Calculation of Vibrational Isotope Effect in Polyatomic Molecules by a Perturbation Method

The perturbation theory devised by Lord Rayleigh for treating vibrating systems provides a convenient method of calculating the vibrational isotope effect in polyatomic molecules, especially those of high symmetry. Special cases of this problem have been treated by other investigators[1] but I believe the following method to be more convenient than any other of comparable accuracy so far proposed.

The difficulty in computing isotope shifts arises when the insertion of the isotope lowers the symmetry of the molecule so that the frequency formulas and normal coordinates for a molecule of lower symmetry would have to be used for a direct calculation. These formulas are always more complicated than those for the symmetric molecule and frequently are not available.

If the displacement of each atom is described by the use of a set of rectangular coordinates q_i with origin at the equilibrium position of the atom and if the change of scale $q_i=(m_i)^{\frac{1}{2}}q_i'$ is made, which introduces the masses into the potential energy, then the kinetic and potential energies are given by

$$2T=\Sigma_i\dot{q}_i^2;\quad 2V=\Sigma_{i,j}B_{ij}q_iq_j.$$

The solution of the normal coordinate problem is obtained when the characteristic values $\lambda_k=4\pi^2\nu_k^2$ (ν_k is the normal frequency) and the transformation

$$Q_k=\Sigma_i l_{ik}q_i$$

with matrix $L=(l_{ik})$ are known. The Q_k's are the normal coordinates.

If a perturbation $2V'=\Sigma_{i,j}C_{ij}q_iq_j$ with matrix $C=(C_{ij})$ is added to the potential energy, perturbation theory (which is analogous to that used in quantum mechanics) gives for the shift $\Delta\lambda_k$ of the kth characteristic value λ_k (λ_k non-degenerate) the expression

$$\Delta\lambda_k=(L^{-1}CL)_{kk}$$

or, on writing out the matrix product

$$\Delta\lambda_k=\Sigma_{i,j}l_{ik}C_{ij}l_{jk}.$$

If λ_k is degenerate, for example double, so that both Q_k and Q_r have the same frequency, it is necessary to solve the secular equation involving these two modes. Thus

$$\begin{vmatrix}(L^{-1}CL)_{kk}-\Delta\lambda & (L^{-1}CL)_{kr}\\ (L^{-1}CL)_{rk} & (L^{-1}CL)_{rr}-\Delta\lambda\end{vmatrix}=0$$

will give the two roots $\Delta\lambda$, which may be equal if the symmetry of the perturbation is high enough so as not to cause splitting of the degenerate frequency. In the above equation

$$(L^{-1}CL)_{kr}=\Sigma_{i,j}l_{ik}C_{ij}l_{jr}.$$

Detailed applications of this method will be reserved for a later paper but the calculation of the isotope effect for the symmetrical vibration (ν_1) of tetrahedral molecules AB_4 is so simple it is given below. Here $Q_1=\frac{1}{2}(r_1+r_2+r_3+r_4)$ if r_i is the radial displacement of the ith atom. If one isotopic B atom, say atom 1, is introduced, the part of the perturbation which is a function of the r's is

$$2V'=KSr_1^2+2K'R(r_1r_2+r_1r_3+r_1r_4),$$

in which K and K' are constants which appear in the potential energy of the unperturbed molecule while

$$S=(m+\Delta m)^{-1}-m^{-1}\cong-\Delta m/m^2,$$

$$R=[m(m+\Delta m)]^{-\frac{1}{2}}-m^{-1}\cong-\Delta m/2m^2,$$

for $\Delta m/m$ small. From the expression for Q_1, $l_{i1}=\frac{1}{2}$ for $q_i=r_1$, r_2, r_3 or r_4 and is zero otherwise. Therefore

$$\Delta\lambda_1=(L^{-1}CL)_{11}\cong-\tfrac{1}{4}(K+3K')\Delta m/m^2.$$

But

$$\lambda_1=(K+3K')/m\quad\text{so that}\quad\Delta\lambda_1/\lambda_1=-\Delta m/4m,$$

which for $\Delta m/m$ small agrees with Salant and Rosenthal's result. In a later paper complete details of the method together with applications to the isotope effect and other phenomena will be given.

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[1] E. O. Salant and J. E. Rosenthal, Phys. Rev. **43**, 581 (1933); **42**, 812 (1932).

A. Langseth, Zeits. f. Physik **72**, 350 (1931).

Separable Systems in Euclidean 3-Space

In 1891 Stäckel[1] showed how to determine the quantities H_i in the Hamiltonian-Jacobi equation

$$\Sigma_i\frac{1}{H_i^2}\left(\frac{\partial\varphi}{\partial x_i}\right)^2+k^2(E-V)\varphi=0,\qquad(1)$$

so that the variables are separable, the solution being of the form $\Sigma_i x_i$ where x_i is a function of x_i alone. In 1927 Robertson[2] showed that for an equation of the form

$$\Sigma_i\frac{1}{H}\frac{\partial}{\partial x_i}\left(\frac{H}{H_i^2}\frac{\partial\varphi}{\partial x_i}\right)+k^2(E-V)\varphi=0,\quad H=H_1\cdots H_n,\qquad(2)$$

to admit by separation of the variables a solution of the form ΠX_i, where X_i is a function of x_i alone, the functions H_i must be of the Stäckel form, and $V=\Sigma[f(x_i)/H_i^2]$, where $f(x_i)$ is an arbitrary function of x_i alone, just as in the case of Eq. (1) as shown by Stäckel; also he showed that the determinant φ of the Stäckel functions φ_{ij} must satisfy the condition

$$\varphi=\Pi[H_i/\psi(x_i)],\qquad(3)$$

where ψ_i is a function of x_i alone.

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[1] Stäckel, *Habilitationsschrift*, Halle.

[2] Robertson, *Bemerkung über separierbare Systeme in der Wellenmechanik*, Math. Annalen, Vol. 98, pp. 749–752.