

The Water Vapor Molecule

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The problem of the vibration rotation spectrum of water vapor is treated by means of the theory of semi-rigid polyatomic molecules developed by Wilson and Howard. The potential energy is expanded as a power series in the normal coordinates and involves three zeroth-order constants, six first-order and six second-order constants. The positions of the band centers are calculated and found to depend upon ten quantities, X_i , X_{ik} , and γ which are functions of the potential constants. A new feature of the treatment is the recognition of a resonance interaction between certain of the overtone bands which arises from the near equality of ν_1 and ν_3 . Eighteen band centers are known experimentally. These serve to determine the X_i , X_{ik} , γ and furnish eight self-consistency checks which are very adequately satisfied. There exists no discrepancy between the Raman and infrared spectra as reported earlier. In order to obtain the geometric displacements corresponding to each normal coordinate it is necessary to examine the spectrum of D_2O . This not only furnishes the required information but also

allows two independent checks upon the theory both of which turn out to be in nearly perfect accord. The interaction between vibration and rotation is considered and the effective moments of inertia are calculated. These are functions of the normal frequencies and of the first-order potential constants. It is shown that $\Delta = I_C - I_A - I_B$ depends only upon the normal frequencies and hence may be computed at once. A comparison between the observed and predicted Δ yields a very satisfactory agreement. The analysis of the rotational structure made by Mecke is supplemented by taking account of the rotational stretching. The resulting molecular constants fix the valence angle to be $104^\circ 31'$ and the O-H distance to be 0.9580\AA . From the effective moments of inertia the first-order potential constants may be evaluated and these, together with X_{ik} determine the second-order potential constants. It is now possible to compute the interaction constant γ and a comparison with the observed γ again results most satisfactorily.

1. INTRODUCTION

THE vibration rotation spectrum of water vapor is a very extensive one and has been the subject of a great many investigations. The first strong line of the rotation series must occur in the far infra-red at about 500μ and the spectrum extends with very few gaps through the near infra-red, where the fundamental vibration frequencies lie, up to about the middle of the visible spectrum. It has been accurately mapped from 135μ to 5700\AA . The far infra-red lines, which correspond to changes in the rotational energy only, have been measured with great precision by Randall, Dennison, Ginsburg and Weber¹ and lead to a determination of the rotational energy levels of the molecule.

It is well known that the water molecule, which has the form of an isosceles triangle, possesses three normal modes of vibration. These fundamental oscillations are shown in Fig. 1. Each of them should be active both in the infra-red and in the Raman spectrum. In point of fact, however, only ν_2 and ν_3 have been observed² in the infra-

red. They lie near 1595 and 3755 cm^{-1} , respectively. These bands are both extremely intense and the third fundamental ν_1 is probably weaker and is masked by the absorption of ν_3 . The principal feature of the Raman spectrum³ is a strong line at about 3650 cm^{-1} which can be ascribed to ν_1 . In addition to the three fundamentals, some fifteen harmonic and overtone bands have been measured. These extend through the near infra-red into the visible region of the spectrum where they are observed as atmospheric absorption lines in the solar spectrum. The accuracy with which these latter bands have been mapped is very high indeed although not essentially better than that attained in measuring the far infra-red rotation lines.

The fine structure of each band, whether fundamental or overtone, is quite extensive since the moments of inertia of the molecule are small and the rotational energies large. The structure appears to be very irregular, as must be expected since no two of the moments of inertia are equal and the molecule belongs to the class of asym-

¹ H. M. Randall, D. M. Dennison, N. Ginsburg and L. R. Weber, *Phys. Rev.* **52**, 160 (1937).

² E. K. Plyler and W. W. Sleator, *Phys. Rev.* **37**, 1493 (1931).

³ D. H. Rank, K. D. Larsen and E. R. Bordner, *J. Chem. Phys.* **2**, 464 (1934); D. Bender, *Phys. Rev.* **47**, 252 (1935).

metric rotators. Mecke⁴ and his co-workers have made a careful study of the rotational structure of all the known bands and have succeeded in analyzing them in the light of the theory of the asymmetric rotator. The results of their work may be stated as follows. Neglecting a rotational stretching effect which will be discussed later, the rotational levels of the molecule in any particular vibrational state may be organized by means of three moments of inertia. These moments, which will be called effective moments of inertia, vary slightly with the vibrational state in question. Mecke showed that they might be expressed as constants plus small corrections which are linear in the vibrational quantum numbers. By this means he extrapolated to the moments of inertia of the nonvibrating molecule and obtained the molecular dimensions. He found the valence angle to be $104^{\circ} 36'$ and the O-H distance to be 0.9558A. A characteristic feature of the effective moments of inertia is that they do not satisfy the relationship $I_A + I_B = I_C$ which must be expected to hold for any coplanar molecule. In a very important contribution to the theory of semi-rigid rotators Wilson and Howard⁵ have shown that the rotational energy levels of a molecule should exhibit just the features observed by Mecke, namely that they may be correlated by means of effective moments of inertia which will vary with the vibrational state.

An analysis of the positions of the centers of the fundamental and overtone bands has been made by Bonner⁶ who used the conventional expression for the vibrational energy,

$$W = W_0 + \sum X_i n_i + \sum_{i \geq k} \sum X_{ik} n_i n_k$$

where n_1 , n_2 and n_3 are the vibrational quantum numbers. The nine constants X_i , X_{ik} , may be determined from the eighteen observed bands and thus allow nine self-consistency checks. These checks are moderately good with one important exception. The fundamental frequency ν_1 , measured as a Raman line, is predicted to lie from forty to fifty wave numbers below its observed position.

⁴ R. Mecke, W. Baumann and K. Freudenberg, *Zeits. f. Physik* **81**, 313, 445, 465 (1933).

⁵ E. B. Wilson and J. B. Howard, *J. Chem. Phys.* **4**, 260 (1936).

⁶ L. G. Bonner, *Phys. Rev.* **46**, 458 (1934).

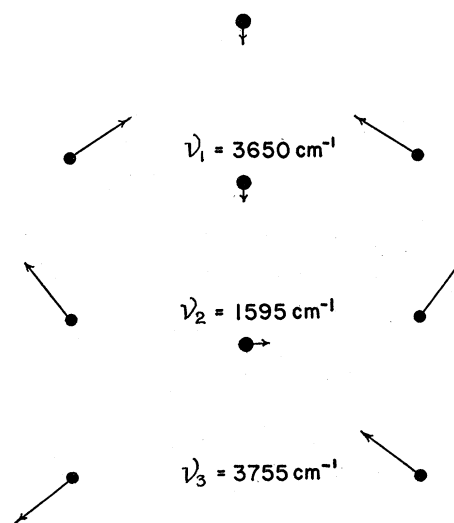


FIG. 1. Fundamental oscillations of the water molecule.

The solution of this difficulty appears to lie in the fact that the two fundamentals ν_1 and ν_3 have nearly the same value, thus paving the way for resonance effects. These effects are not of first order, however, since ν_1 and ν_3 have different symmetry characters and consequently may not interact directly. It is well known that the vibrational energy levels of the nonlinear, symmetrical molecule YX_2 belong to either of two symmetry classes. One of these is even upon reflection in a plane perpendicular to the $X-X$ line and through the Y atom, and it is characterized by n_3 being equal to an even integer. The other class is odd upon reflection and occurs when n_3 is an odd integer. In designating a level it will be convenient to employ the symbol⁷ (n_3, n_1, n_2) . It is thus obvious that the levels which may interact due to the near equality of ν_1 and ν_3 will be of the type (n_3, n_1, n_2) and (n_3+2, n_1-2, n_2) . The hypothesis that a resonance of this sort constitutes an essential feature of the analysis receives immediate confirmation when we examine the overtone bands which occur with greatest intensity. A glance at Table I shows that the strong overtone bands usually appear in pairs, thus (120), (300); (121), (301); (310), (130), etc. The members of these pairs comprise just those levels which could interact by resonance. An analysis of the positions of the

⁷ The order (n_3, n_1, n_2) corresponds with the notation used by Mecke which it seems wise to retain here.

TABLE I. Observed and calculated values of W/hc .

| $(n_1 n_2 n_3)$ | $W/hc(\text{obs.})$ | $W/hc(\text{calc.})$ |
|-----------------|---------------------|----------------------|
| (001) | 1595.0 | — |
| (002) | 3151.0 | — |
| (010) | 3650 | — |
| (100) | 3755.41 | — |
| (101) | 5330.8 | 5330.6 |
| (110) | 7251.0 | 7250.4 |
| (111) | 8807.05 | 8805.52 |
| (120) | 10613.12 | — |
| (300) | 11032.36 | — |
| (121) | 12151.22 | [12148.46] |
| (301) | 12565.01 | [12567.74] |
| (130) | 13830.92 | — |
| (310) | 14318.77 | — |
| (131) | 15347.91 | [15346.27] |
| (311) | 15832.47 | [15834.12] |
| (132) | 16821.61 | 16822.70 |
| (140) | 16899.01 | 16894.25 |
| (320) | 17495.48 | 17482.60 |

energy levels will require in addition to the nine X_i and X_{ik} of the usual theory, one further constant γ which measures the effect of the resonance. It will be shown that, upon determining the ten constants with ten of the observed levels, the remaining eight levels are satisfactorily predicted by the theory.

The general program which we hope to carry out in the present paper is as follows: The Hamiltonian function will be set down and the potential developed as a power series in the normal coordinates. The zeroth-order potential contains three constants, namely, the normal frequencies. The first-order potential consists of

cubic combinations of the coordinates and contains six constants. The second-order potential which involves quartic combinations possesses also six arbitrary constants. A solution is made which yields the energy values of the system and is a function both of the vibrational and of the rotational quantum numbers. The band centers are obtained by setting the rotational numbers equal to zero and in this way the ten constants X_i , X_{ik} and γ which were previously determined from the observed band centers are found as functions of the fifteen potential constants. To proceed further we turn to the rotational energy of the system and calculate the effective moments of inertia of the molecule. These are found to depend linearly upon the vibrational quantum numbers in agreement with Mecke's observations. They are functions of the six cubic constants but not of the quartic constants. The effective moments of inertia as determined experimentally furnish us with nine data, the coefficients of n_1 , n_2 and n_3 for each of the three moments, in addition to the equilibrium values of the moments. These nine data fix the six cubic constants and allow three independent checks of the theory, which are made by comparing the observed and predicted values of $\Delta = I_C - I_A - I_B$. The agreement with the observations is most satisfactory. We now possess sixteen data, the six cubic constants from the effective moments of inertia and the ten X_i , X_{ik} and γ with which to calculate the fifteen potential constants. This implies the existence of one further test of the self-consistency of the theory and upon calculation it proves to be adequately fulfilled.

2. THE HAMILTONIAN

In recent years a number of investigators have attacked the problem of finding the Hamiltonian of a semi-rigid, rotating polyatomic molecule. Of these, the formulation which seems to be most convenient in application is that by Wilson and Howard.⁵ A second derivation of this Hamiltonian by a somewhat shorter and more direct method has been made by one of us (B. T. D.) and will be published shortly. The result of this calculation is to obtain a Hamiltonian which differs only slightly and almost unessentially from the Wilson and Howard function, but which is Hermitian while it may be shown that theirs is not.

Our Hamiltonian, when expressed in the Wilson and Howard notation, is:

$$H = \frac{1}{2} \sum_{\alpha\beta} \mu^\lambda (P_\alpha - p_\alpha) \mu_{\alpha\beta} \mu^{-\lambda} (P_\beta - p_\beta) \mu^\lambda + \frac{1}{2} \sum_k \mu^\lambda p_k \mu^{-\lambda} p_k \mu^\lambda + V.$$

The P_α are components of the total angular momentum and p_α are the components of the local angular momentum in the rotating coordinate system defined by Wilson and Howard. $\mu_{\alpha\beta}$ are the cofactors of a determinant μ which contains the moments of inertia. These quantities depend upon the normal coordinates and will be calculated in detail later. p_k are the momenta conjugate to the normal coordinates q_k .

In the case of the water molecule, some simplifications occur. It will be shown that, of the local angular momenta, the only nonvanishing component will be perpendicular to the plane of the molecule. We denote it by p_3 . The potential function V we develop as a power series in the normal coordinates where the zeroth-order, first-order and second-order portions will contain terms which are, respectively, quadratic, cubic and quartic in the normal coordinates. Since the molecule is assumed to be symmetrical with respect to a plane perpendicular to the line joining the equilibrium positions of the hydrogen atoms and passing through the oxygen, the potential must obviously be an even function of q_3 , where q_3 describes the antisymmetrical motion ν_3 (see Fig. 1). The Hamiltonian, when written out, thus becomes:

$$H = \frac{1}{2} \sum_{\alpha=1}^3 \mu_{\alpha\alpha} P_\alpha^2 + \frac{1}{2} \mu_{12} (P_1 P_2 + P_2 P_1) + \frac{1}{2} \mu^{\frac{1}{2}} p_3 \mu_{33} \mu^{-\frac{1}{2}} p_3 \mu^{\frac{1}{2}} - \frac{1}{2} (p_3 \mu_{33} + \mu_{33} p_3) P_3 + \frac{1}{2} \sum_{k=1}^3 \mu^{\frac{1}{2}} p_k \mu^{-\frac{1}{2}} p_k \mu^{\frac{1}{2}} \\ + \frac{1}{2} (\lambda_1 q_1^2 + \lambda_2 q_2^2 + \lambda_3 q_3^2) + \frac{1}{2} (a_1 q_1^3 + a_2 q_2^3 + a_3 q_1^2 q_2 + a_4 q_1 q_2^2 + a_5 q_1 q_3^2 + a_6 q_2 q_3^2) \\ + \frac{1}{2} (b_1 q_1^4 + b_2 q_2^4 + b_3 q_3^4 + b_4 q_1^2 q_2^2 + b_5 q_1^2 q_3^2 + b_6 q_2^2 q_3^2). \quad (1)$$

The constants $\lambda_1, \lambda_2, \lambda_3, a_1 \cdots a_6, b_1 \cdots b_6$ constitute the fifteen arbitrary potential constants which were mentioned in the Introduction.⁸

3. THE VIBRATIONAL ENERGY

In order to obtain an expression for the band centers we have merely to set the total angular momenta components P_α equal to zero and examine the remainder of the Hamiltonian. It will prove convenient at this point to use, instead of the normal coordinates q_i , the dimensionless variables x_i . The x_i are the arguments of the Hermitian orthogonal functions describing the normal vibrations and are related to q_i as follows: $x_i = 2 \pi [\omega_i c / h]^{\frac{1}{2}} q_i$. The ω_i appearing here and throughout the remainder of the paper are the normal frequencies expressed in waves per cm; c is the velocity of light. The potential energy in these coordinates becomes:

$$V/hc = \frac{1}{2} (\omega_1 x_1^2 + \omega_2 x_2^2 + \omega_3 x_3^2) + (\alpha_1 x_1^3 + \alpha_2 x_2^3 + \alpha_3 x_1^2 x_2 + \alpha_4 x_1 x_2^2 + \alpha_5 x_1 x_3^2 + \alpha_6 x_2 x_3^2) \\ + (\beta_1 x_1^4 + \beta_2 x_2^4 + \beta_3 x_3^4 + \beta_4 x_1^2 x_2^2 + \beta_5 x_1^2 x_3^2 + \beta_6 x_2^2 x_3^2).$$

The relationship between the α_i, β_i and the a_i, b_i of the earlier formula may be easily obtained when needed.

The solution of this part of the problem which describes the vibrating but nonrotating molecule may be readily obtained by the usual perturbation methods. One finds

$$W/hc = W_0/hc + X_1 n_1 + X_2 n_2 + X_3 n_3 + X_{11} n_1^2 + X_{22} n_2^2 + X_{33} n_3^2 + X_{12} n_1 n_2 + X_{13} n_1 n_3 + X_{23} n_2 n_3.$$

⁸ It should be pointed out that the quartic part of the potential may contain three additional terms, namely $q_1 q_2 q_3^2, q_1 q_2^3$ and $q_1^3 q_2$. These terms, since they are odd in at least one coordinate, will not contribute to the energy. They would, however, have had a slight influence in transforming from the Hamiltonian for H_2O to that for D_2O , since the normal coordinates of the latter molecule are not exactly equal to those of the former.

The constants X_i and X_{ik} are the following functions of the potential constants:

$$\begin{aligned}
 W_0/hc &= \frac{1}{2}(\omega_1 + \omega_2 + \omega_3) + \frac{1}{4}(X_{11} + X_{22} + X_{33} + X_{12} + X_{13} + X_{23}), \\
 X_1 &= \omega_1 + X_{11} + \frac{1}{2}(X_{12} + X_{13}), \\
 X_2 &= \omega_2 + X_{22} + \frac{1}{2}(X_{12} + X_{23}), \\
 X_3 &= \omega_3 + X_{33} + \frac{1}{2}(X_{13} + X_{23}), \\
 X_{11} &= \text{K.E.P.} + \frac{3}{2}\beta_1 - \frac{15}{4}\frac{\alpha_1^2}{\omega_1} - \frac{\alpha_3^2}{2\omega_2} - \frac{\alpha_3^2}{8(2\omega_1 + \omega_2)} + \frac{\alpha_3^2}{8(2\omega_1 - \omega_2)}, \\
 X_{22} &= \text{K.E.P.} + \frac{3}{2}\beta_2 - \frac{15\alpha_2^2}{4\omega_2} - \frac{\alpha_4^2}{2\omega_1} - \frac{\alpha_4^2}{8(2\omega_2 + \omega_1)} + \frac{\alpha_4^2}{8(2\omega_2 - \omega_1)}, \\
 X_{33} &= \text{K.E.P.} + \frac{3}{2}\beta_3 - \frac{\alpha_5^2}{2\omega_1} - \frac{\alpha_6^2}{2\omega_2} - \frac{\alpha_5^2}{8(2\omega_3 + \omega_1)} + \frac{\alpha_5^2}{8(2\omega_3 - \omega_1)} - \frac{\alpha_6^2}{8(2\omega_3 + \omega_2)} + \frac{\alpha_6^2}{8(2\omega_3 - \omega_2)}, \\
 X_{12} &= \text{K.E.P.} + \beta_4 - \frac{3\alpha_1\alpha_4}{\omega_1} - \frac{3\alpha_2\alpha_3}{\omega_2} - \frac{\alpha_3^2}{2(2\omega_1 + \omega_2)} - \frac{\alpha_3^2}{2(2\omega_1 - \omega_2)} - \frac{\alpha_4^2}{2(2\omega_2 + \omega_1)} - \frac{\alpha_4^2}{2(2\omega_2 - \omega_1)}, \\
 X_{13} &= \text{K.E.P.} + \beta_5 - \frac{3\alpha_1\alpha_5}{\omega_1} - \frac{\alpha_3\alpha_6}{\omega_2} - \frac{\alpha_5^2}{2(2\omega_3 + \omega_1)} - \frac{\alpha_5^2}{2(2\omega_3 - \omega_1)}, \\
 X_{23} &= \text{K.E.P.} + \beta_6 - \frac{3\alpha_2\alpha_6}{\omega_2} - \frac{\alpha_4\alpha_5}{\omega_1} - \frac{\alpha_6^2}{2(2\omega_3 + \omega_2)} - \frac{\alpha_6^2}{2(2\omega_3 - \omega_2)}.
 \end{aligned} \tag{2}$$

A calculation similar to ours was first made by Bonner.⁶ Our results for that part of the X_{ik} which depends upon the potential constants is in agreement with his when allowance is made for the difference in notation.

The symbol K.E.P. which appears in the above formulas for the X_{ik} represents the contribution from the kinetic energy part of the Hamiltonian. An examination of the Hamiltonian Eq. (1), shows that the K.E.P. may come from a number of terms, many of which turn out to be quite negligible. Thus the difference between $\frac{1}{2}\sum\mu^{\frac{1}{2}}p_k\mu^{-\frac{1}{2}}p_k\mu^{\frac{1}{2}}$ and the zeroth-order expression $\frac{1}{2}\sum p_k^2$ yields nothing to the order of approximation to which we are working. Similarly $\frac{1}{2}\mu^{\frac{1}{2}}p_3\mu_3\mu^{-\frac{1}{2}}p_3\mu^{\frac{1}{2}}$ may be replaced by $\frac{1}{2}\mu_3p_3^2$. This latter quantity which involves the single nonvanishing internal angular momentum p_3 , will in general contribute both to X_{13} and X_{23} . A calculation shows⁹ that for the water molecule the K.E.P. of X_{13} is so small that it may be set equal to zero but that the K.E.P. of X_{23} is $+26.74 \text{ cm}^{-1}$.

The final step in discussing the formula for the positions of the band centers is to consider the influence of the resonance interaction between levels of the type $(n_3n_1n_2)$ and (n_3+2, n_1-2, n_2) . The matrix elements in the Hamiltonian connecting these states are all off diagonal and they are all of second order. Thus the calculation of the X_{ik} will be unaffected, since these depend upon second-order elements on the diagonal but only upon the first-order off-diagonal elements. A second way of stating this is that none of the terms in X_{ik} contain the resonance denominator $(\omega_1 - \omega_3)$. The method of deducing the final energy levels is now to diagonalize separately those portions of the Hamiltonian

⁹ The calculation is easily made when p_3 is explicitly determined as will be done in the next section. μ_3 may be given its equilibrium value $1/I_c$. The physical reason why X_{13} is so little affected is that in water vapor the motions of the hydrogen atoms in the vibration ν_1 are very nearly along the legs of the isosceles triangle. Thus the compound motion of ν_1 and ν_3 together possesses almost no angular momentum. For this reason the K. E. P. of X_{23} is just equal to the corresponding contribution to X_{23} in CO_2 which has been calculated by Weinberg and Eckart, J. Chem. Phys. 5, 517 (1937) and found to be $[\hbar/8\pi^2I_c^0][\omega_3/\omega_2 + \omega_2/\omega_3]$.

matrix which contain the elements in question. The off-diagonal terms of these portions of the Hamiltonian consist of an interaction b . A short calculation shows that

$$b_{n_3+2, n_1-2, n_2}^{n_3, n_1, n_2} = \frac{1}{2} \gamma hc [n_1(n_1-1)(n_3+1)(n_3+2)]^{\frac{1}{2}},$$

where

$$\gamma = \frac{1}{2} \beta_5 - \frac{\alpha_5^2}{\omega_1} + \frac{\alpha_1 \alpha_5}{2\omega_1} + \frac{\alpha_3 \alpha_6}{4(2\omega_1 - \omega_2)} - \frac{\alpha_3 \alpha_6}{4(2\omega_1 + \omega_2)}. \quad (3)$$

It is seen that γ depends only upon the potential constants. There exists a contribution from the kinetic energy part of the Hamiltonian but this turns out to be negligible in the case of the water molecule.

As an example, let us consider the interacting levels (120) and (300). They will be given as the roots of the determinant

$$\begin{vmatrix} X_1 + 2X_2 + X_{11} + 4X_{22} + 2X_{12} - W/hc & \sqrt{3}\gamma \\ \sqrt{3}\gamma & 3X_1 + 9X_{11} - W/hc \end{vmatrix}.$$

The roots may be expressed as $\bar{W}/hc \pm \frac{1}{2} [\delta_0^2 + \delta_1^2]^{\frac{1}{2}}$ where \bar{W}/hc is the mean value of the levels, in this case, $2X_1 + X_2 + 5X_{11} + 2X_{22} + X_{12}$, δ_0 is the separation of the levels without interaction, namely $-2X_1 + 2X_2 - 8X_{11} + 4X_{22} + 2X_{12}$ and δ_1 is the separation caused by the interaction alone, in the present example $2\sqrt{3}\gamma$. The highest frequency bands observed are (140) and (320). These are evidently members of a triplet whose third member is (500) and in this case the determinant which fixes the energy levels is of third order.

The observed positions of the band centers are collected in the Table I. It will be noticed that the numbers given for the bands lying in the near infra-red differ slightly from the values usually appearing in the literature. This arises from the fact that we have corrected the wave-lengths to vacuum.¹⁰ Several measurements³ have been made of the frequency ν_1 which appears in the Raman spectrum and the values which have been reported range from 3648 cm^{-1} to 3654 cm^{-1} . This discrepancy probably has its origin partly in the broadness of the Raman line (about 5 cm^{-1}). We have adopted the even value 3650 cm^{-1} . In order to calculate the ten constants X_i , X_{ik} and γ , we need ten data and these have been selected as indicated in the third column of Table I. In the case of (121), (301) and (131), (311) the individual levels were not used but only their sums and this is denoted by bracketing their calculated values.

¹⁰ M. Rusch, Ann. d. Physik **70**, 373 (1923).

Since there are eighteen bands which have been observed, there will occur eight checks upon the theory. The agreement between the measured and calculated values is very satisfactory and is definitely much better than that obtained by Bonner. We feel that the small differences which do exist are due to the fact that we are approximating the potential function by a power series development which is broken off after the quartic terms. This view is strengthened by the circumstance that the agreement appears to become poorer for the higher levels. The numerical values of the constants in waves per cm are as follows:

$$\begin{array}{lll} X_1 = 3693.89 & X_{11} = -43.89 & X_{12} = -20.02 \\ X_2 = 1614.5 & X_{22} = -19.5 & X_{13} = -155.06 \\ X_3 = 3801.78 & X_{33} = -46.37 & X_{23} = -19.81 \\ |\gamma| = 74.46 & \omega_1 = 3825.32 & \\ & \omega_2 = 1653.91 & \\ W_0/hc = 4631.25 & \omega_3 = 3935.59 & \end{array}$$

The zero-point energy W_0 has been calculated on the basis that the energy constant may be developed as a power series in $n_i + \frac{1}{2}$, thus

$$W/hc = \sum \omega_i (n_i + \frac{1}{2}) + \sum_{i \geq k} \sum X_{ik} (n_i + \frac{1}{2})(n_k + \frac{1}{2}).$$

We are aware that the conventional second-order perturbation theory does not quite give this result as has been pointed out by King.¹¹ We believe that this is due to the fact that the perturbation method involves a development

¹¹ G. W. King, J. Chem. Phys. **5**, 414 (1937).

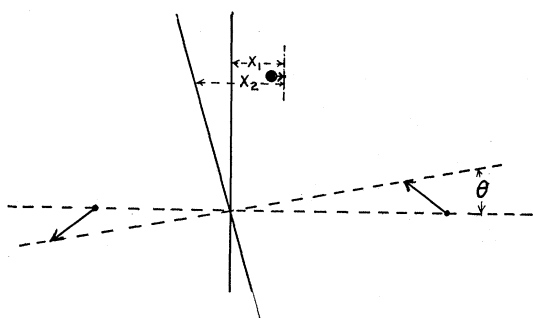


FIG. 2.

which breaks off after a certain number of steps. A similar situation occurs in the theory of the diatomic molecule where the perturbation calculation yields an energy which is not exactly a power series in $(n + \frac{1}{2})$. In this case, however, it is possible to obtain exact solutions for a number of particular potential forms (i.e., the Morse potential) and in every instance the energy is expressed as a function of $n + \frac{1}{2}$.

It will prove necessary for the rotation vibration interaction which is to be treated in the next section that we know the actual geometric displacements corresponding to each of the normal coordinates. The following geometric¹² displacement coordinates will be used. Let us consider the Cartesian axes x and y whose origin lies at the center of gravity of the system and whose x axis is parallel to the line joining the equilibrium positions of the two X atoms. We now choose the x component of the change (increase) of distance between X atoms to be the coordinate q . Let y be the y component of the displacement of the Y atom with respect to the center of gravity of the X atoms. The final coordinate x is illustrated in Fig. 2 and is equal to $x_1 + b\theta$, where x_1 is the x component of the displacement of the Y atom against the center of gravity of the X atoms, θ is the angle between the line joining the X atoms and the x axis, while b is the equilibrium distance between the Y atom and the line joining the X atoms. From the conservation of angular momentum it is easily shown that $x = (1 + \mu b^2 / 2ma^2)x_1$. Here μ is the

reduced mass $2mM/(2m+M)$ and $2a$ is the equilibrium distance between the X atoms.

The kinetic energy of the vibrating system may be calculated in the usual manner and is

$$2T = \left[\mu / \left(1 + \frac{\mu b^2}{2ma^2} \right) \right] \dot{x}^2 + \mu \dot{y}^2 + \frac{m}{2} \dot{q}^2.$$

The general potential function will contain only four constants (since it must be even in the coordinate x) and may be written

$$2V = ax^2 + by^2 + cq^2 + 2dyq.$$

The normal frequencies are given in terms of the roots ($\lambda_i = 4\pi^2\omega_i^2 c^2$) of a determinant and may be expressed as follows:

$$\begin{aligned} \lambda_1 \lambda_2 &= 2(bc - d^2) / m\mu, \\ \lambda_1 + \lambda_2 &= b/\mu + 2c/m, \\ \lambda_3 &= a(1 + \mu b^2 / 2ma^2) / \mu. \end{aligned}$$

The first minors of the determinant yield the relationships between the displacement coordinates and the normal coordinates q_1, q_2, q_3 .

$$\begin{aligned} q &= \delta_{11}q_1 + \delta_{12}q_2, \\ y &= \delta_{21}q_1 + \delta_{22}q_2, \\ x &= \delta_{33}q_3, \end{aligned}$$

where

$$\begin{aligned} \delta_{1i} &= d / [(\frac{1}{2}m\lambda_i - c)^2 \mu + \frac{1}{2}md^2]^{\frac{1}{2}}, \\ \delta_{2i} &= (\frac{1}{2}m\lambda_i - c) / [(\frac{1}{2}m\lambda_i - c)^2 \mu + \frac{1}{2}md^2]^{\frac{1}{2}}, \end{aligned} \quad (4)$$

where the index $i = 1, 2$.

$$\delta_{33} = [1/\mu + b^2/2ma^2]^{\frac{1}{2}}.$$

The following relations exist between the δ_{ik} ,

$$\begin{aligned} \mu \delta_{21}^2 + \frac{1}{2}m \delta_{11}^2 &= 1, & \delta_{11}^2 + \delta_{12}^2 &= 2/m, \\ \mu \delta_{22}^2 + \frac{1}{2}m \delta_{12}^2 &= 1, & \delta_{21}^2 + \delta_{22}^2 &= 1/\mu, \\ 2\mu \delta_{21} \delta_{22} + m \delta_{11} \delta_{12} &= 0, & \mu \delta_{21}^2 - \frac{1}{2}m \delta_{12}^2 &= 0, \\ \delta_{21} \delta_{11} + \delta_{22} \delta_{12} &= 0, & \mu \delta_{22}^2 - \frac{1}{2}m \delta_{11}^2 &= 0. \end{aligned}$$

It is clear that the three normal frequencies of H₂O will not serve to determine these relationships, since there are four potential constants involved. The normal frequencies of D₂O will supply the remaining datum.

The fundamental frequencies of D₂O have been measured¹³ although with somewhat less accu-

¹² A geometric coordinate is one which defines the configuration of the molecule without reference to the masses of the atoms. The constants appearing in the potential function are thus the same for any isotopic molecule.

¹³ The frequency ν_1 appears in the Raman spectrum and was reported by D. H. Rank, K. D. Larsen and E. R. Bordner, J. Chem. Phys. 2, 464 (1934). The bands ν_2 and ν_3 were observed by E. F. Barker and W. W. Sleator, J.

racy than the corresponding work for H₂O and have the values $\nu_1=2666$, $\nu_2=1178.7$, $\nu_3=2789$ cm⁻¹. These frequencies are not the normal frequencies ω , but, as may be seen from Eq. (2), are connected with them by the formulas, $\omega_1=\nu_1-2X_{11}-\frac{1}{2}X_{12}-\frac{1}{2}X_{13}$, etc. We shall treat the problem of obtaining the X_{ik} by a method similar to that used by Bonner. In the diatomic molecule the coefficient of n^2 varies as the square of the frequency when changing from one isotopic molecule to another. We shall accordingly assume that X_{ii} varies as ω_i^2 and X_{ik} as $\omega_i\omega_k$. It will turn out that all three normal frequencies change by about the same factor and consequently we feel that this method, while not rigorously accurate, will lead to no serious errors. A preliminary solution gives the variation of each ω . We find in this way that $\omega_1=2757.86$ and $\omega_2=1210.17$. These numbers, which are derived from the observed fundamentals, may be tested by noticing that the ratio of $\omega_1\omega_2$ for H₂O to $\omega_1\omega_2$ for D₂O must be equal to the square root of the ratio of $m\mu$ for D₂O and H₂O, respectively. A calculation based on H=1.00813, D=2.01473, and O=16.0000 shows that this relation is almost perfectly fulfilled; the observed ratio being 1.89566, while the predicted ratio is 1.89539. Such an excellent agreement implies that our method of obtaining the X_{ik} for D₂O has been a valid one. For purposes of computation ω_1 is increased by 0.20 cm⁻¹ and ω_2 by 0.08 cm⁻¹ in order that the theoretical ratio of $\omega_1\omega_2$ for H₂O and D₂O shall be exactly satisfied.

The third fundamental will be treated slightly differently: ω_3 of D₂O may be obtained by using Bonner's values for the molecular dimensions, $a=0.75625A$ and $b=0.58450A$, together with the ratio of masses. We find $\omega_3=2883.79$. From this,

Chem. Phys. **3**, 660 (1935). Of these two frequencies ν_3 is the less accurately known and was determined as the center of the zero branch associated with the band. We believe that the published value of 2784 cm⁻¹ is subject to the following corrections. In H₂O, the center of the zero branch of ν_3 lies at about 3741 cm⁻¹ whereas the true band center as revealed by the rotational analysis is at 3755.4 cm⁻¹. This difference of 14.4 cm⁻¹ is caused by a type of convergence. Now in the case of the diatomic molecule the convergence factor varies as the cube of the normal frequency and consequently we believe that the correction for the frequency ν_3 of D₂O should be approximately 5.7 cm⁻¹. A reduction to vacuum wavelengths yields the final result, $\nu_3=2789$ cm⁻¹. Fortunately the frequency ν_3 is not involved in the calculation of the potential constants, although it does furnish a test of the self-consistency of the theory.

together with the X_{ik} we calculate that $\nu_3=2787.7$, which is in very satisfactory accord with the observed number 2789.

Collecting these results, we have for D₂O:

$$\begin{aligned}\omega_1 &= 2758.06, & X_{11} &= -22.81, & X_{12} &= -10.56, \\ \omega_2 &= 1210.25, & X_{22} &= -10.44, & X_{13} &= -81.92, \\ \omega_3 &= 2883.79, & X_{33} &= -24.90, & X_{23} &= -10.62.\end{aligned}$$

The zero-point energy of D₂O is then 3385.74 cm⁻¹.

The values of the potential constants and of the δ_{ik} for H₂O now follow readily.

$$\begin{aligned}a &= 10.672 \times 10^5 \text{ dynes/cm} & c &= 3.1344, \\ b &= 7.1810, & d &= 3.1588, \\ \delta_{11} &= +1.14678m^{-\frac{1}{2}}, & \delta_{12} &= +0.82758m^{-\frac{1}{2}}, \\ \delta_{21} &= +0.43910m^{-\frac{1}{2}}, & \delta_{22} &= -0.60845m^{-\frac{1}{2}}, \\ \delta_{33} &= 0.92828m^{-\frac{1}{2}},\end{aligned}$$

where m is the mass of a hydrogen atom, which we will take to be 1.6734×10^{-24} g.

The sign of d is not determined directly but if we assume that the force field must be nearly of the valence type it follows that d is positive. We wish to remark that the accuracy with which the potential constants are known is certainly not as high as would be indicated by the number of significant figures given above. In making calculations, however, it is wise to make sure that no inconsistencies arise from rounding off numbers prematurely.

4. THE VIBRATION ROTATION INTERACTION

The main objective of the present section is to calculate the effective moments of inertia of the molecule. In a very recent paper Shaffer and Nielsen¹⁴ have also undertaken to solve this problem for the nonlinear symmetrical molecule YX₂. They begin, as we do, with the Wilson and Howard Hamiltonian and carry through their computation along lines which in a general way parallel our work. Their final results for the moments of inertia are partly in agreement with ours but contain certain differences which appear to us to be vitally important in a discussion of the problem. Thus we find that the quantity $\Delta = I_C - I_A - I_B$ is independent of the coefficients of the cubic terms in the potential, a result which

¹⁴ W. H. Shaffer and H. H. Nielsen, Phys. Rev. **56**, 188 (1939).

is not attained by Shaffer and Nielsen.* We feel justified in giving a brief account of our calculations, particularly since they appear to be very simple and straightforward.

The moments and production of inertia in the rotating coordinate system defined by Wilson and Howard may be readily expressed as functions of the displacement coordinates x , y and q of the last section. Letting $1/f = (1 + \mu b^2/2ma^2)$, we find:

$$\begin{aligned} A &= \mu b^2 + 2\mu by + \mu^2 f^2 b^2 x^2 / 2ma^2 + \mu y^2, \\ B &= 2ma^2 + 2maq + \frac{1}{2}mq^2 + \mu f^2 x^2, \\ C &= A + B, \\ D &= 2\mu bfx + \frac{1}{2}\mu fx(bq/a + 2y), \\ E &= F = 0. \end{aligned}$$

The $\mu_{\alpha\beta}$ which appear in the Hamiltonian function are

$$\mu_{11} = \frac{B}{AB - D^2}, \quad \mu_{22} = \frac{A}{AB - D^2}, \quad \mu_{12} = \frac{D}{AB - D^2},$$

$$Z_1 = K_1 q_3, \quad Z_2 = K_2 q_3, \quad Z_3 = -K_1 q_1 - K_2 q_2.$$

The $\mu_{\alpha\beta}$ may now be expressed as functions of the normal coordinates. It is convenient to develop them as power series in the q_i and to retain no terms beyond the second.

$$\begin{aligned} \mu_{11} &= 1/\mu b^2 - 2(\delta_{21}q_1 + \delta_{22}q_2)/\mu b^3 + 3f^2\delta_{33}^2q_3^2/2ma^2b^2 + 3(\delta_{21}q_1 + \delta_{22}q_2)^2/\mu b^4, \\ \mu_{22} &= 1/2ma^2 - (\delta_{11}q_1 + \delta_{12}q_2)/2ma^3 + 3\mu f^2\delta_{33}^2q_3^2/4m^2a^4 + 3(\delta_{11}q_1 + \delta_{12}q_2)^2/8ma^4, \\ \mu_{33} &= \mu f^2\delta_{33}^2/2ma^2 - \frac{f^4\mu^2\delta_{33}^4}{2m^2a^4} [(ma\delta_{11} + \mu b\delta_{21})q_1 + (ma\delta_{12} + \mu b\delta_{22})q_2] + 3f^4\mu^2\delta_{33}^4(K_2^2q_1^2 + K_1^2q_2^2)/4m^2a^4 \\ &\quad - f^4\mu^2\delta_{33}^4K_1K_2q_1q_2/2m^2a^4, \\ \mu_{12} &= f\delta_{33}q_3/ma^2b - 3f\delta_{33}q_3(\delta_{21}q_1 + \delta_{22}q_2)/4ma^2b^2 - 3f\delta_{33}q_3(\delta_{11}q_1 + \delta_{12}q_2)/4ma^3b. \end{aligned}$$

A feature of these expressions which will later turn out to be important is that the linear part of $1/\mu_{33}$ is equal to the linear part of $(1/\mu_{11} + 1/\mu_{22})$. This arises directly from the fact that $A + B = C$.

The Hamiltonian (Eq. (1)) may now be re-examined and each term evaluated to the desired order of approximation. The method which is employed is to diagonalize the Hamiltonian with respect to the vibrational part of the matrix elements. The resulting expression may then—in agreement with Wilson and Howard's predictions—be put in the form

$$W = P_1^2/2I_A + P_2^2/2I_B + P_3^2/2I_C + \text{vibrational energy}.$$

The I_A , I_B and I_C are the effective amounts of inertia and are functions of the vibrational quantum

* Note added in proof.—A re-examination of the article by Shaffer and Nielsen leads us to believe that the differences may well be due to several typographical errors and that our results are essentially in agreement.

¹⁵ The physical meaning of this very unequal division is interesting. K_1 and K_2 represent the contributions to the internal angular momentum from the combined motion ν_1 , ν_3 and ν_2 , ν_3 , respectively. In H_2O the motion of the hydrogen atoms (whose amplitude is so much larger than that of the oxygen) is nearly along the legs of the isosceles triangle in both the motions ν_1 and ν_3 but nearly perpendicular to the legs in ν_2 . For this reason the combined motion ν_1 , ν_3 will possess practically no internal angular momentum as compared with that of ν_2 , ν_3 .

$$\mu_{33} = \frac{1}{C - \Sigma Z_k^2}, \quad \mu_{13} = \mu_{23} = 0.$$

The Z_k are obtained in the following manner. The only component of the internal angular momenta p_α which does not vanish is p_3 and has the value

$$p_3 = \mu f(x\dot{y} - \dot{x}y) - (\mu fb/2a)(x\dot{q} - \dot{x}q).$$

This may be expressed as a function of the normal coordinates by means of Eq. (3).

$$p_3 = K_1(q_3\dot{q}_1 - q_1\dot{q}_3) + K_2(q_3\dot{q}_2 - q_2\dot{q}_3),$$

where

$$\begin{aligned} K_1 &= \mu f\delta_{33}(\delta_{21} - b\delta_{11}/2a), \\ K_2 &= \mu f\delta_{33}(\delta_{22} - b\delta_{12}/2a). \end{aligned}$$

It may readily be shown from the relations connecting the $\delta_{\alpha\beta}$ that $K_1^2 + K_2^2 = 1$. A substitution yields the result that for H_2O ,¹⁵ $K_1^2 = 0.000019$ and $K_2^2 = 0.999981$. The quantity Z_k is the coefficient of \dot{q}_k in the formula for p_3 . Thus

numbers. It must be stated that the above equation is true only to second-order approximation; higher orders will bring in quartic combinations of the P_α .

The first part $\frac{1}{2}\sum\mu_{\alpha\alpha}P_\alpha^2$ contains, in addition to the constant $\mu_{\alpha\alpha}^0=1/I_\alpha^0$, terms which are linear in the q_i and terms which are quadratic. These latter are immediately diagonalized, the q_i^2 yielding $h(n_i+\frac{1}{2})/4\pi^2\omega_i c$ while $q_i q_k$ gives no contribution. The linear part of $\mu_{\alpha\alpha}$ may be treated in either of two ways which lead to the same results. The first method recognizes that the presence of a linear term means that the centrifugal forces of rotation have displaced the equilibrium positions of the atoms. We may shift to the new origin by balancing the centrifugal force against the Hooke's law force. This process will eliminate the linear part of $\mu_{\alpha\alpha}$ and will bring in contributions from the cubic part of the potential. The second method is that of the standard second-order perturbation theory; the terms linear in the q_i and those which are cubic in the q_i combine to produce an addition to the energy which may be readily calculated and which is equal to that obtained above.

The second quantity in the Hamiltonian, $\frac{1}{2}\mu_{12}(P_1P_2+P_2P_1)$, yields nothing in this order of approximation. It may likewise be shown that the final term

$$-\frac{1}{2}(p_3\mu_{33}+\mu_{33}p_3)P_3$$

can be replaced by the simpler expression $-\mu_{33}^0 p_3 P_3$.

Obviously $-\mu_{33}^0 p_3 P_3$ contains no elements which are diagonal in the vibrational quantum numbers and therefore no first-order contribution to the energy. In second order it does, however, give an important term which may be calculated from the usual form

$$(\mu_{33}^0)^2 P_3^2 \sum_k' p_{3k}^i p_{3i}^k / (W_i^0 - W_k^0).$$

It should be mentioned that this term does contain a matrix element connecting the resonating states $(n_3 n_1 n_2)$ and (n_3+2, n_1-2, n_2) but that its magnitude for H₂O is negligibly small and need not be considered.

The methods which have just been outlined allow us to obtain the effective $\mu_{\alpha\alpha}$. The effective moments of inertia are found by inverting the $\mu_{\alpha\alpha}$ and are given by the following expressions. We present them as functions of the potential constants $\alpha_1 \cdots \alpha_6$ rather than $a_1 \cdots a_6$. Let $s^2 = h/\pi^2 b^2 c$ and $t^2 = h/4\pi^2 a^2 c$.

$$I_A = I_A^0 [1 - s(3s\delta_{21}^2/4\omega_1 + 3\delta_{21}\alpha_1/\omega_1^{\frac{3}{2}} + \delta_{22}\alpha_3/\omega_2^{\frac{3}{2}})(n_1 + \frac{1}{2}) - s(3s\delta_{22}^2/4\omega_2 + 3\delta_{22}\alpha_2/\omega_2^{\frac{3}{2}} + \delta_{21}\alpha_4/\omega_1^{\frac{3}{2}})(n_2 + \frac{1}{2}) - s(3s\mu b^2 f^2 \delta_{33}^2/8ma^2\omega_3 + \delta_{21}\alpha_5/\omega_1^{\frac{3}{2}} + \delta_{22}\alpha_6/\omega_2^{\frac{3}{2}})(n_3 + \frac{1}{2})],$$

$$I_B = I_B^0 [1 - t(3t\delta_{11}^2/4\omega_1 + 3\delta_{11}\alpha_1/\omega_1^{\frac{3}{2}} + \delta_{12}\alpha_3/\omega_2^{\frac{3}{2}})(n_1 + \frac{1}{2}) - t(3t\delta_{12}^2/4\omega_2 + 3\delta_{12}\alpha_2/\omega_2^{\frac{3}{2}} + \delta_{11}\alpha_4/\omega_1^{\frac{3}{2}})(n_2 + \frac{1}{2}) - t(3t\mu f^2 \delta_{33}^2/2m\omega_3 + \delta_{11}\alpha_5/\omega_1^{\frac{3}{2}} + \delta_{12}\alpha_6/\omega_2^{\frac{3}{2}})(n_3 + \frac{1}{2})],$$

$$\Delta = I_C - I_A - I_B = [hK_1^2\omega_3^2/\pi^2 c\omega_1(\omega_3^2 - \omega_1^2)](n_1 + \frac{1}{2}) + [hK_2^2\omega_3^2/\pi^2 c\omega_2(\omega_3^2 - \omega_2^2)](n_2 + \frac{1}{2}) - [(hK_1^2\omega_1^2/\pi^2 c\omega_3(\omega_3^2 - \omega_1^2)) + (hK_2^2\omega_2^2/\pi^2 c\omega_3(\omega_3^2 - \omega_2^2))](n_3 + \frac{1}{2}).$$

These formulas differ from those of Nielsen and Shaffer only in the parts containing the cubic constants $\alpha_1 \cdots \alpha_6$. Our results, in contrast to theirs, show that $\Delta = I_C - I_A - I_B$ is independent of the cubic constants. The reason why this comes about is easily understood. The cubic coefficients in the effective moments of inertia arise only from the terms in $\mu_{\alpha\beta}$ which are linear in the q_i . These terms, as has been pointed out, satisfy the relation that $1/\mu_{33} = 1/\mu_{11} + 1/\mu_{22}$ and consequently they can contribute nothing to the Δ .

The quantity Δ plays an important role in the theory of the water vapor spectrum since it may be calculated from a knowledge of the normal frequencies and the shape of the molecule only and hence compared directly with the experimental data. Explicitly,

$$\Delta = [0.1644(n_2 + \frac{1}{2}) - 0.0122(n_3 + \frac{1}{2})] \times 10^{-40}. \quad (5)$$

The coefficient of $(n_1 + \frac{1}{2})$ in the expression for Δ is practically zero since the numerical value of K_1^2 is so small.

It will prove convenient to substitute the numerical values for the normal frequencies of the water molecule into the formulas for the effective moments of inertia in order to facilitate a correlation with the experimental data. We thus obtain

$$\begin{aligned} (I_A - I_A^0) \times 10^{40} &= (-0.0151 - 0.0001127\alpha_1 + 0.0001831\alpha_3)(n_1 + \frac{1}{2}) + (-0.0672 + 0.0005493\alpha_2 \\ &\quad - 0.0000376\alpha_4)(n_2 + \frac{1}{2}) + (-0.0149 - 0.0000376\alpha_5 + 0.0001831\alpha_6)(n_3 + \frac{1}{2}), \\ (I_B - I_B^0) \times 10^{40} &= (-0.0290 - 0.0002136\alpha_1 - 0.0001807\alpha_3)(n_1 + \frac{1}{2}) + (-0.0349 - 0.0005421\alpha_2 \\ &\quad - 0.0000712\alpha_4)(n_2 + \frac{1}{2}) + (-0.0280 - 0.0000712\alpha_5 - 0.0001807\alpha_6)(n_3 + \frac{1}{2}). \end{aligned} \quad (6)$$

In the case of the water vapor molecule in which there exists a resonance between the states (n_3, n_1, n_2) and $(n_3 + 2, n_1 - 2, n_2)$ there will occur a mixing of the effective moments of inertia for these states. If I_α^I and I_α^{II} represent the moments of inertia as calculated from Eq. (6) and if I_α^I and I_α^{II} are the actual moments of the resonating states, then it may readily be shown, that

$$\begin{aligned} I_\alpha^I &= I_\alpha^I(\delta + \delta_0)/2\delta + I_\alpha^2(\delta - \delta_0)/2\delta, \\ I_\alpha^{II} &= I_\alpha^I(\delta - \delta_0)/2\delta + I_\alpha^2(\delta + \delta_0)/2\delta, \end{aligned} \quad (7)$$

where in these expressions δ_0 stands for the separation which would exist between the vibrational levels if there were no resonance interaction and $\delta = [\delta_0^2 + \delta_1^2]^{\frac{1}{2}}$ is the actual separation between the levels.

5. CORRELATION WITH EXPERIMENT

The final problem of this investigation will be to compare the experimental fine structure of the water bands with the theoretical formulas for the effective moments of inertia and thereby to obtain the molecular potential constants. Mecke⁴ has analyzed the fine structure lines of each band and has shown that the rotational energy levels are just those which are predicted by the theory of the asymmetrical rotator. He thus calculates the effective moments of inertia for every particular vibrational state. We believe that his values may be somewhat improved by taking into account the rotational stretching of the molecule in the manner proposed by Wilson.¹⁶ It was stated in the last section that the application of a higher order perturbation to the Hamiltonian function would yield terms which are quartic in the components of total angular momenta P_α . The coefficients are functions of

TABLE II. Calculated values of $-\delta W$.

| J | 2_1 | 2_0 | 2_{-1} | 1_1 | 1_0 | 1_{-1} |
|-----------------------------|-------|-------|----------|-------|-------|----------|
| $-\delta W(\text{cm}^{-1})$ | 0.331 | 0.032 | 0.045 | 0.015 | 0.006 | 0.047 |

¹⁶ E. B. Wilson, J. Chem. Phys. 4, 526 (1936).

the normal frequencies only and may be easily evaluated. The final results of our calculation as given in Table II for a limited number of rotational states show that each level will be decreased by what amounts to a small correction.¹⁷

The effective moments of inertia are then obtained from the relations

$$h/2\pi^2cI_A = (2_1 - 1_{-1})_{\text{exp}} + 0.28,$$

$$h/2\pi^2cI_B = (2_0 - 1_0)_{\text{exp}} + 0.03,$$

$$h/2\pi^2cI_C = (2_{-1} - 1_1)_{\text{exp}} + 0.03$$

and are shown in the second, fourth and sixth columns of Table III in units of 10^{-40} g cm². (We take $h = 6.624 \times 10^{-27}$.)*

The observed values of $\Delta = I_C - I_A - I_B$ are given in the seventh column, next to which appear the Δ as calculated from Eq. (5). The agreement is very satisfactory and is best for those levels which lie in regions most favorable for experimental determination. Thus the rota-

¹⁷ The work of Randall, Dennison, Ginsburg and Weber indicates that for the high levels the rotational stretching may be very large (for the state 11_{11} it is about 280 cm⁻¹); in fact, so large that it could not be simply computed.

* Note added in proof.—The physical constants appearing in this paper are taken from a private communication kindly furnished by Professor R. T. Birge.

tional energy levels of the ground state (000) are undoubtedly known with the greatest accuracy. The strong bands (120) to (310) which appear as atmospheric lines in the solar spectrum have also been measured with high precision. The weaker solar bands, as well as the near infra-red bands, have not been as exactly determined. We regard the agreement between Δ_{obs} and Δ_{calc} as being a real and substantial test of the theory and as constituting one of the more important points of this investigation.

The theory also predicts that the effective moments of inertia should be linear functions of the vibrational quantum numbers. A study of the data reveals that this is essentially the case, although small discrepancies exist which are usually of the order of the experimental errors. We have made the following treatment: The seven most accurately observed bands (000) and (120) to (310) are selected and their moments of inertia are fitted to a linear formula by means of a least-square solution which is subject to two supplementary conditions; first that $I_C^0 = I_A^0 + I_B^0$ and second that the Δ is just equal to the calculated Δ . Of course here, as in every case involving the resonating levels, it is necessary to take account of the mixing of the effective moments of inertia caused by the resonance. This is easily done by means of Eqs. (7) and we arrive at the result,

$$I_A \times 10^{40} = 1.0229 + (0.0213)(n_1 + \frac{1}{2}) - (0.1010)(n_2 + \frac{1}{2}) + (0.0486)(n_3 + \frac{1}{2}),$$

$$I_B \times 10^{40} = 1.9207 + (0.0398)(n_1 + \frac{1}{2}) - (0.0249)(n_2 + \frac{1}{2}) + (0.0077)(n_3 + \frac{1}{2}),$$

$$I_C \times 10^{40} = 2.9436 + (0.0611)(n_1 + \frac{1}{2}) + (0.0385)(n_2 + \frac{1}{2}) + (0.0441)(n_3 + \frac{1}{2}).$$

The values for the effective moments of inertia as calculated from the formula just written are given in the third, fifth and seventh columns of Table III. The agreement with the observed values is satisfactorily good and, as in the case of the Δ , is best for those bands which are most accurately known experimentally, thus leading to the belief that the discrepancies may be due to observational errors.

The equilibrium values for the moments of

TABLE III. Observed and calculated values of the effective moments of inertia and of Δ .

| $(n_3 n_1 n_2)$ | I_A OBS. | I_A CALC. | I_B OBS. | I_B CALC. | I_C OBS. | I_C CALC. | Δ OBS. | Δ CALC. |
|-----------------|------------|-------------|------------|-------------|------------|-------------|---------------|----------------|
| (000) | 1.007 | 1.007 | 1.929 | 1.932 | 3.013 | 3.016 | 0.077 | 0.076 |
| (001) | 0.904 | 0.906 | 1.899 | 1.907 | 3.107 | 3.055 | .304 | .241 |
| (100) | 1.057 | 1.056 | 1.928 | 1.939 | 3.048 | 3.059 | .063 | .064 |
| (101) | 0.988 | 0.955 | 1.923 | 1.915 | 3.133 | 3.099 | .222 | .228 |
| (110) | 1.000 | 1.076 | 1.995 | 1.979 | 3.117 | 3.120 | .122 | .064 |
| (111) | 0.977 | 0.976 | 1.896 | 1.954 | 3.200 | 3.160 | .327 | .228 |
| (120) | 1.110 | 1.105 | 2.014 | 2.012 | 3.185 | 3.178 | .061 | .061 |
| (300) | 1.141 | 1.147 | 1.969 | 1.962 | 3.155 | 3.151 | .045 | .042 |
| (121) | 1.000 | 1.003 | 1.978 | 1.987 | 3.240 | 3.217 | .262 | .226 |
| (301) | 1.046 | 1.046 | 1.940 | 1.947 | 3.201 | 3.190 | .215 | .207 |
| (130) | 1.133 | 1.136 | 2.040 | 2.040 | 3.244 | 3.233 | .071 | .057 |
| (310) | 1.161 | 1.158 | 2.006 | 2.014 | 3.217 | 3.219 | .050 | .047 |
| (131) | 1.030 | 1.034 | 2.003 | 2.015 | 3.287 | 3.272 | .254 | .221 |
| (132) | 0.961 | 0.935 | 1.998 | 1.990 | 3.352 | 3.310 | .393 | .386 |
| (140) | 1.107 | 1.224 | 2.056 | 2.064 | 3.283 | 3.286 | .120 | -.004 |
| (320) | 1.183 | 1.231 | 2.006 | 2.055 | 3.365 | 3.282 | .176 | -.006 |

inertia give the O-H distance to be 0.9580A and the valence angle to be $104^\circ 31'$; figures which differ only slightly from those obtained by Mecke⁴ and Bonner.⁶ A comparison of these formulas with Eq. (6) allows us to determine the six cubic constants. We find

$$\alpha_1 = -322 \text{ cm}^{-1}, \quad \alpha_3 = +1, \quad \alpha_5 = -909,$$

$$\alpha_2 = -47, \quad \alpha_4 = +216, \quad \alpha_6 = +160.$$

Knowing the cubic constants together with the numerical values of the six X_{ik} , it is of course possible to obtain the six quartic constants.

$$\beta_1 = +39 \text{ cm}^{-1}, \quad \beta_3 = +35, \quad \beta_5 = +212,$$

$$\beta_2 = +2, \quad \beta_4 = -116, \quad \beta_6 = -108.$$

It is interesting to notice that the perturbing terms in the potential which connect the levels n_1 and n_3 , namely $x_1 x_3^2$ and $x_1^2 x_3^2$, appear to be unusually large. This no doubt accounts both for the resonance between the levels $(n_3 n_1 n_2)$, $(n_3 + 2, n_1 - 2, n_2)$ and for the fact that they appear to be the most intense overtones in the spectrum.

Since we now possess all twelve of the anharmonic potential constants, together with the normal frequencies, we may calculate the interaction constant γ by means of Eq. (3). We find the value $\gamma_{\text{calc}} = -71.5 \text{ cm}^{-1}$ which may be compared with the experimental figure of $|\gamma_{\text{obs}}| = 74.46 \text{ cm}^{-1}$. The agreement, within about 4 percent, is remarkably good and argues strongly for the essential correctness of our interpretation of the water vapor spectrum.