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Anharmonicity Constants of the Potential Function of the Water Molecule

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The vibrational energy levels of a polyatomic molecule with quartic terms in the potential function are determined by matrix mechanics, and the change on substitution of an isotope formulated. Applied to H₂O and D₂O, frequencies at the zero point are obtained that satisfy invariants calculated for harmonic motion.

BONNER¹ derived by a wave-mechanical treatment the first-order perturbations of the energy levels of three coupled oscillators with quartic terms in the potential function, and estimated the isotope effect in D₂O. In the previous calculations² the theoretically interesting cross terms are exceedingly sensitive to changes in the frequencies, so that it was essential to determine the anharmonicity constants for D₂O with certainty.

For use with vibrational levels of low quantum numbers quite probably the energy of an N atomic molecule can be expressed as a Taylor's expansion in $3N$ Cartesian coordinates, x_i :

$$V = \sum_i v_{ii} x_i^2 + \sum_{i,j,k} v_{ijk} x_i x_j x_k + \cdots + v_{i_1 i_2 \dots i_p} x_{i_1} x_{i_2} \dots x_{i_p} \quad (1)$$

$$= \sum_p \sum_i v_{i_1 i_2 \dots i_p} x_{i_1} x_{i_2} \dots x_{i_p}, \quad i_p = 1, 2, \dots, 3N,$$

$p=2$ to the number of terms to be taken in the Taylor's expansion.

$$v_{i_1 i_2 \dots i_p} = \frac{1}{p!} \frac{\partial^p V}{\partial x_{i_1} \partial x_{i_2} \dots \partial x_{i_p}}.$$

If a transformation to coordinates ξ_i be made by

$$x_i = \sum_j q_{ij} \xi_j, \quad Q = \|q_{ij}\|, \quad (2)$$

$$\text{then} \quad V = \sum_p \sum_i \lambda_{i_1 i_2 \dots i_p} \xi_{i_1} \xi_{i_2} \dots \xi_{i_p}, \quad (3)$$

$$\text{where} \quad \lambda_{i_1 i_2 \dots i_p} = \sum_{\mu} v_{\mu_1 \mu_2 \dots \mu_p} q_{i_1 \mu_1} q_{i_2 \mu_2} \dots q_{i_p \mu_p}. \quad (4)$$

By the previously described normal coordi-

nate treatment the matrix Q is chosen so that if $V = V^{(2)} = \|v_{ij}\|$

$$\Lambda^{(2)} = Q' V Q = \Lambda \quad \text{diagonal} \quad \lambda_{ij} = \lambda_i \delta_{ij}; \lambda_i = \omega_i^2.$$

In the $\Lambda^{(p)}$'s the range of the indices is now only $3N-5$ or 6 since rotations and translations occur with zero force constants.

Quadratic cross terms being absent, quantum theory can be simply introduced by matrix mechanics. If \mathbf{P}_i and \mathbf{Q}_i be the well-known infinite matrices which satisfy the commutation rules and diagonalize the Hamiltonian for simple harmonic motion in the i th normal coordinate (whence the masses are unity)

$$\frac{1}{2}(\mathbf{P}_i^2 + \lambda_i \mathbf{Q}_i^2) = \mathbf{W}_i^0 \quad (5)$$

take as matrices \mathbf{P} and \mathbf{Q} for the system

$$\begin{aligned} \mathbf{P} &= \mathbf{P}_1 \times \mathbf{P}_2 \times \mathbf{P}_3 \times \cdots, \\ \mathbf{Q} &= \mathbf{Q}_1 \times \mathbf{Q}_2 \times \mathbf{Q}_3 \times \cdots, \end{aligned} \quad (6)$$

and define

$$\begin{aligned} \mathbf{W}^0 &= \mathbf{W}_1^0 \times \mathbf{I} \times \mathbf{I} \times \cdots + \mathbf{I} \times \mathbf{W}_2^0 \times \mathbf{I} \times \cdots \\ &\quad + \mathbf{I} \times \mathbf{I} \times \mathbf{W}_3^0 \times \cdots. \end{aligned} \quad (7)$$

Since the indices can be permuted without changing the value we can write $\lambda_{1_1 \dots 1_i 2_1 \dots 2_j 3_1 \dots 3_k \dots}$ for a λ with i indices equal to the cardinal number 1, j indices equal to the cardinal 2, k of 3, etc. Then the Hamiltonian³ of the whole system is

$$H = \mathbf{W}^0 + \frac{1}{2} \left\{ \sum_{ijk} \lambda_{1_1 \dots 1_i 2_1 \dots 2_j 3_1 \dots 3_k \dots} \mathbf{Q}_1^i \times \mathbf{Q}_2^j \times \mathbf{Q}_3^k \times \cdots \right\}. \quad (8)$$

³ Professor E. B. Wilson has very kindly discussed the relation of this to the precise Hamiltonian given by E. B. Wilson and T. B. Howard, *J. Chem. Phys.* **4**, 236 (1936), Eq. (33). Our simplified Hamiltonian is only valid as long as rotations can be regarded as linear combinations of Cartesian displacements and represented by a column in the matrix Q (Eq. (2)), which is of order $3N$, not $3N-6$; that is, it is valid for low quantum numbers, to which region its application is restricted.

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¹ L. Bonner, *Phys. Rev.* **46**, 458 (1934).

² "The Potential Function of the Water Molecule," *J. Chem. Phys.* **5**, 405 (1937).

Converting to the wave number energy scale, putting $B_i = (\hbar/(8\pi^2\omega_i))^{1/2}$ and

$$c_{ijk\dots} = \lambda_{ijk\dots}/2\hbar c B_i B_j B_k \dots \quad (9)$$

the energy matrix can be diagonalized by perturbation theory if the potential constants $c_{i_1 i_2 \dots i_p}$, $p \geq 3$, are small compared with ω_i (i.e. with the $c_{i_1 i_2}$'s). First-order corrections are the diagonal elements which come only from the matrices $Q_1^i \times Q_2^j \times Q_3^k \times \dots$ in which no i, j, k is odd.

$$\begin{aligned} E_{n_1 n_2 n_3 \dots} = & \sum_i \omega_i (n_i + \frac{1}{2}) + 3(2n_1^2 + 2n_1 + 1)c_{1111} \\ & + 3(2n_2^2 + 2n_2 + 1)c_{2222} + \dots \\ & + (2n_1 + 1)(2n_2 + 1)c_{1122} \\ & + (2n_1 + 1)(2n_3 + 1)c_{1133} \dots \quad (10) \end{aligned}$$

Collecting terms,

$$E_{n_1 n_2 n_3 \dots} = X_0 + \sum_i X_i n_i + \sum_i X_{ii} n_i^2 + \sum_{i>j} X_{ij} n_i n_j \quad (11)$$

with

$$\begin{aligned} X_0 &= \sum_i \omega_i/2 + 3 \sum_i c_{iiii}, \\ X_i &= \omega_i + 6c_{iiii} + 2 \sum_j c_{iiij}, \\ X_{ii} &= 6c_{iiii}, \\ X_{ij} &= 4c_{iiij}. \quad (12) \end{aligned}$$

To calculate force constants of the molecule we need the frequencies at the bottom of the potential bowl, which from (11) are

$$\omega_i = X_i - X_{ii} - \frac{1}{2} \sum_j X_{ij}. \quad (13)$$

Eqs. (12) were found to determine the change in the X 's when a different transformation to normal coordinates is made, for, although in the isotope effect V is assumed to be the same, Q and hence the λ_{ijk} 's and c 's are different.

If Q^H is the transformation for the molecule with one set of masses

$$Q^{H'} V Q^H = \Lambda^H \text{ diag.} \quad (14)$$

and Q^D is the one for another set of masses

$$Q^{D'} V Q^D = \Lambda^D \text{ diag.} \quad (15)$$

and Z is the product $Q^{H-1} Q^D$ which can be de-

termined accurately enough by successive approximations to the zero-point frequencies, then

$$\begin{aligned} \lambda^{(D)}_{i_1 i_2 \dots i_p} &= \sum_{\mu} q^{(D)}_{i_1 \mu_1} q^{(D)}_{i_2 \mu_2} \dots q^{(D)}_{i_p \mu_p} \nu_{\mu_1 \mu_2 \dots \mu_p} \\ &= \sum_{\nu, \mu} z_{\nu_1 i_1} z_{\nu_2 i_2} \dots z_{\nu_p i_p} q^{(H)}_{\nu_1 \mu_1} q^{(H)}_{\nu_2 \mu_2} \\ &\quad \dots q^{(H)}_{\nu_p \mu_p} \nu_{\mu_1 \mu_2 \dots \mu_p} \quad (16) \end{aligned}$$

$$= \sum_{\nu} z_{\nu_1 i_1} z_{\nu_2 i_2} \dots z_{\nu_p i_p} \lambda^{(H)}_{\nu_1 \nu_2 \dots \nu_p}. \quad (17)$$

The assumption was that the v_{ijk} 's remained unchanged, not the λ_{ijk} 's (linear combinations of the v_{ijk} 's with coefficients containing the masses), but Z and (17) had to be formulated because the v 's are not measurable, only the λ_{ijk} 's of the one molecule, (9) and (11). By the latter, however, only certain λ_{ijk} 's are measured—not all of those that occur on the right of (17). The problem thus cannot be solved rigorously, the anharmonicity constants of the isotope contain more constants (λ_{ijk}) because the λ_{ijk} 's are linear combinations of several v_{ijk} 's. The difficulty is easily overcome. In the case of triatomic molecules with hydrogen the matrix is very nearly diagonal (see 25). Because the matrices⁴ $D(\Gamma_i)^{(3)}$ are of the form $L(\Gamma_i) V(\Gamma_i) L(\Gamma_i)$, Z is also made up of main diagonal blocks, one for each representation, so that outside of these the nondiagonal elements are exactly zero.

If, for a first-order calculation Z is replaced by a diagonal $\|f_i^{1/2}\|$, $f_i = \lambda_i^{(D)}/\lambda_i^{(H)}$ with the f 's considered as parameters whose value can be made as accurate as desired by successive approximations, the summation (17) reduces to

$$\lambda^{(D)}_{i_1 i_2 \dots i_p} = f_{i_1}^{1/2} f_{i_2}^{1/2} \dots f_{i_p}^{1/2} \lambda^{(H)}_{i_1 i_2 \dots i_p}. \quad (18)$$

Substitution in (12) leads to

$$X_i^D = f_i^{1/2} \omega_i^H + 6f_i c_{iiii}^H + 2f_i^{1/2} \sum_j f_j^{1/2} c_{iiij}^H, \quad (19)$$

$$X_{ii}^D = f_i X_{ii}^H, \quad (20)$$

$$X_{ij}^D = f_i^{1/2} f_j^{1/2} X_{ij}^H. \quad (21)$$

Eq. (20) is exact for the σ vibration, since $Z(B_2)$ is of first order and equals $f_{\sigma}^{1/2}$.

⁴ See previous paper, Eq. (12).

APPLICATION TO WATER

Preliminary calculation with frequencies uncorrected for anharmonicity shows that Z can indeed be replaced without great error by the diagonal matrix $\|f_i^{(1)}\|$, $f_i^{(1)}$ being the ratio of the observed frequencies, in which case the unknown anharmonicity constants of D₂O are given by the formulae of the last paragraph. With the latter first-order approximations to the X 's of D₂O the observed frequencies are corrected for anharmonicity giving $\omega_\sigma^D = 2865.4$, $\omega_\pi^D = 2764.7$, $\omega_\delta^D = 1209.7$. The latter are now used to get better values for f_i and hence to get improved X^D 's. The second approximation to $f_\sigma^{1/2}$, 1.3632, already agrees with the value

$$f_\sigma^{1/2} = \left(\frac{2 \sin^2 \alpha}{m_1} + \frac{1}{m_2^H} \right)^{1/2} / \left(\frac{2 \sin^2 \alpha}{m_1} + \frac{1}{m_2^D} \right)^{1/2} = 1.3647 \quad (22)$$

derived in the previous paper. The values of f_π and f_δ are not determined independently of the frequencies as is f_σ because they belong to frequencies in the same representation.

Another way of testing the theory is actually to calculate the position of the fundamental ν_σ^D and compare with the wave-length observed:

$$\begin{aligned} \nu_\sigma^D &= \omega_\sigma^D + 2X_{\sigma\sigma}^D + \frac{1}{2}(X_{\sigma\pi}^D + X_{\sigma\delta}^D) \\ &= f_\sigma^{1/2}\omega_\sigma + 2f_\sigma X_{\sigma\sigma}^H \\ &\quad + \frac{1}{2}f_\sigma^{1/2}(f_\pi^{1/2}X_{\sigma\pi}^H + f_\delta^{1/2}X_{\sigma\delta}^H) \end{aligned} \quad (23)$$

with f_σ = the function of masses and angles (22). Since f_π and f_δ only multiply correction terms, a rough approximation based only on a simple model will suffice. The calculated value is $\nu_\sigma^D = 2781 \text{ cm}^{-1}$, the observed 2784 cm^{-1} .

SYMMETRICAL REPRESENTATION

By means of (19–21) and successive approximations, the observed bands⁵ at $\nu_\pi^D = 2666 \text{ cm}^{-1}$ and $\nu_\delta^D = 1179 \text{ cm}^{-1}$ yield corrected frequencies $\omega_\pi^D = 2773.3$ and $\omega_\delta^D = 1210.5$. These can be tested

⁵ W. V. Norris, H. J. Unger, R. E. Holmquist, Phys. Rev. 49, 272 (1936).

by the formula

$$\omega_\pi^D \omega_\delta^D = \frac{m_2^H}{m_2^D} \left(\frac{m^D}{m^H} \right)^{1/2} \omega_\pi^H \omega_\delta^H = 3.324. \quad (24)$$

From experimental data this is 3.357.

The constants for the energy formula for D₂O are

$$\begin{aligned} \omega_\delta^D &= 2857.0, & X_{\sigma\sigma}^D &= -21.2, & X_{\sigma\pi}^D &= -56.5, \\ \omega_\pi^D &= 2773.5, & X_{\pi\pi}^D &= -37.0, & X_{\sigma\delta}^D &= -11.3, \\ \omega_\delta^D &= 1210.5, & X_{\delta\delta}^D &= -10.4, & X_{\pi\delta}^D &= -10.1. \end{aligned}$$

BETTER APPROXIMATION

So far we have taken Z to be diagonal. Now we can investigate changes when nondiagonal elements are taken into account. With frequencies estimated as above Z is

$$Z = \begin{vmatrix} 0.7166 & 0.0646 \\ 0.0123 & 0.7374 \end{vmatrix}. \quad (25)$$

These values can be improved by successive approximations, but the ratio z_{ij}/z_{ii} remains small enough for z_{ij}^2 to be entirely neglected relative to the main diagonal elements, and the summation (17) reduces to fewer terms. The important constants are

$$\begin{aligned} \lambda^{D_{iiii}} &= z_{ii}^4 \lambda^{H_{iiii}} + \sum_{j \neq i} z_{ii}^3 z_{ji} \lambda^{H_{iii j}}, \\ \lambda^{D_{iiij}} &= z_{ii}^2 z_{ij}^2 \lambda^{H_{iiij}} + \sum_{k \neq j} z_{ii}^2 z_{ij} z_{kj} \lambda^{H_{iijk}} \\ &\quad + \sum_{k \neq i} z_{ij}^2 z_{ik} z_{ki} \lambda^{H_{ijki}}, \end{aligned} \quad (26)$$

so that

$$\begin{aligned} X_{ii}^D &= f_i^{-1} z_{ii}^4 X_{ii}^H + f_i^{-1} z_{ii}^3 \sum_j z_{ji} [6c^H_{iii j}], \\ X_{ij}^D &= f_i^{1/2} f_j^{1/2} z_{ii}^2 z_{jj}^2 X_{ij}^H \\ &\quad + f_i^{1/2} f_j^{1/2} \{ z_{ii}^2 z_{jj}^2 \sum_{k \neq j} z_{kj} [6c^H_{iijk}] + z_{ii} z_{jj}^2 \sum_{k \neq i} z_{ki} [6c^H_{jjik}] \}. \end{aligned}$$

The constants c^H_{iiij} , $c^H_{iijk} \sim \lambda^{H_{iiij}}$, $\lambda^{H_{iijk}}$ occur, which cannot be determined from one molecule. They could be derived by experimental determination of the X_{ij}^D 's in the isotopic molecule. However, they enter with relatively small coefficients and no doubt can be estimated as being equal in magnitude to the λ_{iiij} 's (which are all nearly equal). For water (26) corresponds to

$$\begin{aligned} X_{\pi\pi}^D &= 0.500 X_{\pi\pi}^H + 0.00857 [6c^H_{\pi\pi\pi\delta}], \\ X_{\delta\delta}^D &= 0.553 X_{\delta\delta}^H + 0.0484 [6c^H_{\delta\delta\pi\pi}], \end{aligned}$$

Substitution gives an increase of 2 cm^{-1} in $X_{\pi\pi}^D$ above that calculated by a diagonal Z , and a decrease of 1 cm^{-1} in $X_{\delta\delta}^D$.

Although nondiagonal elements are not entirely negligible, the diagonal elements of Z have changed enough from the f_i 's to counteract the effect.