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A Calculation of the Vibration Frequencies and Other Constants of the H₂O Molecule

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The calculation is based on the Slater-Pauling theory of directed valence, but supplemented by data from the band spectrum of the diatomic OH molecule. The heat of dissociation and valence angle, obtained incidentally, are in good agreement with experiment. The "cross-terms" in the vibrational potential prove to be of subordinate importance. It is found that two of the fundamentals should fall near 2.8μ , and that they should almost coincide. This designation of the observed wide absorption band at

$2.6\text{--}2.8\mu$ as the superposition of two fundamentals agrees with Mecke's interpretation of the H₂O spectrum, but contradicts Johnston and Walker's. The computed value 1660 cm^{-1} of the third fundamental frequency ω_3 differs from experimental determinations by only 4 percent, but any closer agreement than 15 percent is accidental in view of the approximate nature of the theory. Since ω_3 represents a primarily angular vibration, its calculation is a particular test of the concepts of directed valence.

THE water molecule is of interest because it is possible to calculate its vibration frequencies and other constants by a method based on quantum mechanics supplemented by spectroscopic data from the OH and H₂ (but not the H₂O) molecules. This process should not be confused with the less exacting, more customary procedure, used in the preceding paper, of simply adjusting force constants to yield agreement with observed vibration bands. Our calculation of the fundamental frequencies will, of course, include a theoretical evaluation of the coefficients in the vibrational potential,

$$V = \frac{1}{2}[k_1(\Delta r_1)^2 + k_2(\Delta r_2)^2 + 2k_3r_1^0(\Delta\gamma)^2] + k_{12}\Delta r_1\Delta r_2 + 2\frac{1}{2}k_{13}r_1^0(\Delta r_1\Delta\gamma + \Delta r_2\Delta\gamma), \quad (1)$$

where r_1, r_2 are the O—H separations, and γ is the angle H—O—H (cf. Fig. 2 of reference 1). The factors r_1^0, r_1^0 are inserted, as in reference 1, to secure dimensional similarity in the k 's. It turns out that the coefficients k_{12} and k_{13} are relatively unimportant. This fact furnishes at least partial justification for treatment of the "cross-terms" in the potential as small perturbations, as in the preceding paper on the ethyl halides,¹ or even the complete omission of these terms, as in the hypothesis of "valence forces" often made in the literature.

¹ P. C. Cross and J. H. Van Vleck, *J. Chem. Phys.* **1**, 350 (1933). See this reference for more general discussion of molecular vibrations.

According to the quantum theory of directed valence, the potential energy of an H₂O molecule should be approximately of the form

$$V = f(r_1) + f(r_2) + g(r_{12}) + 3(N_{\sigma\sigma} - N_{\pi\pi}) \sin^2(\frac{1}{2}\gamma - \frac{1}{4}\pi). \quad (2)$$

Here $N_{\sigma\sigma}$ and $N_{\pi\pi}$ are, except for sign, exchange integrals between a $1s$ state of H and respectively the $2p\sigma$ and $2p\pi$ states of O, space quantized relative to the corresponding O—H axis.² The terms $f(r_1), f(r_2)$ in (2) are radial O—H potentials, and, to our approximation, are of the same functional form as the potential energy curve for the diatomic OH molecule. The term $g(r_{12})$ represents the repulsion between the two H atoms, whose separation is denoted by r_{12} . The remaining term gives the effect of directional valence, and proves to be considerably more important than $g(r_{12})$. That this term has the form of dependence on γ given in (2) follows from the Slater-Pauling theory of directed valence provided one makes the hypothesis of electron pairing.³

² The notation is chosen in conformity with that used by one of us in *J. Chem. Phys.* **1**, 219 (1933). The reader is referred especially to Sections 5 and 6 of this reference if he desires further information concerning the concepts of the quantum mechanics of directed valence, electron pairing, etc. which we are using. Note especially that our N 's are the negative of exchange integrals.

³ The angular term of (2) is essentially the same as that given by Slater in *Phys. Rev.* **38**, 1139 (1931), except that

Details of the derivation of the last term of (2) are as follows: Let us take the O nucleus as the origin and suppose that the H nuclei lie in the xy plane. Let us further take the bisector of the angle H—O—H to be inclined at 45° to the x axis. Then

$$\cos(r_1, x) = \cos(r_2, y) = \cos(\tfrac{1}{2}\gamma - \tfrac{1}{4}\pi). \quad (3)$$

The configuration of the O atom may, with this choice of axes, be taken⁴ to be $1s^2 2s^2 2p\sigma_z^2 2p\sigma_x 2p\sigma_y$. Here $2p\sigma_z$, for instance, denotes a $2p$ wave function having $m_l=0$ when space quantized relative to the z axis. From the rotational transformation properties of $2p$ wave functions, it follows⁵ that the exchange integral J_{1x} connecting the $1s$ wave function of H atom 1 and the $2p\sigma_x$ wave function of O is

$$J_{1x} = -N_{\sigma\sigma} \cos^2(r_1, x) - N_{\pi\pi} \sin^2(r_1, x) = J_{2y}. \quad (4)$$

Similarly

$$J_{1x} = J_{2x} = -N_{\pi\pi}, \quad (5)$$

$$J_{2x} = J_{1y} = -N_{\sigma\sigma} \sin^2(r_1, x) - N_{\pi\pi} \cos^2(r_1, x). \quad (6)$$

We shall let J denote the sum of the exchange integrals for the pairs (1s of H; 1s of O) and (1s of H; 2s of O). Clearly J has the same value for either H atom and is independent of γ . If we make the hypothesis of electron pairing the exchange energy is⁶

$$J_{1x} + J_{2y} - \tfrac{1}{2}J_{2x} - \tfrac{1}{2}J_{1y} + 2(-\tfrac{1}{2}J_{1x} - \tfrac{1}{2}J_{2x} - J). \quad (7)$$

The terms with coefficients $+1$ in (7) are those which represent pairs. When one expresses the exchange integrals involved in (7) in terms of $N_{\sigma\sigma}$, $N_{\pi\pi}$, γ with the aid of (3–6), one obtains the last term of (2) except for an additive constant $-2J - 2N_{\sigma\sigma} + 3N_{\pi\pi}$. This constant must not be inserted in (2), since it is included in $f(r_1) + f(r_2)$. Namely, the binding energy for OH is

$$f(r_1) = -J - N_{\sigma\sigma} + \tfrac{3}{2}N_{\pi\pi} + \text{polar and Coulomb terms}, \quad (8)$$

so that $f(r_1) + f(r_2)$ absorbs all of the exchange energy at $\gamma = \tfrac{1}{2}\pi$. Eq. (8) is proved from (7) by dropping all terms which involve atom 2, and keeping atom 1 on the x axis. The polar and Coulomb terms are to be added in (8) since (7) aims to give only the exchange energy. We have tacitly assumed that the polar and Coulomb effects do not depend on direction. This appears to be an allowable approximation.

It must be cautioned that in the foregoing, we have

he has introduced explicit numerical values of the N 's. In fact our calculation of the equilibrium position and energy is very similar to that given by Slater except that we use different, and we believe better, numerical constants. Our equilibrium calculations are intended primarily as pre-requisites to the vibrational analysis, which was not considered by Slater.

⁴ By the methods of reference 2 one can show that any other, less symmetrical, choice of spatial quantization for the $2p$ wave functions of oxygen will yield a higher value of the energy if the hypothesis of electron pairing is made.

⁵ See Eq. (6) of reference 2 and related discussion.

⁶ Cf. Eq. (35) of reference 2.

assumed that the O atom always remains in the configuration $s^2 p^4$, or in other words that there is no $s-p$ hybridization for this atom. Any amount of this hybridization tends to intensify the bonds, but the $s-p$ separation of the O atom amounts to over 15 volts, and so the O atom is probably unwilling to make a partial change from $s^2 p^4$ towards sp^5 in order to hold the H atoms tighter. On the other hand, hybridization apparently must be considered in connection with the molecular vibrations of NH_3 , as otherwise it seems impossible to explain the low potential hill⁷ ($\tfrac{1}{4}$ volt) involved in converting one isomer of NH_3 into the other. This difference between H_2O and NH_3 does not appear unreasonable, since the $s-p$ separation is smaller (11 volts) in N than in O and since hybridization is a greater advantage with 3 than with 2 bonds.

We shall assume that $f(r_1)$, $f(r_2)$ and $g(r_{12})$ can be represented by Morse functions. This procedure has been at least partially justified by the success of Eyring's⁸ well-known investigations of activation. The values of $f(r_1)$ and $g(r_{12})$ can then be determined from the potential energy curves yielded by the band spectra of OH and H_2 and are as follows⁹

$$f(r_1) = 120(1 - e^{2.15(0.98-r_1)})^2 - 120,$$

$$g(r_{12}) = -35(1 - e^{1.85(0.75-r_{12})})^2 + 35.$$

Here distances are supposed measured in Angstroms, and the amplitudes have been in terms of a $\text{kg}\cdot\text{cal./g}\cdot\text{mol}$ scale of energy. In evaluating

⁷ D. M. Dennison and G. E. Uhlenbeck, *Phys. Rev.* **41** 313 (1932); N. Rosen and P. Morse, *ibid.* **42**, 211 (1933).

⁸ H. Eyring and M. Polanyi, *Zeits. f. physik. Chemie* **12**, 279 (1931); H. Eyring, *J. Am. Chem. Soc.* **53**, 2537 (1931); Sherman and Eyring, *ibid.* **54**, 2661 (1932).

⁹ Our choice of Morse functions has been determined to fit the vibration frequency and the heat of dissociation rather than the former and the anharmonic correction. For the band spectrum data see Weizel, *Bandspektren*, or Mulliken, *Rev. Mod. Phys.* **4**, 1 (1933). In our formula for $g(r_{12})$ we have not attempted to make allowance for the fact that the polar character of H_2O makes the H atoms each have an excess of positive over negative charge and so exert ionic repulsive forces upon each other. This repulsion is perhaps roughly counterbalanced by the van der Waals force between the H atoms, not included at large separations in the Morse function. Both the ionic and van der Waals forces are probably subordinate to those covered by the Morse function. The van der Waals term is hard to estimate accurately, as Eyring notes (*J. Am. Chem. Soc.* **54**, 3201 (1932)) that the inverse sixth power polarization potential gives excessive values at distances as small as r_{12} . In this reference he compares qualitatively the forces resulting from directional valence and H—H repulsions in H_2O , and notes that the latter are, as we find, not entirely negligible compared with the former.

$g(r_{12})$, we have, like Eyring, supposed that the binding energy of an H₂ molecule is 10 percent Coulomb, and 90 percent exchange. This makes $g(r_{12})$ 35 percent of a Morse function for H₂, inasmuch as exchange terms connecting electrons involved in different pairs involve the coefficient $-\frac{1}{2}$ rather than $+1$, making⁸ the proportionality factor $0.1 - (\frac{1}{2} \times 0.9) = -0.35$. On the other hand $f(r_1)$ and $f(r_2)$ are complete Morse functions for OH.

The values of $N_{\sigma\sigma}$ and $N_{\pi\pi}$ will be taken as 2 and -0.6 volt, respectively. These estimates have been obtained largely from the potential curves of the OH molecule, and are perhaps accurate to 20 percent or so. The details of the method of estimation will be published in a future paper by J. R. Stehn and J. H. Van Vleck,

Incidentally, the agreement with the values 2.3 and -0.6 volts obtained by Coolidge¹⁰ by actual computation of the integrals with Zener's wave functions is gratifying. We believe the spectroscopic method to be perhaps more reliable than the computational one. As a matter of fact, the spectroscopic method gives a value of $N_{\sigma\sigma}$ somewhat below 2 volts, but we have used the round value 2 in order to give some weight to Coolidge's calculations. With our estimate of the N 's, one has

$$3(N_{\sigma\sigma} - N_{\pi\pi}) = 180 \text{ kg} \cdot \text{cal.} / \text{g} \cdot \text{mol.}$$

One must now make a Taylor's development of (2) about the equilibrium position r_1^0, r_2^0, γ^0 . Inasmuch as $r_{12}^2 = r_1^2 + r_2^2 - 2r_1r_2 \cos \gamma$ and $r_1^0 = r_2^0$ this development is

$$\begin{aligned} V = & V(r_1^0, r_2^0, \gamma^0, r_{12}^0) + \left(\frac{\partial f}{\partial r_1} \right)^0 (\Delta r_1 + \Delta r_2) - \frac{3}{2} (N_{\sigma\sigma} - N_{\pi\pi}) \cos \gamma^0 \cdot \Delta \gamma \\ & + \left(\frac{\partial g}{\partial r_{12}} \right)^0 [\sin \frac{1}{2} \gamma^0 \cdot (\Delta r_1 + \Delta r_2) + r_1^0 \cos \frac{1}{2} \gamma^0 \cdot \Delta \gamma] + \frac{1}{2} \left(\frac{\partial^2 f}{\partial r_1^2} \right)^0 [(\Delta r_1)^2 + (\Delta r_2)^2] \\ & + \frac{3}{4} (N_{\sigma\sigma} - N_{\pi\pi}) \sin \gamma^0 \cdot (\Delta \gamma)^2 + \frac{1}{2} \left(\frac{\partial^2 g}{\partial r_{12}^2} \right)^0 [\sin \frac{1}{2} \gamma^0 \cdot (\Delta r_1 + \Delta r_2) + r_1^0 \cos \frac{1}{2} \gamma^0 \cdot \Delta \gamma]^2 \\ & + \left(\frac{\partial g}{\partial r_{12}} \right)^0 \left[\frac{\sin^2 \gamma^0}{16 r_1^0 \sin^3 \frac{1}{2} \gamma^0} (\Delta r_1 - \Delta r_2)^2 + \frac{1}{2} \cos \frac{1}{2} \gamma^0 (\Delta r_1 \Delta \gamma + \Delta r_2 \Delta \gamma) - \frac{1}{4} r_1^0 \sin \frac{1}{2} \gamma^0 \cdot (\Delta \gamma)^2 \right]. \quad (9) \end{aligned}$$

The values of r_1^0, r_2^0 and γ^0 are respectively determined by the requirement that the coefficients of $\Delta r_1, \Delta r_2$ and $\Delta \gamma$ vanish in (9). This gives

$$r_1^0 = r_2^0 = 1.00 \text{ Angstrom}, \quad \gamma^0 = 100^\circ. \quad (10)$$

This value of r^0 agrees with the fact that the experimental determinations are practically the same as the equilibrium distance 0.98 Angstrom

in the diatomic OH molecule. The value of γ^0 is in sufficient accord with the various estimates of from 102° to 111° which have been obtained from band spectra.¹¹ The heat of dissociation into $2\text{H} + \text{O}$ is $V(r_1^0, r_2^0, \gamma^0, r_{12}^0)$, or 205 kg·cal./mol. Expressed in volts, this estimate is 8.9 volts. Thermochemical data lead to a value of about 10 volts.¹² Our theoretical estimate is

order to obtain the factor 2.) For instance, Slater³ secures equally good agreement with entirely different assumed values of the exchange integrals. On the other hand, the calculation of the transverse vibration frequency ω_3 is sensitive to the evaluation of these integrals. Our semi-quantum mechanical, semi-spectroscopic calculation of the heat of dissociation should not be confused with Coolidge's purely quantum mechanical treatment, which led to the excessively low value -5.7 volts. The writers believe that two reasons why Coolidge obtained too low a result may be the following: (a) He assumed the same exponential factor for the carbon $2s$ and $2p$ wave functions, whereas actually

¹⁰ A. S. Coolidge, Phys. Rev. **42**, 189 (1932).

¹¹ For instance, Eucken finds $\gamma^0 = 110^\circ 56'$ while Mecke obtains a value between 102° and 111° .

¹² The good agreement of the calculated and observed heats of dissociation should not be considered any particular triumph, for any theory based on electron pairing will predict approximately twice as great a heat of dissociation for H₂O as for OH. (Cf. J. H. Van Vleck, J. Chem. Phys. **1**, 177 (1933). If we assume electron pairing, it is not necessary to neglect interaction between the H atom and the $2s$ or $2p\pi$ states of O, as there stated, in

raised to 9.4 when correction¹³ is made for the L, S structure of the O configuration s^2p^4 .

By substitution of (10) in (9), we find that the coefficients in (1) have the following numerical values:

$$k_1 = k_2 = 6.96 \times 10^5, \quad k_3 = 0.379 \times 10^5,$$

$$k_{12} = 0.165 \times 10^5, \quad k_{13} = 0.04 \times 10^5.$$

The values of the constants involved in (7) of our preceding paper are

$$a_{11} = a_{22} = 15.6 \times 10^{-25}, \quad a_{33} = 3.86 \times 10^{-25},$$

$$a_{12} = 0.185 \times 10^{-25}, \quad a_{13} = a_{23} = 0.32 \times 10^{-25}.$$

Because of the addition of the cross-terms, the simultaneous equations (8) of the preceding article for determining the molecular vibrations are to be enhanced by the term $\sum_i k_{ij} q_j$, with corresponding modification of the cubic secular equation (10) of the foregoing paper. In virtue of the symmetry of the molecule, this cubic factors into a linear and a quadratic equation in $\lambda^2 = 4\pi^2 c^2 \omega^2$; as follows:

$$\begin{aligned} & (a_{11} - a_{12})\lambda^2 - k_1 + k_{12} = 0, \\ & [(a_{11} + a_{12})\lambda^2 - k_1 - k_{12}][a_{33}\lambda^2 - k_3] \\ & \quad - 2[a_{13}\lambda^2 - k_{13}]^2 = 0. \end{aligned} \quad (11)$$

Substitution of numerical values yields

$$\omega_1 = 3520 \text{ cm}^{-1}, \quad \omega_2 = 3560 \text{ cm}^{-1}, \quad \omega_3 = 1660 \text{ cm}^{-1}. \quad (12)$$

Experimentally regions of intense absorption

the $2s$ states are more firmly held and so have a larger negative exponent. This implies that Coolidge overestimated the exchange repulsion from the $2s$ states. (b) Examination of potential curves for OH suggests that the ionic attraction per atom is somewhat larger than his estimate of 1.1 volts. Coolidge's difficult and noteworthy calculation goes to the refinement of considering more than simple permutations. The results of his paper suggest that possibly the first order Heitler-London calculation is somehow a better approximation without than with allowance for the higher order permutations.

¹³ Under the hypothesis of electron pairing the valence state of H_2O may be shown to be $\frac{3}{4} {}^3P + \frac{1}{4} {}^1D$. The fractional coefficients occur because the pairing prevents L, S of O from being good quantum numbers. When we double the Morse function for OH we allow the O atom twice the activation energy necessary to raise it from 3P to the valence state. Actually the activation energy of O is the same for OH as for H_2O , so that our estimate of the heat of dissociation should be increased by one quarter of the interval ${}^1D - {}^3P$, or by 0.5 volt.

occurs at 1600 and 3700 cm^{-1} .¹⁴ It is not at all surprising that the calculated radial vibrations come near 3600 cm^{-1} for this is merely because the primarily radial vibrations have nearly the same frequency as that characteristic of OH. Conclusions of more interest are the following:

(1) The coefficients k_{12}, k_{13} in (1) are comparatively small, so that inclusion of the "cross-terms" does not greatly modify the calculated frequencies. In fact, if one sets $k_{12} = k_{13} = 0$, the computed frequencies become 3560, 3520, 1660 cm^{-1} instead of (12). The frequencies ω_1 and ω_2 have the significance of being associated with unsymmetrical and symmetrical primarily radial vibrations: i.e., ω_1 has $\Delta r_1 = -\Delta r_2, \Delta \gamma = 0$ while ω_2 , like ω_3 , has $\Delta r_1 = \Delta r_2$.

(2) The difference $\lambda_1^2 - \lambda_2^2$ is given approximately by the equation

$$\begin{aligned} \lambda_1^2 - \lambda_2^2 = & \frac{2(-a_{11}k_{12} + a_{12}k_1)}{a_{11}^2 - a_{12}^2} \\ & - \frac{2[a_{13}^2(k_1 + k_{12}) - a_{13}k_{13}(a_{11} + a_{12})]}{a_{33}(a_{11} + a_{12})^2}. \end{aligned} \quad (13)$$

The second term is quite small in the case of water, contributing only about 10 percent of the total separation. It is interesting to note that the contribution of the k_{12} term is about twice as large as that of the a_{12} term, and is of the opposite sign. The value of a_{12} is the following function of γ^0 :

$$a_{12} = -\mu_3 \cos \gamma^0 + \frac{\mu_3^2 \sin^2 \gamma^0}{2(\mu - \mu_3 \cos \gamma^0)}, \quad (\mu = \mu_1 = \mu_2). \quad (14)$$

The second term of (14) is about $\frac{1}{6}$ as large as the first one. Attempts have been made in the literature to calculate γ^0 for H_2O from the experimental values of λ_1^2 and λ_2^2 by means of the relation

$$\cos \gamma^0 = -\frac{M_{\text{H}} + M_{\text{O}}}{M_{\text{H}}} \frac{\lambda_1^2 - \lambda_2^2}{\lambda_1^2 + \lambda_2^2} \quad (15)$$

obtained by setting $a_{12} = -\mu_3 \cos \gamma^0$ and $a_{13} = a_{23} = k_{12} = k_{13} = 0$ in Eq. (11). It is obvious that such a method of obtaining the equilibrium angle is not reliable since small values of the cross-

¹⁴ W. W. Sleator, *Astrophys. J.* **48**, 125 (1918).

terms k_{12} will completely alter the character of the right side of (13).¹⁵

(3) The difference $\omega_1 - \omega_2$ is so small that it is comparable with the rotational structure. Hence it is not surprising that the frequencies ω_1 , ω_2 have not yet been resolved experimentally. Actually, the band at 3700 cm⁻¹ is extremely diffuse. Johnston and Walker¹⁶ claim to have located ω_2 at 984 cm⁻¹ from the Raman effect, but such a value of ω_2 is entirely out of the question unless the theory is devoid of all meaning. Our interpretation of the band as a superposition of ω_1 , ω_2 is similar to that proposed by Mecke.^{17, 18}

(4) The HOH² molecule, involving the isotope H², may be assumed to have the same potential function as the HOH molecule. If the force constants k_1 , k_3 are adjusted to give absorption

¹⁵ In molecules where the central atom is not of large mass compared to the attached ones, the difference $\lambda_1^2 - \lambda_2^2$ is not small, and must be calculated from the exact formulas (11) rather than from the approximate relation (13). When the central atom and attached masses are comparable, as in the examples studied by Lechner, (Monats. f. Chem. **61**, 395 (1932)) the terms involving a_{12} overshadow those proportional to k_{12} and k_{13} . Hence Lechner's calculation of equilibrium angles would not be materially modified by inclusion of cross-terms in the potential.

¹⁶ H. L. Johnston and M. K. Walker, Phys. Rev. **39**, 535 (1932). Our ω_1 , ω_2 , ω_3 correspond to Johnston and Walker's Dennison's) ν_3 , ν_1 , ν_2 , respectively.

¹⁷ R. Mecke. Zeits. f. physik. Chemie **16**, 431 (1932).

¹⁸ Note added in proof: Papers by Mecke, Baumann and Freudenberg (Zeits. f. Physik **81**, 313, 445, 465 (1933)) have just appeared which give a very careful analysis of the rotation-vibration bands of water. They find ω_1 and ω_2 at 3756 and 3600 cm⁻¹, respectively. Thus $\omega_2 - \omega_1$, according to their analysis, has a different sign and larger numerical magnitude than in our theoretical estimate $\omega_2 - \omega_1 = 40$ cm⁻¹. This, however, need not cause concern, since $\omega_2 - \omega_1$ is still small, in qualitative accord with theory, and quantitative accuracy

regions at approximately 3750 cm⁻¹ for ω_1 and ω_2 and at 1600 cm⁻¹ for ω_3 of the HOH molecule, the fundamental bands of HOH² should occur at 3750, 2720, and 1400 cm⁻¹.

(5) The agreement between the calculated and observed values of ω_3 is particularly gratifying, for ω_3 represents an angular mode of vibration not found in OH, and originates in the resistance of directional valence to any bending of the molecule from the equilibrium angle. It must be remembered that the calculations, from their very nature, do not claim any great precision, and agreement only to within 15 percent¹⁹ or so would not have been disconcerting. The calculations on ω_3 thus confirm the essential correctness of the Slater-Pauling concept of directed valence.

in the theoretical calculation of a difference as small as $\omega_2 - \omega_1$ is not to be expected in view of the many approximations which it is necessary to make, notably the assumption of electron pairing. Also, the experimental determination of ω_2 is not free from difficulty, and Mecke mentions that the region from 3300 to 3600 cm⁻¹ has so far defied exact analysis. An interesting problem is presented by the fact that Mecke finds ω_2 to be an inactive frequency except when involved in combinations with ω_1 . If one assumes that the motions of the water molecule can be represented by the vibrations of a system of three particles, each with a constant charge, then one must expect ω_2 to be an active frequency. However, it is probable that the water molecule becomes increasingly ionic in character when r_{13} and r_{23} are simultaneously diminished. If so, migrations of charge back and forth between the O and H atoms accompany the vibrations. It is thus conceivable that equal displacements in r_{13} and r_{23} at nearly constant γ may give rise to little change in moment, due to a cancellation of the change due to migration and the change calculated for a model in which the atoms have constant charges. In this fashion ω_2 might be inactive.

¹⁹ The error in ω_3 can be less than in the exchange integrals because ω_3 is roughly proportional to $(N_{\sigma\sigma} - N_{\pi\pi})^{\frac{1}{2}}$.