Some Properties of the Mixing Parameter in the Analysis of Molecular Vibrations

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A mathematical proof is given for the range $-\pi/4 < \Phi < +\pi/4$ of the mixing parameter Φ in the case of vibrational problems of order two. The parameters Φ and $\overset{*}{\Phi}$ corresponding to the cases before and after isotopic substitution of atoms in molecules are shown to be related as $\tan \Phi = A \tan \overset{*}{\Phi} - B$, where A and B are terms depending upon the molecular structure and vibrational frequencies.

Solutions to various problems associated with molecular vibrations essentially deal with the evaluation of elements of the normal coordinate transformation matrix L. The parameter formalism [1–3] involves splitting of the L matrix into two parts, one (L_0) calculable purely from the kinetic energy matrix G and the other (C) to be determined so that

$$L = L_0 C\,. \tag{1}$$

The properties which enable a lower triangular structure for L_0 superior to other possible forms have been explained by Freeman [4]. Further, it has been recently shown by Muller [5] that this form of L_0 is identical with the famous 'high frequency separation method of Wilson' in the $n=2$ cases. The matrix C should be orthogonal and can be expressed in terms of angular parameter Φ as [1–3]

$$C = \begin{bmatrix} \cos\Phi & -\sin\Phi \\ \sin\Phi & \cos\Phi \end{bmatrix}. \tag{2}$$

In an alternate form for the C matrix [6, 7] the terms $\cos\Phi$ and $\sin\Phi$ are represented by $(1+c^2)^{-1/2}$ and $-c(1+c^2)^{-1/2}$ respectively, thus yielding the relation $c = -\tan\Phi$. Among the various properties of the matrix C, their general physical significance [8] and mass dependence in certain special cases [7] have been analysed recently. The present discussion focusses attention on the possible ranges within which the parameter Φ should lie and the change in the actual value of the parameter due to isotopic substitution of atoms in the case of vibrational species of order $n=2$.

Since $\Phi = \pi/2$ or $-\pi/2$ corresponds to a reversing of the symmetry coordinates as against the case when $\Phi = 0$, the range for Φ has been suggested by Török [9] to be $-\pi/4$ to $+\pi/4$ in a logical manner. A more rigorous proof for this may be given using the well known equation [1–3]

$$\tilde{C}\,\tilde{L}_0\,F\,L_0\,C = \Lambda\,. \tag{3}$$

Here, F is the matrix of force constants and Λ is a diagonal matrix of elements Λ_i related to the vibrational frequencies. The condition for the diagonalisation of the left hand side,

$$\tan 2\Phi = 2(\tilde{L}_0 F L_0)_{12}/[(\tilde{L}_0 F L_0)_{11} - (\tilde{L}_0 F L_0)_{22}] \tag{4}$$

demands the solution for Φ to be contained in the range $-\pi/4$ to $+\pi/4$ corresponding to any of the mathematically possible force fields, whatever be the form of L_0.

However, under the present lower triangular form for L_0, the magnitudes of Φ (or c) are found to be extremely small in all $n=2$ cases wherever the L matrix has been uniquely obtained by the use of sufficient number of additional data [3, 6, 10–12] (thus greatly supporting the validity of the well known L matrix approximation method of setting $L = L_0$, by Müller [13]). Referring by asterisks to the case after isotopic substitution of atoms, the relation between C and $\overset{*}{C}$ can be best obtained using the equation corresponding to the invariance of the F matrix under isotopic substitution, obtained from Eq. (3) as

$$\tilde{\overset{*}{C}}\,\tilde{\overset{*}{L}}_0\,\tilde{L}_0^{-1}\,C\,\Lambda\,\tilde{C}\,L_0^{-1}\,\overset{*}{L}_0\,\overset{*}{C} = \overset{*}{\Lambda}\,. \tag{5}$$

Putting $L_0^{-1}\overset{*}{L}_0 = P$ and employing the lower triangular structure for L_0 and $\overset{*}{L}_0$, an expression for the off-diagonal element can be written as

$$\begin{aligned}&(P_{11} - P_{21}\,c + P_{22}\,c\,\overset{*}{c})\,(P_{11}\,\overset{*}{c} - P_{21}\,c\,\overset{*}{c} - P_{22}\,c)\,\Lambda_1 \\ &+ (P_{11}\,c + P_{21} - P_{22}\,\overset{*}{c})\,(P_{11}\,c\,\overset{*}{c} + P_{21}\,\overset{*}{c} + P_{22})\,\Lambda_2 = 0\,.\end{aligned} \tag{6}$$

Here, the parameters c and $\overset{*}{c}$ correspond to $-\tan\Phi$ and $-\tan\overset{*}{\Phi}$ respectively. The magnitudes of c and $\overset{*}{c}$, being extremely small under the present form of L_0, allow neglecting of their second and higher order powers and lead to a simplified form of Eq. (6) as

$$c = A\,\overset{*}{c} + B \tag{7}$$

where

$$A = [(P_{11})^2\Lambda_1 + (P_{21})^2\Lambda_2 - (P_{22})^2\Lambda_2]/[P_{11}P_{22}(\Lambda_1 - \Lambda_2)]$$

and

$$B = P_{21}\Lambda_2/[P_{11}(\Lambda_1 - \Lambda_2)]$$

are constants depending upon the structure and the vibrational frequencies for each molecule. Equation (7) indicates that c and $\overset{*}{c}$ are linearly related. The analogous form of Ep. (7) in terms of the angular parameters will be

$$\tan\Phi = A\tan\overset{*}{\Phi} - B\,. \tag{8}$$

Identical forms of Eqs. (6), (7) and (8) containing $\dot{\Lambda}_1$ and $\dot{\Lambda}_2$ can also be written. Such equations will be useful in drawing c versus $\dot{c}$ (or Φ versus $\dot{\Phi}$) curves, evaluating the actual values of the parameters and then in employing them in Eq. (3) to evaluate unique force constants.

Another interesting application of these equations is in the evaluation of the ratios Λ_1/Λ_2 and $\dot{\Lambda}_1/\dot{\Lambda}_2$, once the exact values of Φ and $\dot{\Phi}$ are made available by the use of some additional experimental data. Thus, for example if the coriolis coupling constants ζ_{11} and $\dot{\zeta}_{11}$ are known from the analysis of bands corresponding to Λ_1 and $\dot{\Lambda}_1$, then the Φ and $\dot{\Phi}$ values can be immediately calculated[10] and these results used to predit the position of the bands corresponding to Λ_2 and $\dot{\Lambda}_2$ using Equation (6). It should however be cautioned that the experimental uncertainties in the data used to evaluate the parameter can reduce the accuracy of such results.

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