Force constants from intensity analysis of molecules CH$_3$Cl and CD$_3$Cl

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Abstract. The secular equation $(GF - E\lambda)L = 0$ contains more force constants than can be calculated from the equations formulated using the frequencies. For a 3 × 3 matrix, there are 6 force constants but only 3 frequencies. Attempts were made by others to estimate all the 6 constants to satisfy the frequencies and Coriolis constants and rotation distortion constants. However, many attempts are not made in these estimations to satisfy the intensities. A full complement of equations is derived to evaluate all the force constants combining the intensity equations $I = L'A$ with $LL' = G$ and evaluated the force constants of A_1 species of CH$_3$Cl and CD$_3$Cl. A simple analysis of a 2 × 2 matrix shows that $F_{12}/F_{22} = G_{12}^{-1}/G_{22}^{-1}$ as reported earlier.

1. Introduction

It is well known that the secular equation $(GF - E\lambda)L = 0$ contains more force constants than can be calculated from the number of equations available. A 3 × 3 matrix contains 6 force constants and only 3 equations corresponding to the three frequencies $\lambda(= 4\pi^2\sigma^2c^2)$ that can be formulated. Many attempts have been made over the years to arrive at all the 6 constants by making a number of approximations. These centre round determining L elements from

$$LL' = G \tag{1}$$

and substituting them in

$$L'FL = \Omega \tag{2}$$

Ω is a diagonal matrix of λ's. L' is transpose of L which connects symmetry coordinates and normal coordinates. But, L is an unsymmetrical matrix containing 9 elements, and G is symmetrical containing 6 elements and hence are not sufficient to determine all the F elements. Many of the approximations are made on the L elements. For instance, Torkington (1949) assumed that all the non-diagonal L elements can be neglected. Thirugnanasambandam and Karunanidhi (1976) published a number of papers extending over a large number of molecules, using an approximation $F_{ij}/F_{jj} = K_{ij}/K_{jj}$. K's are kinetic constants. They also, incorporated the idea of reflex angles suggested by Ford and Orville Thomas (1967) and adjusted the symmetric force constants. Combining these equations and frequencies, all the force constants

were obtained and using the L elements from them they calculated the Coriolis interaction constants, rotation distortion constants and mean square amplitudes. Hence, they claimed that this approximation was correct. Aldous and Miller (1962) adjusted the force constants to a set of combined frequencies, Coriolis interaction constants and rotation distortion constants, by trial and error. Gans (1977) reviewed all these methods and called the whole thing a state of art.

Rotation of a molecule slightly distorts it. Coriolis interaction constants and rotation distortion constants are results of this perturbation. They are extensively used in high resolution spectroscopy. Equations were derived by Meal and Polo (1956) to connect them to the L elements of the unperturbed molecules.

Intensity of a line in a molecular spectrum is as important as frequency and ,can be related to the L elements. But not many attempts have been made to calculate the intensity using the force constants obtained from the various approximations. A brief review of the theory connecting L elements and intensities is, perhaps, called for.

Intensity of a Raman line is due to change in the polarizability of the molecule during an oscillation. Eliashevich and Wolkenstein (1945) suggested that the polarizability of a molecule is a linear sum of the polarizabilities of the bonds. Long (1953) who derived elegant equations connecting polarizability and Raman intensity made the following assumptions.

(i) The polarizability tensor of a molecule is sum of the polarizability tensors of the bonds. (ii) α_1 is the polarizability along length of the bond and α_2 and α_3 perpendicular to it. To make the calculations tractable α_2 is made equal to α_3 and any α_{xy} of the molecule of n bonds is given by

$$\alpha_{xy} = \sum(\alpha_{1n} - \alpha_{2n})nxny + \alpha_{2n}\delta_{xy} \tag{3}$$

nx and ny are direction cosines of the nth bond and δ is Kronecker function. (iii) During an oscillation, the bonds change in length and orientation. It is assumed that while the polarizability of a bond changes as it is stretched, orientation does not change it. (iv) When a bond is stretched its polarizability changes, but the polarizability of a neighbouring bond does not change unless its length also is affected due to molecular oscillation. This is called zero order approximation.

On the basis of this model, equations like

$$I_1 = A_1 L_{11} + A_2 L_{21} + A_3 L_{31} \tag{4}$$

were derived. A's contain values of bond polarizabilities and their derivatives. I^2 is line intensity. Intensity analysis is intended to determine A's and from them the bond polarizabilities and their derivatives.

There are three limitations to this analysis. While the intensities of strong lines can be determined with sufficient accuracy (1% or less), lines of medium intensity can be obtained with an error of the order of 10% and lines of low intensity are of really uncertain value. The I's which are square roots of intensity have a sign ambiguity. L's are determined from force constants that cannot be obtained with any certainty. We have solved this problem by writing (4) in the form,

$$I = L'A \tag{5}$$

and its transpose in the form $I' = A'L$ so that

$$I'I = A'LL'A = A'GA. \tag{6}$$

In the expanded form,

$$I_1^2 + I_2^2 + I_3^2 = A_1^2 G_{11} + A_2^2 G_{22} + A_3^2 G_{33} + 2A_1 A_2 G_{12}$$
$$+ 2A_2 A_3 G_{32} + 2A_3 A_1 G_{13}.$$

Now we have avoided L's. $I_1^2 + I_2^2 + I_3^2$ is insensitive to low intensity. Sign ambiguites of I's are avoided. Taking an isotopic molecule and assuming that the A's are the same for it, we have two equations, as we are using two isotopic substituted molecules.

Molecules in the gaseous or liquid states are oriented at random. Hence, from the Raman spectrum of A_1 species one can obtain α_i^2 and γ_i^2 the trace and anisotropy of the polarizability tensor for each mode of oscillation.

We shall now take CH_3Cl and CD_3Cl for which force constants have been determined by many. For A_1 species, their symmetry coordinates for C_{3v} symmetry of tetrahedral angles are,

$$S_1 = D$$
$$S_2 = 1/\sqrt{3}(d_1 + d_2 + d_3)$$

and

$$S_3 = 1\sqrt{6}(\theta_1 + \theta_2 + \theta_3 - \beta_1 - \beta_2 - \beta_3)$$

D is the length of CCl bond, d is CH (or CD) bond length, θ's are angles between CH bonds and β's the angles between CCl and CH.

In (4), $A_3 = \delta\alpha_3/\delta S_3$. Since the trace of the polarizability tensor is independent of orientations of the bonds, $A_3 = 0$. Now A_1 and A_2 can be determined from the two equations (6) as will be explained in §3.

To this part equation (1) can be added which are six in number. Equations (4) are really not independent as the L's combine to form an equation like (6). Hence, we have 8 equations to solve for 9 L's. Similar equations like (4) can be obtained from IR intensities. Hence, one of them can be taken to have a full complement of 9 equations to solve for 9 L's and from them the force constants using (2). Now α_i are square roots of α_i^2, that can be obtained from Raman intensity analysis. Hence, they have sign ambiguity. One can express them like

$$\alpha_1 = A \cdot L_1$$
$$A = (A_1 A_2); \quad L_1 = (L_{11} L_{21}).$$

While A is a constant, both α_1 and L_1 have sign ambiguity and their signs are connected in some way which is not clear. If we fix α_1 as positive, L_1 can be positive or negative. But either way, they give correct G's and F's. Hence, in our analysis, we fix the signs of α_1 as positive. Therefore, the way is clear to derive all the 9 equations to get the 9 values of L and calculate physically correct force constants. Without this clarification of sign ambiguity, it has not been possible to use the intensities either for evaluation of electrooptical parameters or for calculating force constants. Though Coriolis interaction constants and rotation distortion constants are not determined with any greater accuracy than intensities, they could be extensively used to determine the force constants as they do not suffer from this serious defect of sign ambiguity.

Now, we want to point out, that this analysis is not affected by any of the approximations of bond polarizability theory. Here, for instance, $A_1 = \delta\alpha/\delta S_1$;

$A_2 = \delta\alpha/\delta S_2$ α is the trace of polarizability of the whole molecule. We need to invoke the approximations of the model only if we want to calculate bond polarizabilities and their derivative. As it is, we are not excluding interactions between the bond polarizabilities, nor are we assuming $\alpha_2 = \alpha_3$. But we have to admit that we are implying the polarization of the molecule as the sum of polarizabilities of the bonds in putting $A_3 = 0$.

For the present, we are limiting our analysis only to A_1 type oscillations, as the purpose of this paper is mainly to present 9 equations to solve for 9 L elements.

2. Derivation of equations for L elements

We shall first show the derivation of a 2×2 matrix as it facilitates understanding the procedure for a 3×3 matrix, which is complex.

Expanding (1) and (4),

$$I_1 = A_1 L_{11} + A_2 L_{21}; \quad I_2 = A_1 L_{12} + A_2 L_{22}; \quad G_{11} = L_{11}^2 + L_{12}^2;$$

$$G_{22} = L_{21}^2 + L_{22}^2; \quad G_{12} = L_{11} L_{21} + L_{12} L_{22}.$$

Also, we are limiting this analysis only to isotopic pairs of molecules for which intensities are available to avoid approximations of bond polarizability theory.

It is seen that the order of L elements in (4) and (1) is different.

Taking the inverses

$$A = (L^{-1})'I \tag{7}$$

and

$$G^{-1} = (L^{-1})'L^{-1}. \tag{8}$$

Now, the order of the L^{-1} elements is the same as in (7) and (8). On solving for L^{-1} elements,

$$I_{12}^2 L_{11}^{-1} = A_1 I_1 \pm I_2 (\Delta_1)^{\frac{1}{2}} \tag{9a}$$

$$I_{12}^2 L_{21}^{-1} = A_1 I_2 \pm I_1 (\Delta_1)^{\frac{1}{2}} \tag{9b}$$

$$I_{12}^2 L_{12}^{-1} = A_2 I_1 \pm I_2 (\Delta_2)^{\frac{1}{2}} \tag{9c}$$

$$I_{12}^2 L_{22}^{-1} = A_2 I_2 \pm I_1 (\Delta_2)^{\frac{1}{2}} \tag{9d}$$

$$I_{12}^2 = I_1^2 + I_2^2$$

$$\Delta_1 = G_{11}^{-1} I_{12}^2 - A_1^2$$

$$\Delta_2 = G_{22}^{-1} I_{12}^2 - A_2^2$$

Now,

$$\Delta_1 \Delta_2 = (G_{11}^{-1} I_{12}^2 - A_1^2)(G_{22}^{-1} I_{12}^2 - A_2^2)$$

$$= G_{11}^{-1} G_{22}^{-1} I_{12}^4 + A_1^2 A_2^2 - I_{12}^2 (G_{11}^{-1} A_2^2 + G_{22}^{-1} A_1^2).$$

Now

$$G_{11}^{-1} = G_{22}/(G_{11} G_{22} - G_{12}^2)$$

$$G_{22}^{-1} = G_{11}/(G_{11} G_{22} - G_{12}^2)$$

$G_{11}G_{22} - G_{12}^2$ is the determinant of the G matrix, and is the reciprocal of the determinant of the G^{-1} matrix. Hence,

$$\Delta_1 \Delta_2 = G_{11}^{-1} G_{22}^{-1} I_{12}^4 + A_1^2 A_2^2 - I_{12}^2 (G_{11}^{-1} G_{22}^{-1} - (G_{12}^{-1})^2)(G_{11} A_1^2 + G_{22} A_2^2).$$

Expanding (6),

$$I_1^2 + I_2^2 = I_{12}^2 = G_{22} A_2^2 + 2G_{12} A_1 A_2 + G_{11} A_1^2$$

or

$$G_{11} A_1^2 + G_{22} A_2^2 = I_{12}^2 - 2G_{12} A_1 A_2.$$

Then, substituting in the above equation for $\Delta_1 \Delta_2$,

$$\Delta_1 \Delta_2 = (G_{12}^{-1} I_{12}^2 - A_1 A_2)^2. \tag{10}$$

Now, for a 3×3 matrix,

$$A_i = L_{1i}^{-1} I_1 + L_{2i}^{-1} I_2 + L_{3i}^{-1} I_3 \tag{11}$$

and

$$G_{11}^{-1} = (L_{11}^{-1})^2 + (L_{21}^{-1})^2 + (L_{31}^{-1})^2. \tag{12}$$

Write

$$(G_{11}^{-1})' = G_{11}^{-1} - (L_{31}^{-1})^2 \tag{13}$$

Similarly,

$$A_1' = A_1 - L_{31}^{-1} I_3 = L_{11}^{-1} I_1 + L_{21}^{-1} I_2. \tag{14}$$

From (12) and (13)

$$I_{12}^2 L_{11}^{-1} = A_1' I_1 \pm I_2 (\Delta_{31})^{\frac{1}{2}} \tag{15a}$$

$$I_{12}^2 L_{21}^{-1} = A_1' I_2 \pm I_1 (\Delta_{31})^{\frac{1}{2}}. \tag{15b}$$

Here,

$$\Delta_{31} = (G_{11}^{-1})' I_{12}^2 - A_1'^2.$$

Similarly

$$\Delta_{32} = (G_{22}^{-1})' I_{12}^2 - A_2'^2$$

We can write similar expressions involving Δ_{32}. From (10)

$$(\Delta_{31} \Delta_{32})^{\frac{1}{2}} = (G_{12}^{-1})' I_{12}^2 - A_1' A_2'. \tag{16}$$

Expanding (16) and simplifying

$$K_1 (L_{32}^{-1})^2 - 2(K_{12} L_{31}^{-1} + l_2 I_3) L_{32}^{-1}$$
$$- (X_{12} - K_2 (L_{31}^{-1})^2 + 2l_1 I_3 L_{31}^{-1}) = 0 \tag{17}$$

Here,

$$X_{12} = (G_{11}^{-1} G_{22}^{-1} - (G_{12}^{-1})^2) I_{12}^2 - A_{12}^2$$

$$A_{12}^2 = G_{11}^{-1} A_2^2 + G_{22}^{-1} A_1^2 - 2A_1 A_2 G_{12}^{-1}$$

$$K_1 = (G_{11}^{-1} I^2 - A_1^2); \quad K_2 = (G_{22}^{-1} I^2 - A_2^2); \quad K_{12} = (G_{12}^{-1} I^2 - A_1 A_2)$$

$$l_1 = (A_1 G_{22}^{-1} - A_2 G_{12}^{-1}); \quad l_2 = (A_2 G_{11}^{-1} - A_1 G_{12}^{-1}); \quad I^2 = I_1^2 + I_2^2 + I_3^2$$

solving for L_{32}^{-1},

$$K_1 L_{32}^{-1} = (K_{12} L_{31}^{-1} + l_2 I_3) \pm (l_{12} \Delta_{31})^{\frac{1}{2}} \tag{18}$$

and

$$K_2 L_{31}^{-1} = (K_{12} L_{32}^{-1} + l_1 I_3) \pm (l_{12} \Delta_{32})^{\frac{1}{2}}. \tag{19}$$

One can similarly obtain,

$$K_1 L_{33}^{-1} = (K_{13} L_{31}^{-1} + l_4 I_3) \pm (l_{13} \Delta_{31})^{\frac{1}{2}} \tag{20}$$

and

$$K_2 L_{33}^{-1} = (K_{23} L_{32}^{-1} + l_6 I_3) \pm (l_{23} \Delta_{32})^{\frac{1}{2}} \tag{21}$$

with

$$l_{12} = (K_1 K_2 - K_{12}^2)/I^2; \quad l_{13} = (K_1 K_3 - K_{13}^2)/I^2; \quad l_{23} = (K_2 K_3 - K_{23}^2)/I^2$$

where

$$K_{13} = G_{13}^{-1} I^2 - A_1 A_3; \quad K_{23} = G_{23}^{-1} I^2 - A_2 A_3$$

$$l_4 = A_3 G_{11}^{-1} - A_1 G_{13}^{-1}; \quad l_6 = A_3 G_{22}^{-1} - A_2 G_{23}^{-1}$$

$$l_3 = A_1 G_{33}^{-1} - A_3 G_{13}^{-1}; \quad l_5 = A_2 G_{33}^{-1} - A_3 G_{23}^{-1}$$

Also,

$$K_3 = G_{33}^{-1} I^2 - A_3^2$$

K_3, l_3 and l_5 will be useful to write L_{31}^{-1} and L_{32}^{-1} in terms of L_{33}^{-1}.

Expanding $(G_{11})'$, A_1', etc

$$\Delta_{3i} = -I^2 (L_{3i}^{-1})^2 + 2 A_1 I_3 L_{3i}^{-1} + G_{11}^{-1} (I^2 - I_3^2) - A_1^2.$$

Subscript 3 in Δ indicates that they contain L_{31}, L_{32}, L_{33} and I_3. Similarly one can obtain Δ_{21}, Δ_{22} and Δ_{23} using L_{21}, L_{22}, L_{23} and I_2.

It is seen that equations for L_{31}^{-1}, L_{32}^{-1} and L_{33}^{-1} are functions of I_3 only. Similarly, it can be shown that $(L_{21} L_{22} L_{23})$ are functions of I_2 and $(L_{11} L_{12} L_{13})$ are functions of I_1 only. It is significant that these vectors are multiplied only by the corresponding I's in (10). It can be shown that the eliminant of L_{33}^{-1} from (20) and (21) corresponds to one of the equations (18) or (19). Thus, from (18)–(20), we have only two independent equations. It is possible to get L_{33}^{-1} and L_{32}^{-1} in terms of L_{31}^{-1}, for instance. It is significant that (12) give relations between L^{-1}'s along the rows while equations (18) to (21) give relations between L^{-1}'s along the columns. This is the additional feature that we obtain by combining the frequencies and the intensities.

Using equations for A_2', $(G_{22}^{-1})'$, A_3' and $(G_{33}^{-1})'$ one can write similar to 15

$$I_{12}^2 L_{12}^{-1} = (A_2 - I_3 L_{32}^{-1}) I_1 \pm I_2 (\Delta_{32})^{\frac{1}{2}} \tag{15a}$$

$$I_{12}^2 L_{22}^{-1} = (A_2 - I_3 L_{32}^{-1}) I_2 \pm I_1 (\Delta_{32})^{\frac{1}{2}} \tag{15b}$$

$$I_{12}^2 L_{13}^{-1} = (A_3 - I_3 L_{33}^{-1}) I_1 \pm I_2 (\Delta_{33})^{\frac{1}{2}} \tag{15c}$$

$$I_{12}^2 L_{23}^{-1} = (A_3 - I_3 L_{33}^{-1}) I_2 \pm I_1 (\Delta_{33})^{\frac{1}{2}}. \tag{15d}$$

From (15), (17) and (18), one can obtain all the L^{-1} elements except say, L_{31}^{-1}, in terms of L_{31}^{-1}. Since they are complex, it is found worthwhile verifying them using a

numerical model.

$$I' = (2\ 3\ 4)$$

$$(L^{-1}) = \begin{matrix} 2\ 1\ 3 \\ 4\ 5\ 6 \\ 7\ 9\ 8 \end{matrix}$$

$$A = (L'^{-1})I$$

$$(L'^{-1})L^{-1} = G^{-1}.$$

3. Calculation of force constants of CH_3Cl and CD_3Cl

We shall confine our calculations to A_1 type oscillations as both Raman and Infrared intensities are available from the literature and as the authors claim accuracy for their values. Also, force constants are calculated from these molecules using Coriolis constants. From Raman intensities we take only α and from IR all the I's as given in table 1. Since for α_3, the authors declare 100% uncertainty we take it to be zero.

The first step is to calculate A_1 and A_2 using $\sum \alpha_i^2 = 2\cdot3$ for CH_3Cl and $1\cdot22$ for CD_3Cl.

Expanding (6),

$$2\cdot3 = A_1^2(0\cdot0671) + A_2^2(0\cdot6141) - 2A_1 A_2(0\cdot0289)$$

$$1\cdot22 = A_1^2(0\cdot0671) + A_2^2(0\cdot3154) - 2A_1 A_2(0\cdot0289)$$

The values in the brackets are G_{11}, G_{22} and G_{12}. On solving $A_1 = 2\cdot1840$; $A_2 = 1\cdot9050$. The corresponding IR value $B_1 = 2\cdot274$. Similar to (15) and (11) one can write

$$(I_2^2 + I_3^2) L_{21}^{-1} = (B_1 - I_1 L_{11}^{-1})I_2 \pm I_3 \Delta_{11}^{\ddagger} \tag{22}$$

$$A_1 = L_{11}^{-1}\alpha_1 + L_{21}^{-1}\alpha_2. \tag{23}$$

Then,

$$\Delta_{11} = -I^2(L_{11}^{-1})^2 + 2B_1 I_1 L_{11}^{-1} + G_{11}^{-1}(I_2^2 + I_3^2) - B_1^2$$

similar to Δ_{31}.

On solving (22) and (23), $L_{11}^{-1} = 4\cdot0788$ for CH_3Cl and $4\cdot4242$ for CD_3Cl. In solving for B_1 from IR intensities we do not have the advantage of putting $B_3 = 0$. It was necessary to use both A_1 and E type equations to obtain B_3. But since the value of B_1 is sufficiently large, the error in its evaluation is small. Hence the values of L^{-1} obtained using both A_1 and B_1 can be taken to be correct.

The G^{-1} values used are those calculated from the K's published by

Table 1. Infrared and Raman intensities and frequencies.

	α_1	α_2	I_1	I_2	I_3	λ_1	λ_2	λ_3
CH_3Cl	0·4472	1·4491	0·7135	0·7404	0·4008	0·1904	3·126	0·6523
CD_3Cl	0·4000	1·0296	0·5987	0·6081	0·5080	0·1716	1·659	0·3762

λ's are in units of 10^{29}/s, α's and I's are in natural units.

Table 2. Force Constants of A_1 species in millidynes/A° of CH_3Cl and CD_3Cl.

	PW		TY	Th		O
	CH_3Cl	CD_3Cl	CH_3Cl	CH_3Cl	CD_3Cl	CH_3Cl
F_{11}	3·6739	3·9140	3·88	3·3903	3·5147	4·81
F_{22}	5·4014	5·0637	5·63	5·4792	5·5487	5·672
F_{33}	0·2149	0·1803	0·57	0·1903	0·2004	0·646
F_{12}	1·2962	0·9616	−1·41	0·1233	0·2129	0·72
F_{13}	−0·2460	−0·3562	−0·25	−0·1656	−0·2861	−0·40
F_{23}	0·3244	0·1718	0·41	0·0083	0·0173	0·622

PW: Present work; TY: Subedar and Tyagarajan (1979); Th: Thirugnanasambandam and Karunanidhi (1976); O: Overend (quoted by Aldous and Miller 1962).

Thirugnanasambandam and Karunanidhi. But we take tetrahedral angles for convenience. The force constants published by them are given in table 2 to compare with our symmetry force constants. Now the characterstic constants.

$K_1, K_2, K_3, K_{12}, K_{13}, l_{12}, l_{13}, l_3$ and l_4 are calculated from the equations given. From L_{11}^{-1}, using

$$K_1 L_{12}^{-1} = K_{12}^{-1} L_{11}^{-1} + l_2\alpha_2 \pm (l_{12}\Delta_{11})^{\frac{1}{2}} \tag{24}$$

$$K_1 L_{13}^{-1} = K_{13}^{-1} L_{11}^{-1} + l_4\alpha_2 \pm (l_{13}\Delta_{11})^{\frac{1}{2}} \tag{25}$$

L_{12}^{-1} and L_{13}^{-1} are calculated.
Then using

$$A_2 = \alpha_1 L_{12}^{-1} + \alpha_2 L_{22}^{-1}$$

$$O = \alpha_1 L_{13}^{-1} + \alpha_2 L_{23}^{-1}, \quad L_{22}^{-1} \text{ and } L_{23}^{-1}$$

are evaluated. Using

$$A_1 = \alpha_1 L_{11}^{-1} + \alpha_2 L_{21}^{-1}$$

L_{21}^{-1} is obtained. L_{22}^{-1} and L_{23}^{-1} can also be calculated using L_{21}^{-1} in place of L_{11}^{-1} in (24) and (25). The values obtained in the two ways check well. Then, with G_{11}^{-1}, G_{22}^{-1} and G_{33}^{-1} the other L^{-1}'s are evaluated. Then F's thus calculated are given in table 2 along with those from the other authors. Thirugnanasambandam *et al* used their equations $F_{ij}/F_{jj} = K_{ij}/K_{jj}$. Subedar and Tyagarajan (1979) combined the frequencies and rotation distortion constants.

On comparison one finds that our F_{12} is rather large. It is not possible to adjust any of the parameters in our format to get smaller values. But, for CH_3F, Aldous and Miller (1962) who have used frequencies and Coriolis interaction constants together obtained 0·72 and Overend *et al* (quoted by Aldous and Miller 1962) obtained 1·31. Hence, our force constants are perhaps reasonable.

4. Intensity analysis of a 2 × 2 matrix

For diatomic molecules of C_{2v} symmetry, the A_1 species consists of one symmetric stretching mode and a bending mode. The isotopic part of the Raman spectrum can

be shown to be like

$$\alpha_1 = A_1 L_{11} \tag{26a}$$

$$\alpha_2 = A_1 L_{12} \tag{26b}$$

A_2, as it represents the orientational part of the polarizability tensor is equal to zero. Squaring and adding these equations

$$\alpha^2 = \alpha_1^2 + \alpha_2^2 = A_1^2 G_{11}. \tag{27}$$

Writing equations similar to (9)

$$\alpha^2 L_{11}^{-1} = A_1 \alpha_1 \pm \alpha_2 (G_{11}^{-1} \alpha^2 - A_1^2)^{\frac{1}{2}}.$$

Now

$$G_{11}^{-1} \alpha^2 - A_1^2 = (G_{11} G_{22}/\delta) A_1^2 - A_1^2 = A_1^2 G_{12}^2/\delta \tag{9a}$$

δ is determinant of the G matrix. Then

$$\alpha^2 L_{11}^{-1} = A_1 (\alpha_1 \pm \alpha_2 G_{12}/\delta^{\frac{1}{2}}) \tag{28}$$

similarly

$$\alpha^2 L_{21}^{-1} = A_1 (\alpha_2 \pm \alpha_1 G_{12}/\delta^{\frac{1}{2}}). \tag{29}$$

It was shown in an earlier paper (Swarnakumari and Rao 1984) that for pairs L_{11}^{-1}, L_{21}^{-1} and L_{12}^{-1}, L_{22}^{-1} the sign before δ should be mutually exclusive.

Now

$$\alpha^2 L_{12}^{-1} = + \alpha_2 (G_{22}^{-1} \alpha^2)^{-\frac{1}{2}} \tag{9c}$$

which reduces to

$$L_{12}^{-1} = + (\alpha_2/A_1)\delta^{-\frac{1}{2}} \tag{30}$$

$$L_{22}^{-1} = - (\alpha_1/A_1)\delta^{-\frac{1}{2}} \tag{31}$$

Then,

$$F_{22} = (L_{12}^{-1})^2 \lambda_1 + (L_{22}^{-1})^2 \lambda_2 = G_{22}^{-1}(\alpha_2^2 \lambda_1 + \alpha_1^2 \lambda_2)/\alpha^2 \tag{32}$$

$$F_{12} = L_{11}^{-1} L_{12}^{-1} \lambda_1 + L_{21}^{-1} L_{22}^{-1} \lambda_2 = \alpha_1 \alpha_2 \delta^{-\frac{1}{2}}(\lambda_2 - \lambda_1)/\alpha^2$$
$$+ G_{12}^{-1}(\alpha_2^2 \lambda_1 + \alpha^2 \lambda_2)/\alpha^2. \tag{33}$$

Generally α_2 is very small compared to α_1, which leads to

$$F_{12}/F_{22} = G_{12}^{-1}/G_{22}^{-1}. \tag{34}$$

This is the result proposed by Thirugnanasambandam and Karunanidhi (1976). The equations for F_{12} and F_{22} are very significant consisting of products of frequencies and intensities. Perhaps, it will be possible to extend this derivation to a 3 × 3 matrix.

For 2 × 2 matrices other than for A_1 species, the expressions for F's are not simple (Swarnakumari and Rao 1984). Force constants for F species for molecules like CH_4 were also published earlier (Ravindranath *et al* (1986)).

Finally it may be mentioned that intensity analysis is the only way to solve force constants in the spectra of liquids and crystals. In the present study, it has been possible to compare our results with those obtained using Coriolis interaction constants as the intensities relate to molecules in the gaseous state.

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