The Potential Function of the Water Molecule

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however, are slightly shifted in position. The long wave-length component has a shoulder on its long wave-length side which is more pronounced in the solution than in the liquid. But there is no broad absorption, so characteristic of the alcohols and acids, which is sensitive to dilution with carbon tetrachloride.

It appears therefore that the broad bands of the two acids, like the corresponding bands of the alcohols, are due to a coupling in the liquid state between the hydroxyl parts of the molecules. Since the coupling is very likely of the hydrogen or hydroxyl bond type recently discussed by Bernal and Megaw,[8] a study of these bands may make possible an experimental distinction between the two types of bonds. But if a distinction lies, as Bernal and Megaw suggest it does, in the absence of a characteristic hydrogen vibration

[8] Bernal and Megaw, Proc. Roy. Soc. **A151**, 384 (1935).

in the hydrogen bond and, correspondingly, in its presence in a hydroxyl bond, the similarity of the spectra of the alcohols and acids shows that their bondings are alike.[9] And certainly not enough is known about these bonds to say that the apparently greater strength or wider range of the acid polymer bands is sufficient to distinguish .between a hydrogen bond in which a proton interchange between oxygens can take place and a hydroxyl bond in which it cannot. For the present the infrared evidence supports the view that, with respect to the behavior of hydrogen, the alcohol and acid polymer bonds are alike.

[9] Compare, for example, Bernal and Megaw's remarks on acetic acid (reference 7, page 420) in which they use the absence of observed Raman lines caused by characteristic hydroxyl frequencies to indicate the presence of a hydrogen bond as distinct from a hydroxyl bond. The same argument based on the evidence of infrared absorption would lead to no such distinction in type between the alcohol and acid liquid lattice bonds.

The Potential Function of the Water Molecule

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For use with frequencies corrected for anharmonicity the energy of a molecule is expressed by a complete quadratic form. Reduction of the force constants in Cartesian coordinates to an independent set by relations due to symmetry and mutual forces is carried out by a systematic matrix method which is particularly useful in correcting for anharmonicity and for finding functions of the frequencies and masses invariant in isotopic molecules. For H$_2$O and D$_2$O these relations being satisfied, the potential function is indeed assumed to be unchanged, all constants are computed, and compared with those of various models. In the S$-$P$'$picture of the H$_2$O molecule the H$-$H repulsion, ionic terms in OH bonding and exchange integrals in the angular function prove to be the values expected theoretically.

A LARGE number of experimentally determined vibrational levels have been roughly correlated by the use of potential functions of simple models, but satisfactory agreement necessitates the use of a complete potential function. The spectra of a single molecule usually do not yield enough independent data to evaluate all the necessary constants. The many attempts at choosing functions with as many constants as frequencies are by definition only approxima-

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tions; cross terms have to be neglected which often turn out to be large. It would be possible to determine all constants by substitution of isotopes provided the potential energy remains unchanged. There are enough experimental data for H$_2$O and D$_2$O to test whether the isotope makes significant changes in the potential function relative to the vibrational levels, and if not, to determine all the constants of a general quadratic potential expression for energy. It is instructive to evaluate the true values of cross terms of various models showing that it needs an intuitive choice very close to normal coordinates

before the neglect of such terms does not affect low frequencies. It is also shown that as regards correlation with the S−P structure it is useless to calculate cross terms without proper correction for anharmonicity.

The isotope effect on vibrational levels will be investigated in two steps; first the classical frequencies at the bottom of the potential bowl will be determined using a complete quadratic expression, then anharmonicity corrections will be calculated from higher terms. For triatomic molecules the first step, that of changing to normal coordinates, has already been presented in many forms, but we shall take the opportunity to outline a method which works well for more complicated molecules, leading to formulae of "invariants" that can be used for the identification of bands and for the accurate prediction of the isotope effect. On replacing an atom by an isotope each vibrational frequency will not in general be multiplied by an "isotope factor" (function of masses only) unless it is alone in a representation; rather there will be factors by which certain invariants will change. Formulae of this sort are useful since they are quite accurate when applied to the observed frequencies, because unknown anharmonicity corrections largely cancel.

FREQUENCIES WHEN THE ENERGY IS A COMPLETE QUADRATIC

Since we do not intend to neglect any constants there is no need to choose unusual coordinates. Simple Cartesian coordinates x_i for each atom are the clearest, and the corresponding constants will then be easily visualized and more easily interpreted than those resulting from an exotic choice of special coordinates. The simplifications of common sense and, in more complicated cases, of intuition are introduced as a straightforward algebraic formulation of group theory.

Let v_{ij} and t_{ij} be the constants in the bilinear forms for the potential and kinetic energies of an N atomic molecule

$$-2V = \sum_{ij} v_{ij} x_i x_j, \tag{1}$$

$$2T = \sum_{ij} t_{ij} \dot{x}_i \dot{x}_j, \tag{2}$$

summed from $i, j = 1$ to $3N$ so that

$$v_{ij} = -\frac{\partial^2 V}{\partial x_i \partial x_j}$$

and $V = \|v_{ij}\|$ is symmetrical.[1]

The classical problem can be formulated as a diagonalization process to which the simplifications of group theory are most easily applied. The Lagrangian equations are

$$\sum_j (t_{ij} \ddot{x}_j + v_{ij} x_j) = 0 \tag{3a}$$

and if harmonic motion of frequency ω is assumed, these reduce to

$$\sum_i v_{ij} x_j = \lambda \sum_i t_{ij} x_j, \quad \lambda = \omega^2. \tag{3b}$$

If $q^{(\lambda)}$ be a vector whose elements are the amplitudes of simple harmonic oscillation, in a normal coordinate, with frequency ω, the above set of $3N$ linear Lagrangian equations can be written as one,

$$T^{-1} V q^{(\lambda)} = D q^{(\lambda)} = \lambda q^{(\lambda)}, \tag{3c}$$

in which T and V are the matrices of the bilinear forms (1) and (2), and $T^{-1}V = D$. A matrix Q is defined whose columns are the $3N$ vectors $q^{(\lambda)}$, and Λ as a diagonal matrix whose elements correspond to the $3N$ λ's, any one of which satisfies (3b). The frequencies and amplitudes (coefficients of the linear transformation equations to normal coordinates) will be found by solving the matrix equation

$$Q^{-1} D Q = \Lambda, \tag{3d}$$

which is shorthand for the $3N$ sets of $3N$ linear equations (3c). Given D the problem is to find the matrix of transformation to normal coordinates Q, and the set of frequencies Λ. On the other hand, in our present state of knowledge, D is the unknown.

The frequencies Λ may or may not be all measurable, and since as yet the amplitudes Q are unobserved, D, hence V, cannot be calculated from the experiment, except in the few special cases where the number of independent ele-

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[1] When there is degeneracy, as in a triatomic molecule of D_{3h}, it is convenient to use complex numbers. In that case the words "symmetrical" and "orthogonal" occurring below must be replaced by "Hermitian" and "unitary."

ments in D equals the number of observed frequencies, unless certain frequencies of one or more isotopic molecules with identical V's are known. To do this it is convenient to simplify (3d) to equations in independent constants, which is done in two steps of partial diagonalization. The number of different elements may be reduced by Cauchy relations, resulting from symmetry. If the molecule is not in a force field six roots λ corresponding to rotation and translations will be zero. The rank of the $3N$th order matrix is thus $3N$-6; hence there are 6 relations between the constants entirely different from those resulting from symmetry.

By a simple device the problem can be reduced to the diagonalization to Λ of a symmetrical matrix, requiring only an *orthogonal* transformation S which is much easier to work with than Q. In analogy to the usual treatment of reducing the bilinear expression for the kinetic energy to the canonical form, take $L^2 = T^{-1}$ and $S = L^{-1}Q$ and substitute in (3d)

$$S'(LVL)S = \Lambda. \qquad (4)$$

The matrix $D^{(1)} = LVL$ is symmetrical and has the same roots as D. If Cartesain coordinates were chosen T and L are diagonal, $l_i = 1/\sqrt{m_i}$, and $d_{ii}^{(1)} = v_{ii}/(m_i m_i)^{\frac{1}{2}}$.

If there is any symmetry partial diagonalization to blocks, each one referring to all oscillations of the same symmetry type, can be accomplished by a change of coordinates which can be picked so that the matrix of transformation has elements independent of the actual values of the potential constants. Such "symmetry coordinates" are often obvious, but in complicated cases when intuition is not developed enough, they can be deduced by group theory.

Let G be a matrix induced in configuration space by one of a group of symmetry operators. For example in Fig. 1 a rotation of π about the symmetry axis z (operator $C_2(z)$) induces

$$G(C_2z) = \left\| \begin{matrix} \cos \pi & \sin \pi \\ & \\ -\sin \pi & \cos \pi \end{matrix} \right\| \times \left\| \begin{matrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{matrix} \right\| \qquad (5)$$

where the order of coordinates is $z_1y_1z_2y_2z_3y_3$: the first matrix is the usual rotation of coordinates,
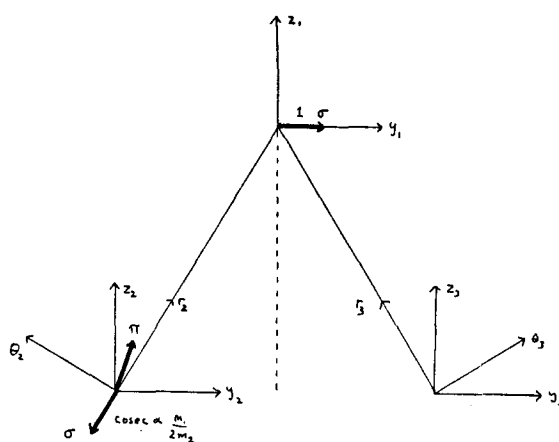

FIG. 1.

and the second the permutation of the atoms. Such an operation merely changes the phase of a characteristic oscillation $q^{(\lambda)}$ so that

$$Gq^{(\lambda)} = \gamma q^{(\lambda)}, \qquad (6)$$

where γ is a root of unity. In the case of degeneracy $q^{(\lambda)}$ has to be properly chosen from the infinite set of degenerates $q^{(\lambda)}$'s to satisfy (6).

The diagonalization to blocks is done by a unitary matrix R of columns $r^{(i)}$ which will reduce G (preferably the most complicated one) to a diagonal form, $\|\gamma_{ii}\|$ where γ_{ii} are roots of unity since G is always unitary. The matrix R will reduce all the matrices of the group if and only if there is no degeneracy.

$$Gr^{(i)} = \gamma_{ii}r^{(i)}. \qquad (7)$$

Comparing (7) and (6) $q^{(\lambda)}$ is a linear combination of columns of R belonging to the same γ or representation, the coefficients of this combination being determined only by the force constants and not by symmetry. The elements in a column of R may be pictured as amplitudes of an oscillation of the system which has the correct symmetry properties: obviously a normal vibration is a linear combination of all such simply constructed modes *that have the same symmetry*. For a triatomic molecule belonging to D_{3h} the transformation R deduced as above by diagonalizing either the operator C_3 or S_6 is actually the required transformation to normal coordinates, $R \equiv S$: the diagonalization is complete. In general, by the introduction of symmetry

coordinates, as defined by R, the matrix

$$D^{(2)} = R'D^{(1)}R = D^{(2)}(\Gamma_1) + D^{(2)}(\Gamma_2) + \cdots \quad (8)$$

is divided into main diagonal blocks $D^{(2)}(\Gamma_i)$, one for each representation Γ_i. In the case of a triatomic molecule of symmetry C_{2v} the matrix R is

$$R = \frac{1}{\sqrt{2}} \begin{Vmatrix} \sqrt{2} & 0 & 0 \\ 0 & 1 & 1 \\ 0 & 1 & -1 \end{Vmatrix} \times \begin{Vmatrix} 1 & 0 \\ 0 & 1 \end{Vmatrix}, \quad (9)$$

when the order of coordinates is $y_1z_1y_2z_2y_3z_3$. The columns and rows of $D^{(2)}$ are then distributed among the representations in the same way as columns of R are, in this case $B_2A_1B_2A_1A_1D_2$. Symmetry is enforced on D by putting all non-diagonal blocks of $D^{(2)}$ identically zero, to give all the (Cauchy) relations between the v_{ij}'s that can be obtained from symmetry considerations, which relations are substituted in the main diagonal blocks. Since L commutes with R, $L^{-1}D^{(2)}L^{-1}$ is the matrix of force constants to be used with symmetry coordinates, of which many are still dependent.

Independent constants are now obtained by considering only mutual forces between the atoms, i.e., by removing rotations and translations. Algebraically this corresponds to knowing the roots λ for the latter are zero. This is not so if the molecule is in a force field, such as in a liquid or crystal lattice, in which case no further reduction beyond symmetry is possible. Since rotations and translations belong to definite representations each block $D^{(2)}(\Gamma_i)$ can be treated separately: indeed for simplicity different coordinates may be used in different blocks. It is easy to write down the $q^{(\lambda)}$'s for these motions of zero frequency, e.g., that for translation parallel to the axis of symmetry is $\sim(0\ 1\ 0\ 1\ 0\ 1)$. Vectors $f^{(\lambda)}$ representing the amplitudes in symmetry coordinates are made from these

$$f^{(\lambda)} = R'L^{-1}q^{(\lambda)}. \quad (10)$$

For representation Γ_i a unitary matrix $F(\Gamma_i)$ is set up with a column $f^{(\lambda)}$ for each rotation and translation belonging to that representation, the remaining columns being chosen as simply as

possible to complete F and make it unitary. In our example

$$F(A_1) = \begin{Vmatrix} (m_1/M)^{\frac{1}{2}} & (2m_2/M)^{\frac{1}{2}} & 0 \\ (2m_2/M)^{\frac{1}{2}} & -(m_1/M)^{\frac{1}{2}} & 0 \\ 0 & 0 & 1 \end{Vmatrix}, \quad (11)$$

$$M = m_1 + 2m_2.$$

The matrices (one for each representation)

$$D^{(3)}(\Gamma_i) = F'(\Gamma_i)D^{(2)}(\Gamma_i)F(\Gamma_i) \quad (12)$$

now contain the simplest possible set of independent mutual force constants and reduced masses, and of course have the same roots as the original D. They have a main diagonal block of order equal to the number of true vibrations in Γ_i, the remainder of the matrices being zero.

To summarize, a change of coordinates x_i to reduced mass symmetry coordinates ξ_i has been made in configuration space,

$$x_i = q_{ij}\xi_j, \quad (13)$$

$$\|q_{ij}\| = Q = LRF, \quad (14)$$

where the transformation L was made to make the dynamical matrix D symmetrical, so that all subsequent transformations could be orthogonal: the change R divided the problem into separate representations, and F gave mutual forces, that is, coordinates fixed relative to the center of gravity. The last two are not commutative, but the first two are.

APPLICATION TO THE MOLECULE AB_2 OF C_{2v}

For representation B_2, $D^{(2)}(B_2)$ is of the third order. Two columns of $F(B_2)$ belong to a rotation and a translation: hence the third is fixed and corresponds to the relative amplitudes of motion in the σ vibration. Contrary to many published diagrams, in the σ vibration atoms 2 and 3 always move along the bonds, and atom 1 perpendicular to the symmetry axis, and the relative amplitudes are functions of the masses and angles only. The ratio of the electric moments of isotopic molecules is a function only of the masses.

Since F is uniquely determined the diagonalization is complete,

$$D^3_{(\Gamma_t)} = \begin{Vmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \lambda_\sigma \end{Vmatrix}. \qquad (15)$$

Equating (15) element for element we get in a very simple way the relations between the v_{ij}'s necessary to keep the center of gravity stationary and to prevent rotation, i.e., the mutual force constants. From these the trace comes out to be

$$\lambda_\sigma = \left(\frac{2\sin^2\alpha}{m_1} + \frac{1}{m_2}\right)(v_{r_2r_2} - v_{r_2r_3}). \qquad (16)$$

This is an expression of the same form as obtained previously for specialized models. Using *all* the terms of a quadratic potential function the only modification is in the force constant, which is neither that of the diatomic molecule AB nor that of a diatomic molecule AB with the same electronic structure as in AB_2, for as will be shown in (31) it contains a component of the interaction of atoms 2 and 3. As is the case with any frequency alone in a representation the force constants and masses occur in separate factors. The ratio of frequencies of any isotopic molecules, retaining the symmetry, is a function of the masses and angle only (the superscripts H and D refer to two isotopes of B)

$$\frac{\omega_\sigma^H}{\omega_\sigma^D} = \left(\frac{2\sin^2\alpha}{m_1} + \frac{1}{m_2^H}\right)^{\frac{1}{2}} \Big/ \left(\frac{2\sin^2\alpha}{m_1} + \frac{1}{m_2^D}\right)^{\frac{1}{2}}. \quad (17)$$

This formula and (18) have been shown before; here we show they are true for the general quadratic, and hence for a general potential function provided frequencies corrected for anharmonicity are used. In the case of H$_2$O the right-hand side has a value of 1.3647 using an angle[2] of 104° 41′. With the observed frequencies corrected for anharmonicity as described below the ratio is 1.3632.

A satisfactory agreement of the observed ratio to (17) shows that very probably the force constant $v_{r_2r_2} - v_{r_2r_3}$ is the same in the isotopic molecule. Assuming this we can use (17) to calculate the angle from the two observed frequencies.

[2] K. Freudenberg and R. Mecke, Zeits. f. Physik **81**, 465 (1933).

$$\sin^2\alpha = \frac{m_1}{2}\left(\frac{\lambda_\sigma^D}{m_2^H} - \frac{\lambda_\sigma^H}{m_2^D}\right) \Big/ \lambda_\sigma^H - \lambda_\sigma^D, \quad (18)$$

which gives $2\alpha = 107°\ 22'$ in fair agreement with the angle obtained from rotational analysis,[2] 103° 20′ to 107° 20′. The formula (18) is very sensitive to the frequencies, and the σ vibration of D$_2$O has not been measured under high resolution.

In the symmetrical representation A_1 the third-order matrix has rank two since one root belonging to translation parallel to the symmetry axis is zero. Using yz coordinates a simple $F(A_1)$ can be found removing this motion, reducing $D^{(3)}(A_1) = F(A_1)D^{(2)}(A_1)F(A_1)$ to a second-order matrix whose roots are λ_π and λ_δ.

$$D^{(3)}(A_1) = \frac{1}{m_2}\begin{Vmatrix} \mu^2 z_+ & -\mu w_- \\ -\mu w_- & y_- \end{Vmatrix}, \qquad (19)$$

where
$$z_+ = v_{z_2z_2} + v_{z_2z_3}, \quad w_- = v_{y_2z_2} - v_{y_2z_3},$$
$$y_- = v_{y_2y_2} - v_{y_2y_3}, \quad \mu = (M/m_1)^{\frac{1}{2}}.$$

Further diagonalization depends on the actual force constants. It turns out that for this molecule transformation to $r\theta$ coordinates (Fig. 1) reduces the nondiagonal element enough to neglect it relative to the larger root λ_π. However, without numerical knowledge of the force constants, the possible affect of isotope on them can be tested. From the determinant of (19)

$$\lambda_\pi\lambda_\delta = (M/m_1m_2^2)(z_+y_- - \omega_-^2), \qquad (20)$$

so that
$$\frac{\omega_\pi^H\omega_\delta^H}{\omega_\pi^D\omega_\delta^D} = \frac{m_2^D}{m_2^H}\left(\frac{M^H}{m^D}\right)^{\frac{1}{2}}, \qquad (21)$$

a function independent of angles or internuclear distances. For H$_2$O $-$ D$_2$O it is 1.895. With Bonner's frequencies[3] for H$_2$O and values for D$_2$O all corrected for anharmonicity the observed ratio is 1.884.

This good agreement is encouraging enough to use H$_2$O and D$_2$O data to calculate the potential constants. Only three of the four frequencies ω_π^H, ω_δ^H, ω_π^D, ω_δ^D need be used. It is most convenient to select three, calculate the fourth by (21) and use all four with invariants of (19)— that is the traces and determinant. If we put

[3] L. Bonner, Phys. Rev. **46**, 458 (1934).

$m_2\lambda_i = \kappa_i$ the traces of $D^{(3)}(A_1)$ for the two molecules yield

$$z_+ = \kappa_\pi^H + \frac{\kappa_\delta^H - \kappa_\pi^D}{\mu_H^2 - \mu_D^2} - \kappa_\delta^D, \qquad (22)$$

$$y_- = \kappa_\pi^H + \kappa_\delta^H - \mu_H^2 z_+.$$

The determinant gives

$$w_- = \pm(z_+ y_- - \lambda_\pi\lambda_\delta(m_1 m_2^2/M))^{\frac{1}{2}}. \qquad (23)$$

Force constants in $r\theta$ coordinates are more significant from a theoretical standpoint (yz coordinates were used above because of the simplicity of the equations); they can be calculated from the transformation

$$\begin{Vmatrix} \cos\alpha & \sin\alpha \\ -\sin\alpha & \cos\alpha \end{Vmatrix} \begin{Vmatrix} z_+ & w_- \\ w_- & y_- \end{Vmatrix} \begin{Vmatrix} \cos\alpha & -\sin\alpha \\ \sin\alpha & \cos\alpha \end{Vmatrix}$$

$$= \begin{Vmatrix} \rho_+ & \varphi_+ \\ \varphi_+ & \theta_+ \end{Vmatrix}, \qquad (24)$$

where $\rho_+ = v_{r_2 r_2} + v_{r_2 r_3}$,

$$\theta_+ = v_{\theta_2\theta_2} + v_{\theta_2\theta_3} = 2v_{\theta_2\theta_2} \quad \text{from (12)},$$
$$\varphi_+ = v_{r_2\theta_2} + v_{r_2\theta_3} = 2v_{r_2\theta_3} \quad \text{from (12)}. \qquad (25)$$

Only ρ_+ need be calculated by matrix multiplication, the trace and determinant of (24) give

$$\theta_+ = z_+ + y_- - \rho_+, \quad \varphi_+^2 = \rho_+\theta_+ - (z_+ y_- - w_-^2). \quad (26)$$

Actual values of these force constants were calculated using Bonner's values of the corrected frequencies ω_σ^H, ω_π^H, ω_δ^H obtained from analysis of a large number of infrared bands. In the next paper the anharmonicities for D_2O are calculated and applied to the observed frequencies.[4] As only one of these need be chosen, ω_δ^D was selected as ω_π^D was determined from the Raman spectrum about which there may be some doubt. In the Raman spectrum of H_2O the observed value of π vibration (uncorrected for anharmonicity) is 3654 in the Raman spectrum,[5] whereas the value calculated from infrared is 3604 cm^{-1}, a difference of 54 cm^{-1}. Assuming ω_δ^H, ω_δ^D, ω_π^H (infrared) formula (21) would be exactly satisfied by a π vibration (uncorrected for anharmonicity) of 2638 which differs from

[4] W. V. Norris, H. J. Unger, R. E. Holmquist, Phys. Rev. **49**, 272 (1936).
[5] D. F. Bender, Phys. Rev. **47**, 252 (1935), *et al.*

the observed Raman line 2666 cm^{-1} by 27.7 cm^{-1}. Allowing for an isotope effect the same discrepancy between the Raman and infrared frequencies seems to occur in D_2O as in H_2O.

From the values

$$\omega_\delta^H = 3899.0 \text{ cm}^{-1}, \quad \omega_\delta^D = 1210.5 \text{ cm}^{-1},$$
$$\omega_\pi^H = 3807.5 \text{ cm}^{-1}, \quad (\omega_\pi^D = 2745.6) \text{ cm}^{-1},$$
$$\omega_\delta^H = 1654.5 \text{ cm}^{-1},$$

the force constants are calculated to be (units of megadynes/cm)

$$z_+ = 0.3567, \quad \rho_+ = 0.8211, \quad v_{r_2 r_2} = 0.8269,$$
$$y_- = 0.6169, \quad \theta_+ = 0.1526, \quad v_{r_2 r_3} = -0.00585,$$
$$w_- = 0.3114, \quad \varphi_+ = -0.0469, \quad v_{\theta_2\theta_2} = 0.07632,$$
$$\rho_- = 0.8325, \quad v_{r_2\theta_3} = -0.02346.$$

For further calculation of intensities or anharmonicities the numerical value of the matrix $P(A_1)$ which diagonalizes $D^{(3)}(A_1)$ is wanted. Being orthogonal it is of the form

$$P(A_1) = \begin{Vmatrix} \cos\vartheta & \sin\vartheta \\ -\sin\vartheta & \cos\vartheta \end{Vmatrix} \qquad (27)$$

with ϑ given by the equation

$$\sin 2\vartheta = \frac{-2}{m_2}\left(\frac{m}{m_1}\right)^{\frac{1}{2}} \frac{w_-}{\lambda_\pi - \lambda_\delta}. \qquad (28)$$

The motion of the hydrogen atoms in the π vibration makes an angle $\tan^{-1}\mu^{-1}\tan\vartheta - \alpha$ with the bond direction, which is 17° 28′ for H_2O and 17° 17′ for D_2O.

The evaluation of the terms in the general quadratic expression form a nucleus for a collection of correct force constants—augmented with similar results from H_2S, H_2Se, methane, ethylene, etc., which should indicate the order of magnitude of similar constants, especially cross terms, to be used in the calculation of frequencies in molecules where the potential function cannot be obtained from theory or experiment. Of especial interest is the bending constant, which, in agreement with an empirical rule derived from linear molecules, is about 10 percent of the bonding constant: the high value of 17 percent $v_{r_2 r_2}$ of H—H repulsion is in

TABLE I. *The energy, $f(r)$, of OH bonding.*

MEGADYNES/CM	CURVA-TURE f''	SLOPE (PER CM) f'/r
i Observed in OH molecule	0.7757	0
ii Observed in H_2O, Eq. (31)	.8386	0.0109
iii Predicted by Badger's rule	.800	—
iv Predicted by (32)	—	0.0073
v Predicted by Morse function for OH	.8252	0.0075
vi Predicted by introduction of ionic terms in the Morse function	.8356	0.0070
vii Predicted by introduction of ionic terms in the Morse function	.8306	.011
viii Predicted by addition of ionic terms	.8386	.013

accordance with indications from other molecules. In water, at any rate, the valence and central models contribute equally to the molecular function.

The constants determined above are probably reliable, as they favorably withstand two tests. The frequencies of HDO can be calculated since both V and T are now known, but the presentation of this confirmation will have to be postponed since comparison with experiment also requires the determination of anharmonicity constants for HDO.

In the second test the actual constants are compared with those of a theoretically constructed molecule based on the S—P picture of directed valence. Since the constants differ somewhat from those estimated by Van Vleck and Cross[6] for such a model, it is interesting to see to what parameters in the energy functions the actual values correspond. In this each hydrogen is joined independently to the oxygen as it is in OH chiefly by the overlapping $f(r)$ of the orbital of the hydrogen $1s$ electron with one of the three p orbitals in oxygen which are oriented at right angles. The mutual effect of the hydrogen is $1s-1s$ repulsion $g(r_{12})$ increasing the angle. The stiffness of the angle $h(\alpha)$ is due to two important exchange integrals—the actual bonding A to one p orbital and exchange with the other two $\frac{1}{2}B$, formulated by Slater[7] as

$$h(\alpha) = 3(A - B) \sin^2 (\alpha/2 - \pi/4). \quad (29)$$

Lacking exact computation the potential function is estimated as a central force model of Morse functions of OH and H_2 with a valence

[6] J. H. Van Vleck and P. Cross, J. Chem. Phys. **1**, 387 (1933).
[7] J. C. Slater, Phys. Rev. **38**, 1109 (1931).

force model using Slater's angular function,

$$v = f(r_1) + f(r_2) + g(r_{12}) + h(\alpha). \quad (30)$$

By (3)

$$f'' = v_{r_2 r_2} + \cos \alpha v_{r_2 r_3} - \tfrac{1}{2} \sin 2\alpha \, v_{r_2 \theta_3}$$
$$= 0.8386 \text{ megadynes/cm},$$

$$f'/r = -\sin^2 \alpha(-2v_{r_2 r_3} + \tan \alpha \, v_{r_2 \theta_2})$$
$$= 0.0109 \text{ megadynes/cm},$$

$$g'' = v_{r_2 r_3} + \tfrac{1}{2} \cot \alpha \, v_{r_2 \theta_3}$$
$$= -0.0149 \text{ megadynes/cm},$$

$$g'/r = \sin \alpha(-2v_{r_2 r_3} + \tan \alpha \, v_{r_2 \theta_2})$$
$$= -0.0143 \text{ megadynes/cm}, \quad (31)$$

$$h''/r = v_{\theta_2 \theta_2} - 4v_{r_2 r_3} - 4 \cot 2\alpha \, v_{r_2 \theta_3}$$
$$= 0.0751 \text{ megadynes/cm},$$

$$h'/r^2 = -\sin 2\alpha(-2v_{r_2 r_3} + \tan \alpha \, v_{r_2 \theta_3})$$
$$= 0.0181 \text{ megadynes/cm},$$

The fact that g'' and g'/r have the correct sign (showing hydrogen repulsion) alone is gratifying, since this is not so when frequencies uncorrected for anharmonicity are used. The value of the force constant f'' being almost that in OH substantiates the conception of directed valence bonding, but even the discrepancy is in good agreement with more detailed considerations. First, the increase of the constant with decrease in internuclear distance, $r_{OH} = 0.964$, $r_{H_2O} = 0.955$A, is in agreement with Badger's rule as shown in Table I (*iii*).

Were the bonding function the same in H_2O as OH, for such small displacements

$$f'_{H_2O} = f'_{OH} + \Delta r f''_{OH}, \quad (32)$$

a relation not satisfied by the data (Table I, *iv*). The discrepancy is probably due to increased ionic character in the H_2O molecule, a phenomenon predicted by theory. A correction for a small increase in ionic character say x percent can be estimated[8] by multiplying the Morse function by $100+x$. A Morse function alone gives values, in agreement with (32), shown in the line v of Table I, while 1.5 percent ionic character raises f'' to the correct value but leaves f'/r still too low (*vi*). The change due to the introduction of small amounts of "ionic" wave functions affects the exponential factor in

[8] Eyring and Polanyi, Zeits. f. physik. Chemie **B12**, 279 (1931).

the Morse function rather than the dissociation energy, 1.5 percent ionic character giving in this case the correct values, *vii* of Table I.

Still a third way of calculating the change follows from the additivity of the differentials of terms in the potential energy. Pure ionic attraction would correspond to

$$V = e^2/r, \tag{33}$$

$$\frac{\partial V}{\partial r} = -\frac{0.230}{r^2} 10^{-5} \text{ dynes}, \tag{34}$$

$$\frac{\partial^2 V}{\partial r^2} = \frac{0.46}{r^3} \text{ megadynes/cm}, \tag{35}$$

and 2.5 percent ionic character giving about the right correction to both constants (*viii*, Table I).

The hydrogen repulsion $g(r_{12})$ can be similarly estimated from the Morse function for H_2, for which the parameters are determined from the values $\omega_e = 4371.9$ and $D_e = 4.722$ ev. As shown by Van Vleck and Cross x percent ionic character in the energy of nonbonded atoms can be represented by a Morse function multiplied by a factor $x/100 \times \frac{1}{2}(1-x/100)$. At the internuclear distance $2r \sin \alpha = 1.512A$ 20 percent ionic character gives the observed $g'' = -0.0149$, and $g'/r = -0.0116$ whereas the observed g'/r is -0.0148.

The more detailed picture of the *angular* function (29) can be confirmed in two independent ways by the data: the agreement reveals the extent to which the data are self-consistent.

$$h''/r^2 = 6(A-B)/r^2 \sin 2\alpha, \tag{36}$$

$$h'/r^2 = -3(A-B)/r^2 \cos 2\alpha, \tag{37}$$

giving for $(A-B)/r^2$ the values 2.96 and 3.26 ev/A, in agreement with the values of the exchange integrals calculated by Coolidge.[9] Using the value used in the computations, one has $(A-B)/r^2 = 2.9$. The actual calculation of Coolidge did not give the correct energy, probably due to lack of ionic terms. However, the above agreement is not fortuitous since ionic terms would not contribute to the angular (orientation) part, $h(\alpha)$, unless they were large.

CONCLUSIONS

The hydrogen isotope does not change the potential function of H_2O to within the accuracy of measurement of the vibrational levels. If this is assumed the angle can be calculated as $107° 22'$, agreeing with the value obtained from rotational analysis, and all force constants in a general quadratic potential function can be determined, showing that valence and central force constants are equally important, and that cross terms are not negligible with respect to the lowest frequency. These constants are of the magnitude predicted by the $S-P$ picture of molecular structure in regard to the OH bonding, $H-H$ repulsion and stiffness of orientation.

These computations were achieved by a matrix method of handling changes of coordinates, of general application, leading to accurate formulae for studying the isotope effect, identifying bands and determining the angle. As shown in the following paper the method is especially useful in calculating the perturbation of the energy levels due to higher and cross terms in the potential functions, and the effect of the isotope thereon.

[9] A. S. Coolidge, Phys. Rev. **42**, 189 (1932).