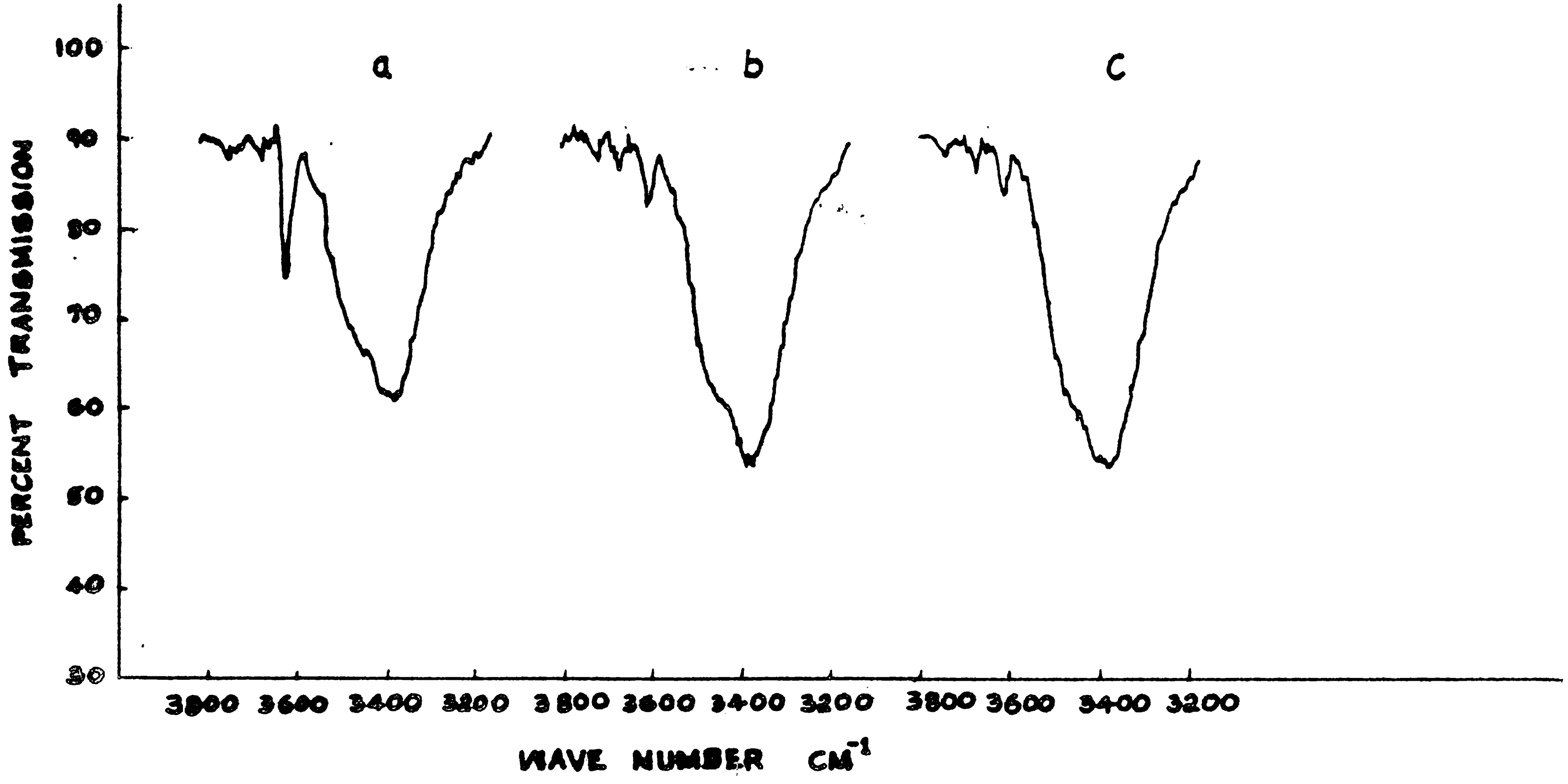
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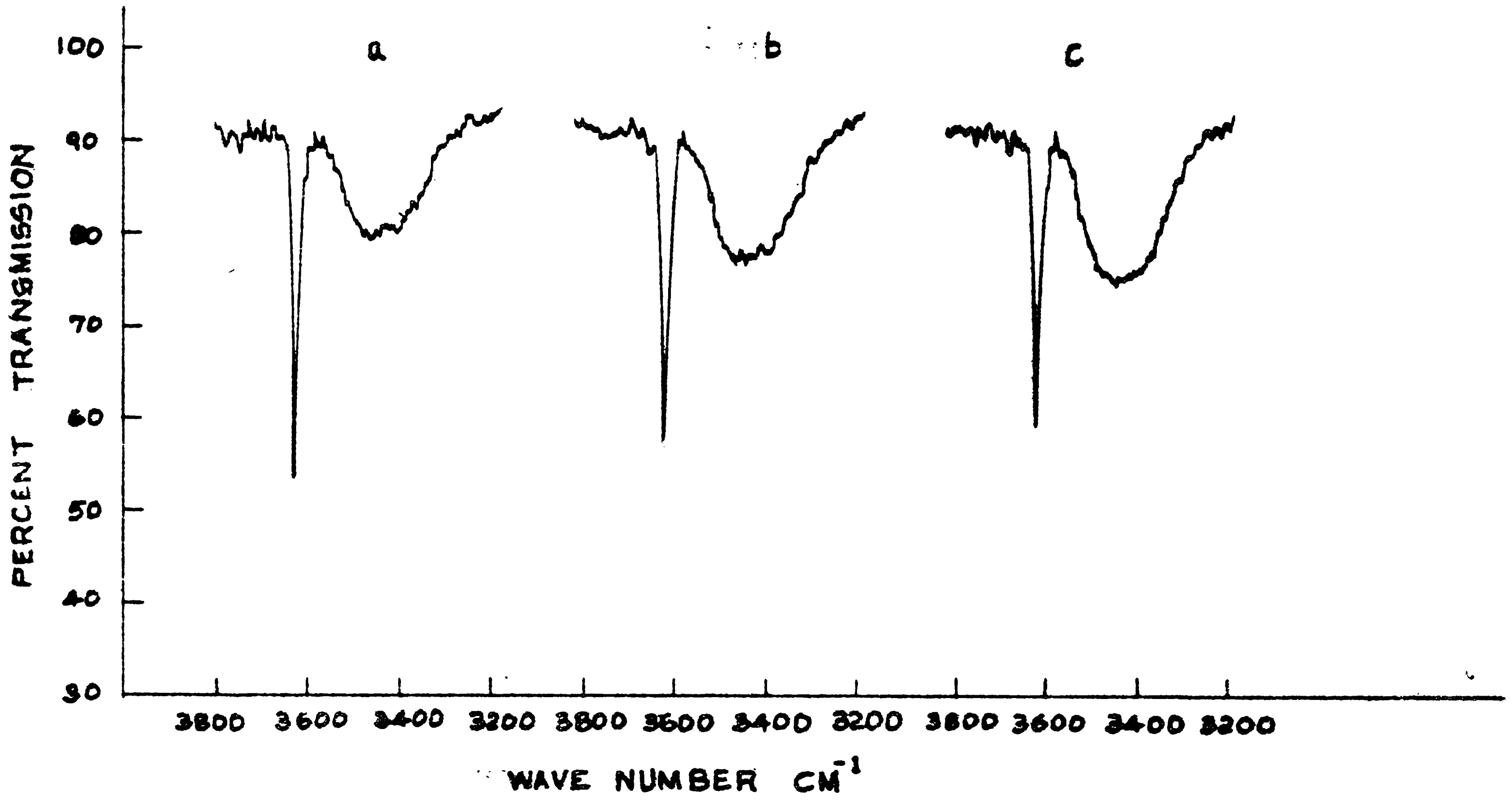
FIG. 5.2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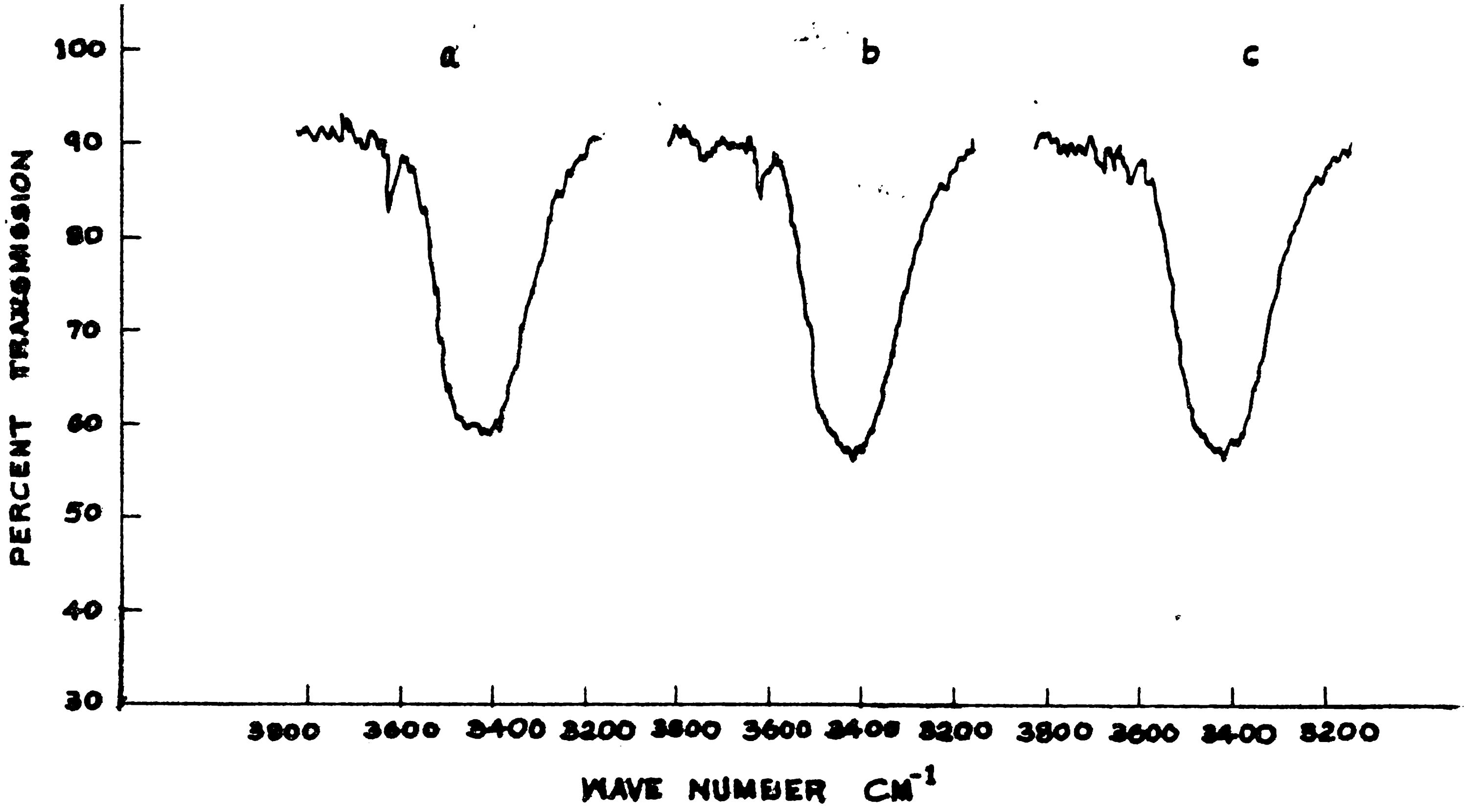
WAVE NUMBER CM^{-1}

FIG. 5.3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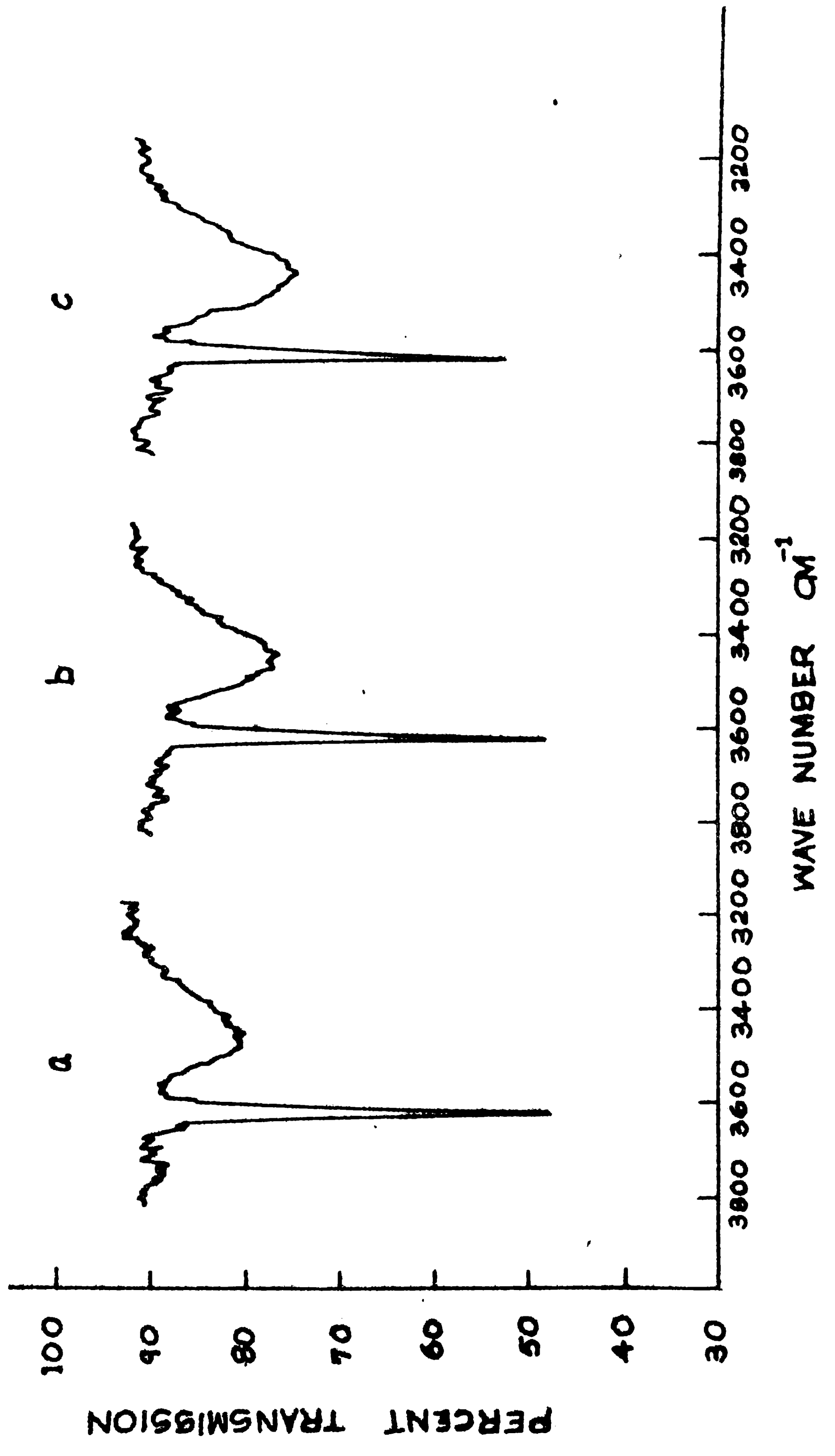
3200
WAVE NUMBER CM^{-1}

FIG. 5.4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PERCENT TRANSMISSION
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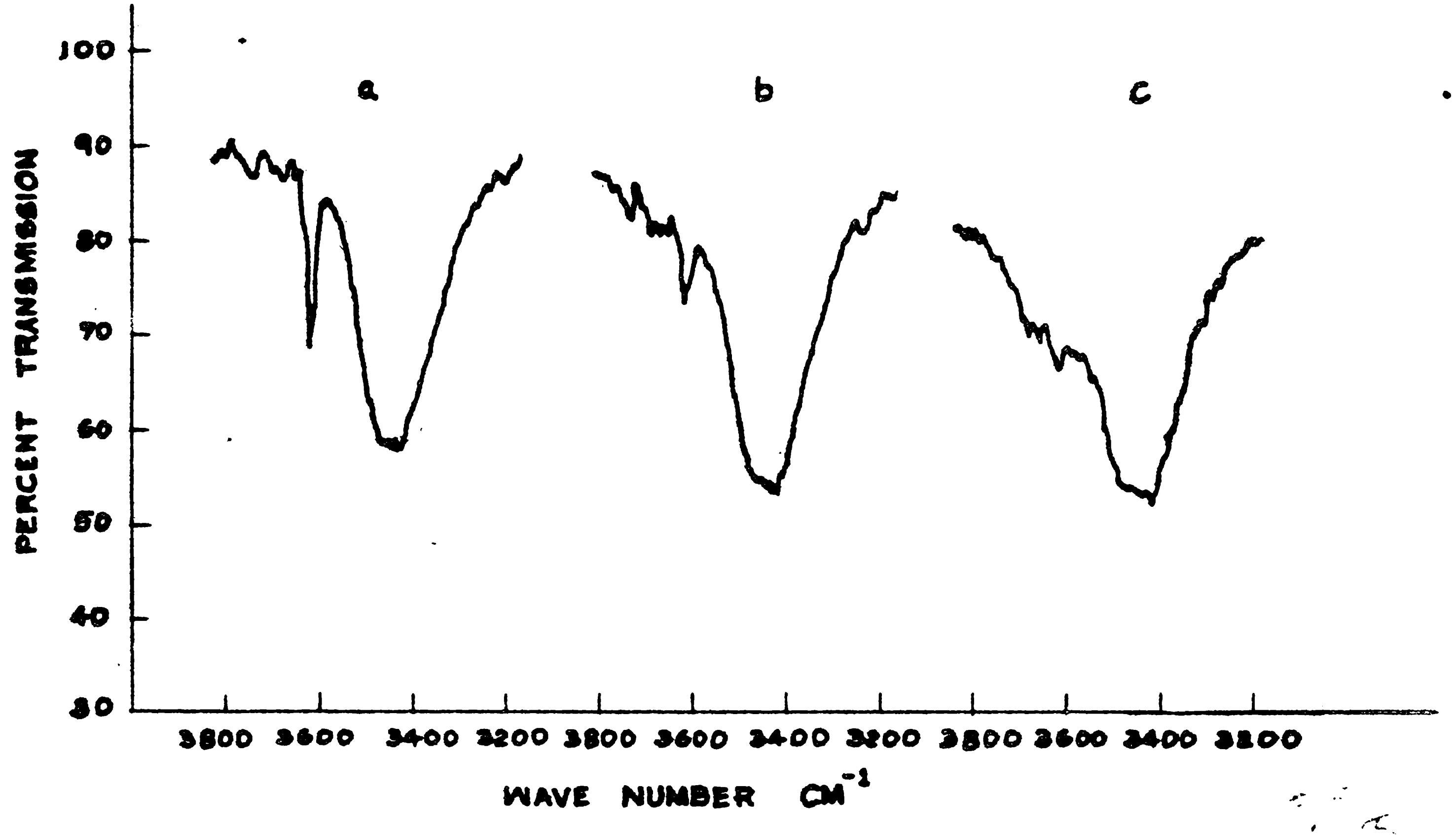
3800 3600 3400 3200
3800 3600 3400 3200
WAVE NUMBER CM^{-1}

FIG. 5.5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PERCENT TRANSMISSION
a
b
c
3800 3600 3400 3200 3800 3600 3400 3200 3800 3600 3400 3200
WAVE NUMBER CM⁻¹

FIG. 5.6

Variable path length micrometer cells are used with a fixed cell thickness of 0.5 mm. For each measurement of the ternary system a background trace of the corresponding blank solution (the solution that contained the same concentration of the acceptor) is run so that it is superimposed on the sample beam. All the samples used for IR Measurements are of pure quality and they are distilled again before use.

6. Results and Discussion

The equilibrium constants of p-cresol with acetone, ethyl methyl ketone, diethyl ketone are evaluated by the above method and the results are given in Tables (5.1) and (5.2). Very low concentrations of the acceptor of the order of 0.02 M to 0.1 M are used for the evaluation of K, and slightly higher concentrations of the order of 0.5 M to 1 M are used to determine the molecular extinction coefficient ϵ_{max}. The donor concentration is kept at a constant low value of 0.0192 mol/lit which is particularl advantageous to avoid any possibility of self association of the donor molecules.

In Table (5.3) the equilibrium constants obtained by the present method are compared with previous literature values. It can be noted that the results of the present investigations are in satisfactory agreement with the previous ones. This fact proves the validity of the simple and straight forward method followed in this investigation. The lower K value when carbon tetrachloride is used as the solvent instead of cyclohexane clearly demonstrates the influence of solvent in hydrogen bond formation. This observation supports the proposition (37) that weak specific interaction can occur between carbon tetrachloride and ketones.

TABLE 5.1

MOLECULAR EXTINCTION COEFFICIENT $\epsilon_{max.}$ FOR THE BONDED OH BANDS OF KETONE - P-CRESOL SYSTEMS

C°_{p} = 0.0192 mole/lit.

Acceptor	Concentration of the acceptor C°_{a} mol/lit.	Absorption maxima a max.	$\epsilon_{max.}$
Acetone	1.224	0.2210	231.5
	0.816	0.2218	231.5
Ethyl Methyl ketone	1.0022	0.206	215
	0.8018	0.206	215
Di-ethyl ketone	0.9461	0.234	245
	0.7569	0.234	245

TABLE 5.2

EQUILIBRIUM CONSTANT K C_p° = 0.0192 mole./lit

Acceptor	Concentration of the acceptor C_a° mole/lit.	Absorption maxima $e_{max.}$	Concentration of the hydrogen bond complex C_x mole/lit.	K
Acetone	0.0408	0.0505	0.0044	8.2
	0.0612	0.0689	0.0059	8.12
	0.0816	0.0839	0.0073	8.24
Ethyl Methyl ketone	0.0601	0.0607	0.0059	8.18
	0.0802	0.0763	0.00718	8.25
	0.1002	0.0887	0.00824	8.24
Di-ethyl ketone	0.0379	0.0559	0.0046	9.5
	0.0568	0.0753	0.0061	9,45

TABLE 5.3

COMPARISON OF EQUILIBRIUM CONSTANT K OBTAINED BY THE PRESENT METHOD WITH LITERATURE VALUES

Acceptor	Donor	Solvent	K	Ref.No.
Acetone	P-cresol	Carbontetrachloride	8.23	0*
"	"	Cyclohexane	12.81	29
"	Phenol	Carbontetrachloride	8.5	42
"	"	"	8.35	43
"	"	"	8.47	35
Ethyl Methyl ketone	P-cresol	Carbontetrachloride	8.22	0
"	"	"	9.3	36
"	"	"	10.0	36
"	Phenol	"	8.0	43
Di-ethyl ketone	P-cresol	Carbontetrachloride	9.48	0
"	Phenol	"	7.35	35

*0 - present study.

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CHAPTER VI

ORGANIC POLYMER THIN FILMS BY GLOW DISCHARGE POLYMERIZATION METHOD

Electrodless glow discharge polymerization unit and a special low temperature infrared cell were fabricated and organic polymer thin film was prepared. Infrared spectrum of the polymer film was studied and the characteristic lines of the polymer were identified. An attempt was also made to explain the polymerization mechanism taking place during glow discharge.

1. INTRODUCTION

In the early 1960s several workers discovered (1) that polymeric films produced in a plasma attain properties such as chemical inertness, good adhesion to the substrate, high thermal stability, homogenity and absence of pores and superior dielectric characteristics which could be utlised in several important practical applications. In the last decade a good deal of work has been reported describing the properties of organic polymeric films synthesized by plasma process and many applications for these films have been suggested. Plasma deposited organic films of this type found wide application as dielectrics in electronic industry as protective coating for metals and other reactive surfaces and more recently in reverse osmosis membrane fabrication. A good survey of this work has been summerized in the reviews of J.R. Hollahan and A.T. Bell (2) and also in the proceedings of the Symposium on Plasma Chemistry of Polymers (3).

The plasma state of matter can be defined as a partially ionised state of gas composed of ions, electrons and neutral species. Plasma polymerization can take place in the gaseous plasma created by a glow discharge, a corona discharge, an electron beam or a laser.

Organic or organometallic vapours introduced into the plasma are converted into ions, free radicals, or excited molecules. The reaction of these species with the monomer and with themselves leads to the formation of highly crosslinked and branched polymers.

2. WHAT SUBSTANCES DO FORM POLYMERS?

One outstanding advantage of a plasma process for the formation of organic polymer films is the wide variety of organic compounds that may be polymerized by this technique. Because of the very high energy available in the plasma, practically any organic or organometallic compound including those which are devoid of functional groups normally required in conventional polymerization can be polymerized. Several reports contain surveys of the types of compounds that are capable of forming polymer films (4-7). These include saturated and unsaturated aliphatics aromatics and a variety of organometallics. Smolinsky and Heiss (6) have given a qualitative rating of the tendency of a variety of monomers with diverse functional groups to form acceptable polymeric films. In this study, organosilanes were found to form the most desirable films while aliphatic halogen compounds were reported not to form films at all. Bradley and Hammar (5) found thatvenyl ferrocene and 1, 3, 5 - trichlorobenzene had the greatest tendency to form films while carbontetrachloride, hexachlorobenzene and ammonia did not form films at all. Based on their own results they concluded that a polymer could be obtained when the monomer contained either a carbon-hydrogen bond, a carbon-carbon double bond or an aromatic ring unless it was prehalogenated. A similar study undertaken by Yasuda and Lamaze (8) examined the polymerization of 90 monomers in an electrodeless discharge. These monomers were found to fall into two classes according to their effect on the pressure in the flow system. One class of monomers increased the pressure in the flow system when they were introduced into the plasma afterglow and the other class of monomers caused a decrease in the pressure of the flow plasma system.

Hollahan and McKeever (9) described the formation of a polymer film when a mixture of CO, H_2 and N_2 was exposed to an rf electrodeless discharge. The nitrogen content of the polymer film was found to be directly proportional to the flow rate of nitrogen gas through the plasma region. The effects of diluting the monomer with a carrier gas such as argon or other rare gases has also been explored. The results indicated that the presence of inert gas can change the properties of the plasma as well as the structure of the film (10, 11).

3. EXPERIMENTAL METHODS

A wide variety of reactors and experimental arrangements have been used to prepare polymer films in electric discharge. These may be classified according to whether the gas is static or flowing and whether internal or external electrodes are used.

Reactors with internal electrodes can be worked with dc power supplies as well as ac supplies operating over the range of Hz 50 Hz to 2450 MHz. When a dc discharge is used, the polymer films form principally on the electrode acting as the cathode. In the presence of an ac field, films form on both electrodes. In the absence of flow of gas through the system it has been observed that the gas pressure can either rise or fall when the discharge is first turned on (5, 12-14). The direction of the pressure change depends upon the monomer used and is a reflection of the relative rates of monomer-fragmentation and polymerization. The rate of polymer deposition has been found to increase up to an assymptotic limit as the initial monomer pressure is increased. For a fixed initial monomer pressure, the polymerization rate increases with increasing discharge power or current density. It has also been observed that the deposition rate can be increased by cooling the electrodes. The monomer may be fed continuously through the system in the presence or absence of a carrier gas (15, 16). It has been claimed that operating in the flowthrough mode has advantage of reducing the building up of contaminants in the film (15).

A schematic representation of a flow system used with an electrodeless discharge (17) is shown in Fig.(6.1). Several modes of operation have been described. The monomer may be fed directly through the plasma zone (9, 18, 20) or the monomer and a carrier gas may be fed through the plasma zone (7, 8, 21) or the monomer may be introduced into the after glow of an inert gas (17, 22). Using the first configuration it has been found that the polymerization rate increases towards a maximum value as the discharge power is increased. Above a certain power level, all the monomer can be converted to polymer. For high polymerization rates it has been observed that a very fine polymer powder is formed in addition to the deposition of a film. By contrast, excitation of a carrier gas and subsequent introduction of monomer leads to a lower polymerization rate and avoids the formation of a powder.

4. CHARACTERIZATION OF PLASMA POLYMERIZED FILMS

The methods used to characterize organic films deposited in plasma systems and the properties of these films have been summarized in the review article of Kolotyrkin et.al and A.M. Mearns (1, 23). In general, the properties of polymeric films synthesized in plasma may be summarized as follows: Films are amorphous, pinhole free, and highly cross-linked. The polymers have superior thermal stability, high melting points and low solubility.

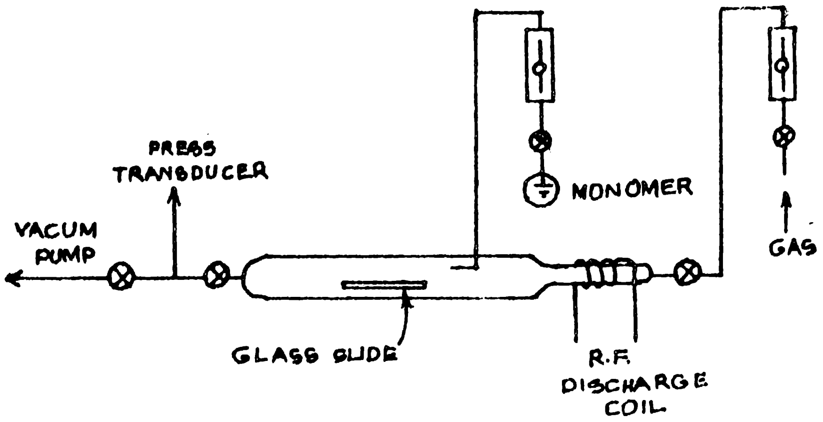


FIG. 6.1

SCHEMATIC REPRESENTATION OF A FLOW SYSTEM USED WITH AN ELECTRODELESS DISCHARGE

They contain high concentrations of unpaired spins and undergo rapid surface oxidiation when exposed to atmosphere. Lower molecular weight materials which are more soluable and softer can be formed under conditions of high pressure and lower current densities (19, 24).

Among the various techniques used to characterize plasma - polymerized films, infrared spectroscopy has yielded maximum information. Discussions of their spectra of such polymers can be found in references (9, 15, 18, 20, 25). The conclusions reached from these spectra indicate high degrees of cross linking, unsaturation and features similar to those found in polymers prepared by conventional means. Kronick et.al (25) have carried out detailed infrared investigations of these films by frustrated multiple internal reflection spectroscopy (FMIR). The general conclusions derived from their work are that, independent of whether the monomer is aromatic, olefinic, conjugated or unconjugated or fully saturated, the solid product is a dense, highly branched and cross-linked polymer containing considerable unsaturation in the form of both olefinic bonds and free valencies. The presence of carbonyl bonds were also observed when the films were exposed to the atmosphere. The absorptions due to bonds in the carbonyl and hydroxyl regions were found to increase in intensity with the time of exposure to the atmosphere.

Differential scaning calorimetry (DSC) and thermal gravitmetric analysis (TGA) have been used to examine the thermal characteristics of plasma polymerized films.(20).

5. MECHANISMS OF PLASMA POLYMERIZATION

In view of the larger number of elementary reactions taking place in an electric discharge, the formulation of a mechanism for polymer formation and the verification of this mechanism are very difficult tasks to accomplish. There are two major approaches to explaining plasma polymerization. In the first approach, polymerization is assumed to take place on an electrode or other solid substrate as a result of monomer adsorption and the subsequent bombardment of the monomer by active species and radiation produced in the plasma. The second approach assume that free radicals or ionic species are produced in the gas phase and that these may interact among themselves or with the monomer to produce active species of larger molecular weight i.e. oligomers. The formation of a film occurs when both the original species and the oligomers diffuse to the substrate surface where they can react further. A second distinction which can be noted is the selection of ions or free radicals as the active species responsible for polymerization.

The interpretations of plasma polymerization and the proposed mechanism presented in the literature can be distinguished according to whether electrodes are present within the discharge or not. Williams and Hayes (15) have studied the polymerization of twelve vinyl monomers in a bell jar apparatus containing parallel electrodes which are excited at 10 MHz. It was postulated that the active species were formed when monomer molecules adsorbed on the electrodes were bombarded by either electrons or ions derived from the plasma. The fragments formed in this manner were assumed to initiate polymerization within the adsorbed layer. Further evidence of the importance of monomer adsorption was the observation that the polymerization rate increased with monomer pressure upto a limiting value for a given current density. Denaro et.al (24) have noted that under conditions of high current density the formation of particles of polymer could be observed in the vapour phase. However, the amount of polymer formed in this way was found to be negligible compared to the amount of material that formed on the electrode surface. The initiation of polymer formation was assumed to take place through free radicals produced by collisions between the free electron present in the plasma and the monomer vapour.

A somewhat different polymerization mechanism has been proposed for those experiments in which an electrodeless discharge was used. The deposition rate was found to be independent of the power of the reactor [illegible] and increased with the square of the monomer partial pressure (8). Based upon the observed pressure dependence it was proposed that polymerization occurred in the gas phase.Thompson and Mayhan (20) have studied the rate of polymerization of styrene in an electrodeless discharge. It was observed that the rate of polymerization depends on the power coupled into the plasma and at power levels of 36 W, particles of polymer were observed to form in the gas phase and fall to the bottom of the reactor. Careful observation of the films present on the wall of the reactor showed the presence of these particles in the film. On the basis of this evidence, polymerization in the gas phase was considered to be important compared to polymerization on the surface.

From this review it is apparent that a comprehensive mechanism for explaining plasma polymerization is not available. But it can certainly be concluded that ions and radicals are formed in the gas phase and these species most certainly interact both with themselves as well as with the monomer gas to produce intermediates of increasingly greater molecular weight. This set of reactions can lead to the formation of polymer chains present in the gas phase and to the ultimate formation of the fine polymer powders reported by a number of authors.

From the brief survey given above it is clear that neither the properties of the polymer nor the mechanism of polymerization has been studied in a systematic manner. There are many perameters that determine the quality and rate of production of polymers. In the same way there are many factors that cause the degradition of the films. In many cases even the structure of polymers is not certain. As such a programme for detailed study of polymeric thin films is taken up by the author and is being continued. A brief report of the work in progress is given below.

5. EXPERIMENTAL SET UP

A high frequency oscillator oscillating in the range 3 - 10 MHz was constructed using 807 beam power tetrodes. The circuit diagram used for the power supply and the oscillator are shown in Figs. (6.2) and (6.3) respectively. A tuned plate tuned grid (TPTG) circuit was used for the oscillator. The high tension was fed directly to the plate through the centre of the plate coil and through a 10 KΩ resistance to the grid G_1. The grid condenser used was 0.01 μF, cathode biasing values being 200 Ω and 0.02 μF. The centre of G_2 coil was earthed through 100 Ω and 0.02 μF biasing. The high frequency voltage in the plate coil was stepped up by a coil having 30 turns. The ratio of $y/x \simeq 3$ to 4, x and y being the number of turns of the plate coil and step up coil respectively. Two thin copper foils were attached to the two ends of the discharge tube and these copper foils and the step up coil were connected in series. An air condenser C_1 was used in parallel to match the frequ-

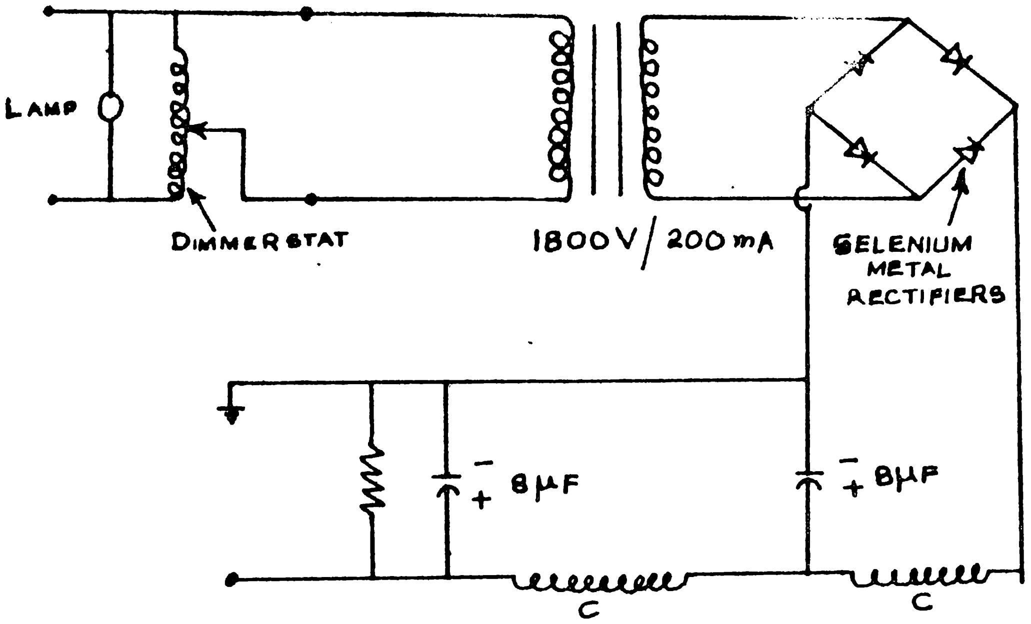


FIG. 6.2
POWER SUPPLY CIRCUIT

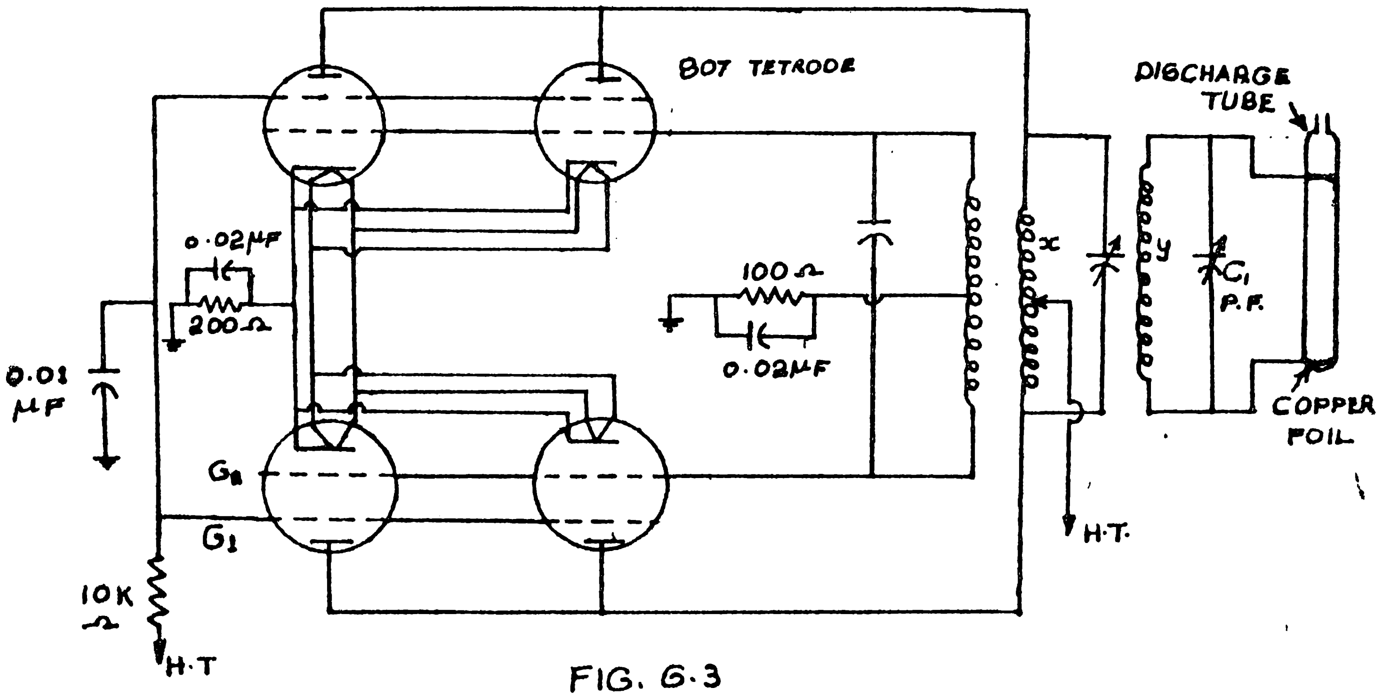


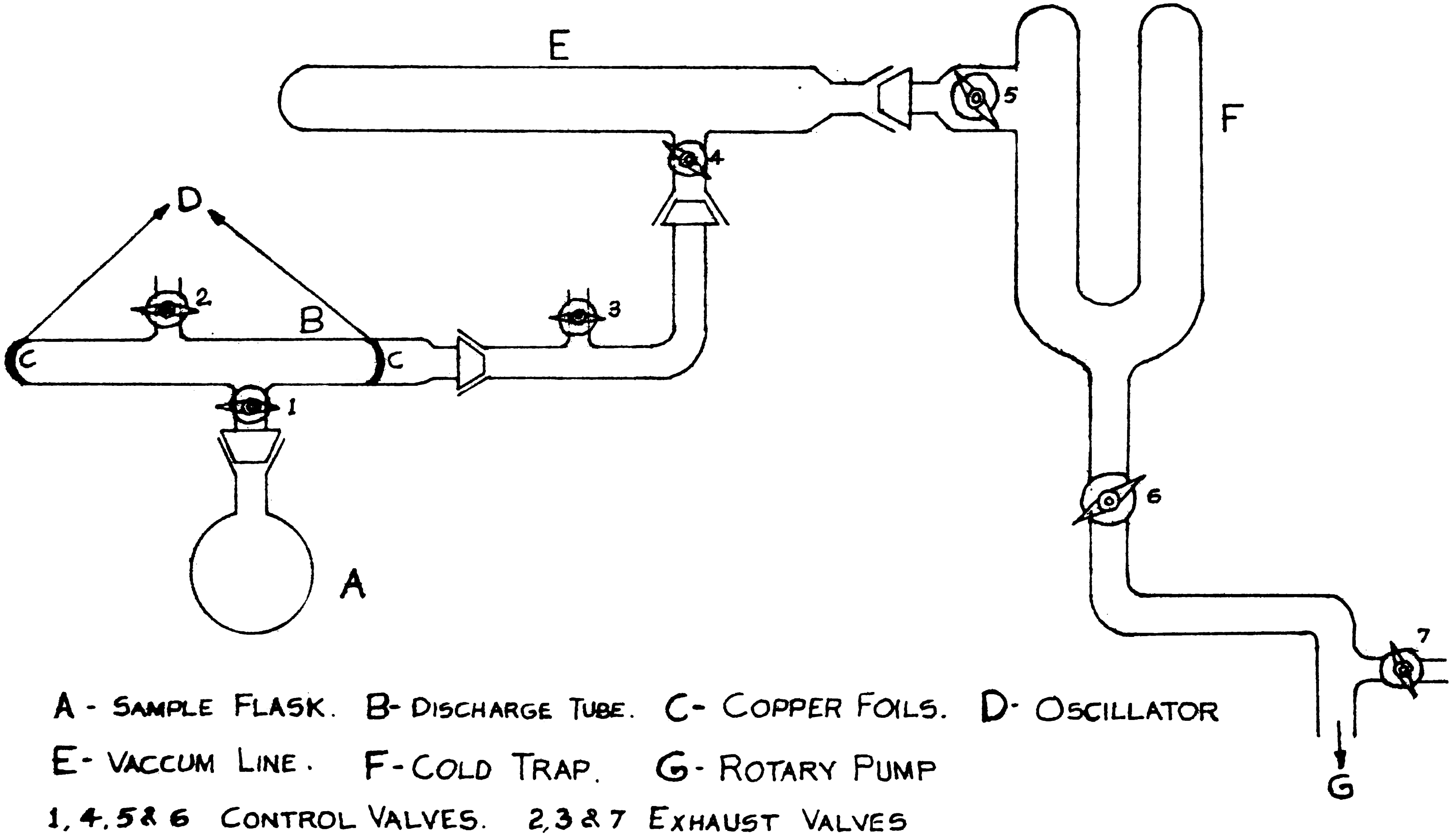
FIG. 6.3
HF. OSCILLATOR CIRCUIT

ency of the secondary circuit to that of the oscillator. The power supply for the oscillator has a power transformer capable of giving 2 Kv, 200 m ampe. The voltage of the secondary of the transformer was applied to selenium metal rectifiers. Further it was filtered through the choke (15 H). input filter system and filter condensers (8 µF). The monomer vapour of the sample at at a pressure of about 1 torr was fed through the control valve to the discharge tube B which is previously evacuated to 1 x 10^{-2} torr. The monomer vapour was discharged by the R.F. oscillator connected to the outer electrodes of the discharge tube and the polymerized film was deposited on the sodium chloride substrate placed inside the discharge tube.

A low temperature ir cell (Fig.6.5) with sodium chloride windows was also fabricated for low temperature work. The side tube carrying a jet is for the ejection of the polymer vapour on to the central window. the whole cell can be detached and placed inside the sample compartment of ir spectrophotometer to take low temperature ir spectra.

Polymer Thin Film of P-Toluidine

To start with p-toluidine was selected as the monomer for polymerization for several reasons. It is reported that the polymerization efficiency in glow dis-



A - Sample Flask. B- Discharge Tube. C- Copper Foils. D- Oscillator

E- Vaccum Line. F- Cold Trap. G- Rotary Pump

1, 4, 5 & 6 Control Valves. 2, 3 & 7 Exhaust Valves

Fig.6.4. Experimental Set-up For The Preparation Of Polymer Thin Films

charge for p-toluidine is 40 gms/kw hr (5). In this type of work the vapour pressure of the monomer is usually controlled by temperature in the absence of mechanical control. The vapour pressure of p-toluidine at room temperature is about 1 torr which is the desired range of pressure. Using the low temperature ir cell a thin layer of the monomer was obtained on the central window and its ir spectrum was recorded. Using the set up shown in fig. (6.4) in place of the low temperature ir cell the polymer thin film was obtained on a NaCl plate placed in the path of the discharge. On passing the discharge the film deposited not only on the window but also on the sides of the discharge tube. The colour of the film was dark brown and it was not easily removed from the NaCl plate showing that it has got good adhesion to the substrate. p-toluidine is highly soluble choloroform whereas the polymer film is very sparingly soluble in choloroform showing thereby that the composition of coloured film is different from the parent substance. The ir spectrum of the sample was recorded. The experiment was repeated several times and in all cases the spectra obtained were identical. The spectrum of the polymer along with the monomer is given in fig. (6.5). and the vibrational frequencies are tabulated in Table (6.1).

The ir spectra of p-toluidine in the liquid and solid state were studied by several authors (26-28). The prominent lines of the spectrum are the 3400 and 3330 cm^{-1}

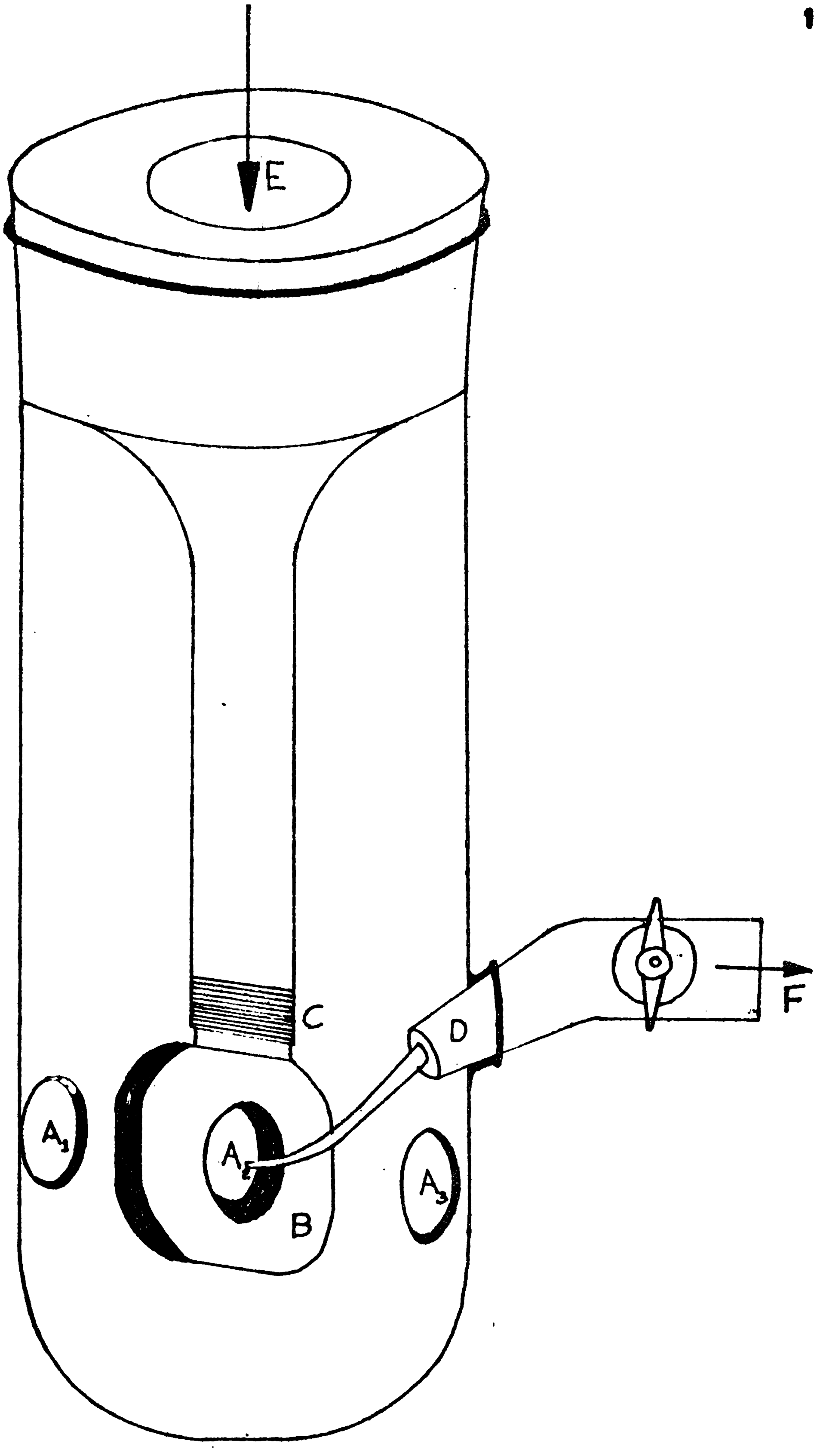


FIG. 6.5. LOW TEMPERATURE IR CELL

A1, A2, A3 - NaCl WINDOWS. B- COPPER DISC. C- COWAR GLASS JOINT. D-VAPOUR JET. E- COOLING AGENT. F- DISCHARGE TUBE.

lines representing NH antisymmetric and symmetric stretching vibration five CH stretching vibrations at 3092, 3058, 3025, 2920 and 2853 cm^{-1}, phenyl ring vibrations at 1620 and 1510 cm^{-1}, C-N stretching vibrations at 1270 cm^{-1} and the disubstituted ring vibrations at 810 and 750 cm^{-1}. Almost all these lines are present in the monomer spectrum given in fig. (6.5).

A comparative study of the monomer and polymer spectra brings out the following deviations in the polymer spectrum from the monomer spectrum. There is only one line at 3360 cm^{-1} for N-H stretching vibration in the polymer spectrum in place of two lines at 3400 and 3330 cm^{-1} in the monomer spectrum. Three lines corresponding C-H vibrations which are present in the monomer are also present in the polymer. The 1620 and 1510 cm^{-1} lines corresponding to the ring vibrations are unaffected in polymer spectrum. Also the strong line at 1270 cm^{-1} corresponding to C-N stretching vibration was found to be missing in the polymer spectrum. Out of the two bands at 810 and 750 cm^{-1} representing the disubstitution of benzene ring the line at 750 cm^{-1} is shifted to 680 cm^{-1}. An additional weak band was observed at 3570 cm^{-1} in the polymer spectrum and the intensity of this band increased with long exposure of the film to the atmosphere. This can be the O-H band due to absorption of atmospheric water vapour (29). Additional bands are present at 1300 and 1250 cm^{-1} also.

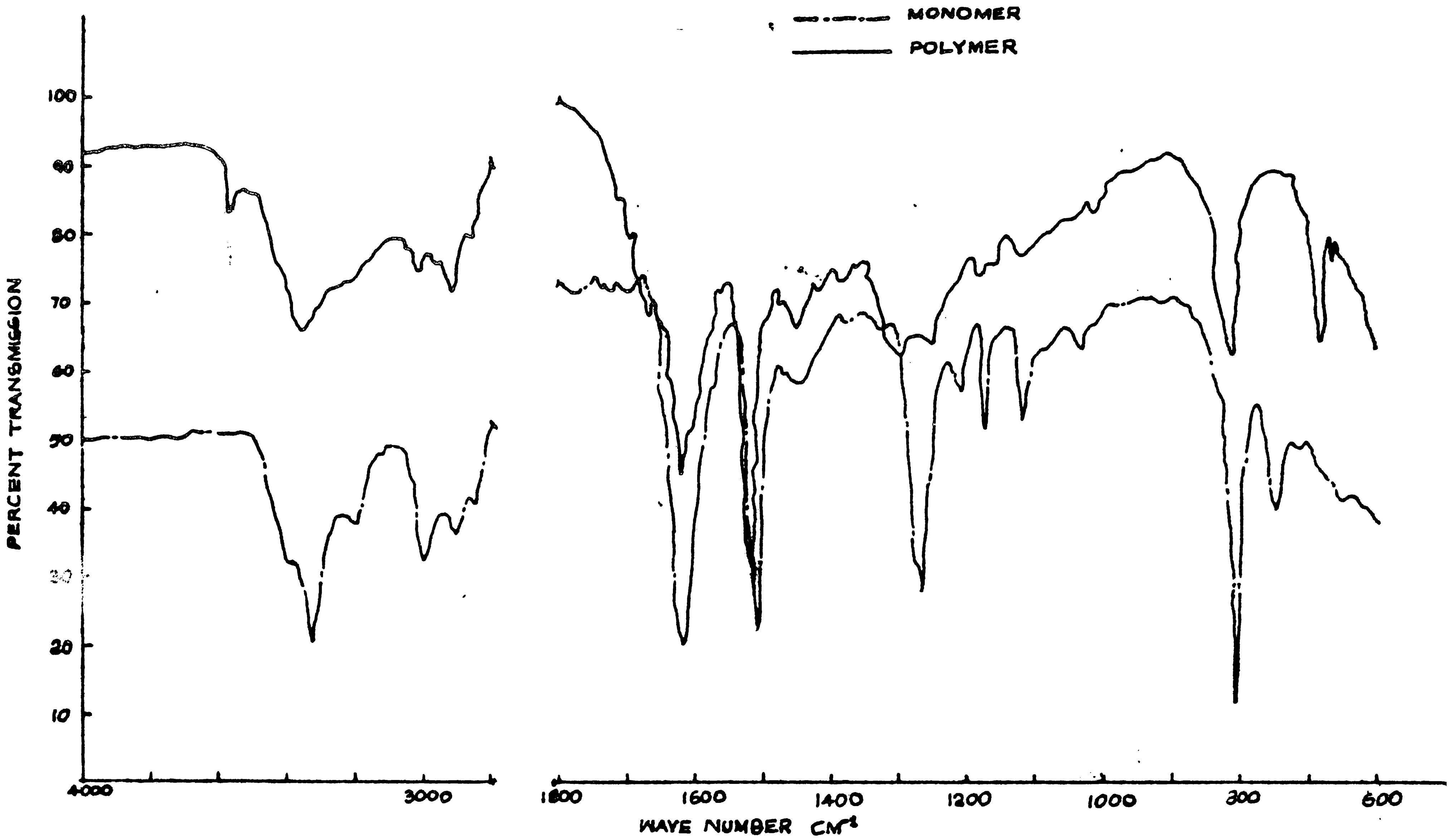
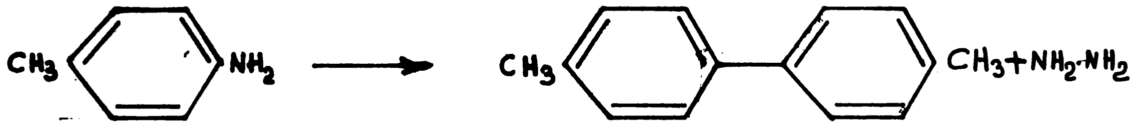


FIG.6.6 I.R SPECTRA OF P-TOLUIDINE AND GDP P-TOLUIDINE

Eventhough the chemical reaction during polymerization can take place in different ways, from the above comparative study of the spectra, it is suggested that polymerization takes place through the following reaction mechanism.



Monomer Polymer Unit

The polymer formed is a mixture of 4, 4, dimethyl diphenyl and hydrazine. In the Hydrazine (NH_2NH_2) molecule the N-H asymmetric and symmetric vibrations are reported to be at 3350 and 3325 cm^{-1} (30). In the polymer spectrum of Fig. (6.6) these two lines are not resolved out. It may be reasonably concluded that the line at 3400 cm^{-1} is shifted to 3360 cm^{-1} and because of the proximity of the strong line at 3330 cm^{-1} shifted to higher frequency side, there resulted only one strong broad line centred around 3360 cm^{-1}. This frequency shift from 3400 to 3360 cm^{-1} may be a result of change in hybridization at the N atom from SP^2 in p-toluidine to SP^3 in hydrazine molecule (30). The disappearance of the strong line corresponding to C-N stretching vibration, in the polymer spectrum indicated that NH_2 group is knocked off. Since the ring vibrations are preserved in the polymer spectrum it is clear that the phenyl ring is not affected. The additional weak bands at 1300 and 1250 cm^{-1} cannot be assigned with the available data but the line at 1250 cm^{-1} seems to represent N-N vibration (31). The shifting of p-substituted band at 750 cm^{-1} to 680 cm^{-1} indicates the replacement of light NH_2 group by a heavy phenyl group.

p-toludine is taken as a test case and it is found that the above experimental set up can be successfully used to prepare polymer films by electrodelese glow discharge polymerization process. It has been shown that spectroscopic investigations of these films can throw light into the possible mechanism of polymerization. It is expected to extend this work to low temperature and to the preparation and study of other organic polymers.

TABLE 6.1

INFRARED FREQUENCIES OF P-TOLUIDINE AND GDP P-TOLUIDINE

Frequency cm^{-1}		Assignment of important lines
P-Toluidine	GDP P-Toluidine	
*	3570 W	(OH)
3400 W	3360 M	(NH)
3330 M		
3210 W		(NH) association
3000 M	3000 W	
2920 M	2920 W	(CH)
2850 W	2850 W	
1875 W		
1620 S	1620 S	
1510 S	1510 S	ring vibrations
1450 W	1450 W	
	1300 W	
1270 S		(CN)
	1250 W	
1215 W		
1180 W	1180 W	
1120 W	1120 W	
1030 W	1030 W	
810 S	810 M	Substituted benzene vibration
750 M	680 M	

* S- strong, M-Medium, and W-weak.

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