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 eigenvector matrix elements with mass coupling defined as $G_{12}/C_{12}$ 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. The points thus defined lie along a straight line in the case of molecules of $XY_2$ type possessing large mass coupling (e.g. $N_2O$, $NF_2$, $OF_2$, $CF_2$ 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. In such cases, the elements of the matrix $L=L_0$ can easily be calculated from the $G$ matrix employing the Wilson condition $L\bar{L}=G$. However, to represent the actual case, one may write

$$L=L_0 C$$  \hspace{1cm} (1)

where $C$ is an orthogonal matrix. Defining $C$ as

$$C=\frac{1}{\sqrt{1+c^2}} \begin{bmatrix} 1 & c \\ -c & 1 \end{bmatrix}$$  \hspace{1cm} (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 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.

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 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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