Mass Dependence of the Vibrational Eigenvector Matrix Elements in $XY_2(C_{2v})$ Type Molecules

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Interesting linear relationships (one for hydrides and another for nonhydrides) are found to exist between a certain parameter c characterising the vibrational eigenvector matrix L and the mass ratio m_Y/m_X in the case of bent symmetric XY_2 type molecules with small mass coupling.

The variation of the ratio L_{12}/L_{21} of the eigen vector matrix elements with mass coupling defined as $G_{12}/|G|^{1/2}$ in vibrational problems of order two in molecular types $XY_2(C_{2v})$, $XY_3(D_{3h})$ and $XY_4(T_d)$ has been recently analysed by Müller et alii [1]. The points thus defined lie along a straight line in the case of molecules of XY_2 type possessing large mass coupling (e. g. NO_2, NF_2, OF_2, CF_2 etc.). For molecules with relatively small mass coupling (e. g. ClO_2, SO_2, H_2O, H_2Se etc.) the points do not lie along the line.

For molecules with small mass coupling, the L matrix approximation ($L_{12}=0$) is known to give a reasonable set of force constants [2, 3]. In such cases, the elements of the matrix $L=L_0$ can easily be calculated from the G matrix employing the Wilson condition [4] $L\tilde{L}=G$. However, to represent the actual case, one may write

$$L = L_0 C \qquad (1)$$

where C is an orthogonal matrix [5]. Defining C as [6]

$$C = \frac{1}{\sqrt{1+c^2}} \begin{bmatrix} 1 & c \\ -c & 1 \end{bmatrix} \qquad (2)$$

one may expect the deviation of the parameter c from zero to reflect the deviation of the matrix L from L_0 in the actual case.

Recently, a criterion based on the minimisation of the average bending energy has been found to hold extremely well in fitting the actual force fields of $XY_2(C_{2v})$ type molecules [7] obtained with the help of sensitive additional data like isotopic frequencies and Coriolis coupling constants. Values of the parameter c in these cases, when plotted directly against the mass ratio m_Y/m_X, indicate an interesting linear relationship as shown in Figure 1. Thus, for molecules with small mass coupling also certain regularities between the L matrix elements and the mass ratio can be established.

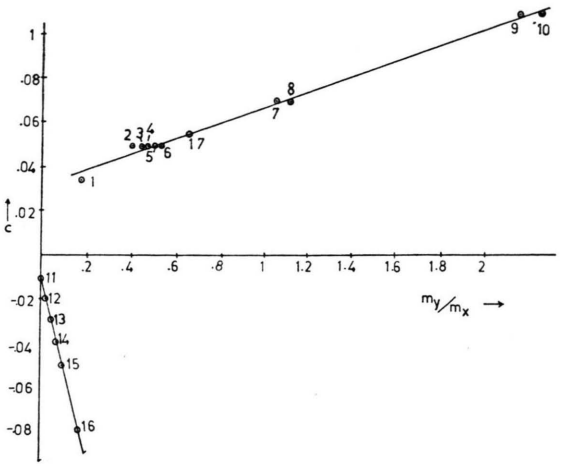

Fig. 1. Variation of c with m_Y/m_X in molecular types $XY_2(C_{2v})$. 1. SeO_2, 2. $^{37}ClO_2$, 3. $^{35}ClO_2$, 4. $^{34}S^{16}O_2$, 5. $^{34}S^{18}O_2$, 6. $^{32}S^{18}O_2$, 7. $^{32}S^{35}Cl_2$, 8. $^{32}S^{37}Cl_2$, 9. $^{35}Cl_2O$, 10. $^{37}Cl_2O$, 11. H_2Se, 12. H_2S and T_2Se, 13. H_2O and D_2S, 14. T_2S, 15. D_2O, 16. T_2O, 17. SiF_2. The values of c for examples 1 to 16 are given in Ref. [7]. The value of c for example 17 was calculated using the method given in [7].

One interesting feature of this graph is that all the c values are positive for nonhydrides and negative for hydrides.

In a very recent work by Swetharanyam and Ramaswamy [8] it has been reported that a linear relationship between a similar parameter $\Phi=(\tan^{-1}c)$ and the cube root of mass ratios exists in the case of $XY_4(T_d)$ type molecules. Since it is impossible to pinpoint the force field or the c values by virtue of the inherent spreads in the experimental values as well as errors due to anharmonicity, the observations of such regularities in the values of L_{12}/L_{21} or c with molecular structures are bound to help refinement of our knowledge of many of the molecular constants. A very interesting result arising from such observations is that the L_{ij} elements show almost complete dependence upon molecular geometry and atomic masses at least in such simple cases.

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