tend to coalesce. In an intermediate case, as shown by the calcium hydride diagram, the branches start out as in case **a** and then with increasing J values, tend toward case **b**. The beryllium chloride bands appear to follow the calcium hydride diagram and this might explain why the R_1 and R_2 branches have the $(v'+\frac{1}{2})(v''+\frac{1}{2})$ coefficients that they do. The R_1 branch turns at about $J=59$ and therefore should have a large coefficient, but the R_2 branch must turn at a relatively much lower J value and thus have a much smaller coefficient. The fact that both branches have practically the same coefficients may be due to the coalescing effect of the case **b** type; consequently, the R_1 branch tends to be drawn in and have a smaller coefficient than expected and the R_2 branch tends to be drawn out and have a larger coefficient.

The heats of dissociation of the upper and lower states, calculated in the customary way from the vibrational formula for the Q_1 heads, are 3.47 and 4.33 volts, respectively. From these values and that of the constant term in the vibrational formula, the atomic excitation comes out to be 2.59 volts which is in fair agreement with the $^1D \rightarrow P^1$ separation in beryllium of 2.70 volts. Hence, it is concluded that the electronic configurations in the upper and lower states are Be—$(2s)(3d)^1D+$Cl—$3p^5\cdot{}^2P$ and Be—$(2s)(2p)^1P+$Cl—$3p^5\cdot{}^2P$.

A. E. Parker[6] has recently reported another $^2\Pi \rightarrow {}^2\Sigma$ BeCl band system which lies in the yellow-green region of the spectrum. Neither state of this system is common to the ones given above but it seems quite certain that this yellow-green system has the same final state dissociation products and arises from the electronic transition of $^1S-P^1$ in the beryllium atom.

The authors wish to thank Dean Henry G. Gale and Dr. George Monk of the University of Chicago for permitting one of us to use the large grating in the Ryerson Laboratory.

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[6] A. E. Parker, Phys. Rev. **45**, 752 (1934), and also in private communication.

The Vibrational Spectrum of Water Vapor

Lyman G. Bonner, *Gates Chemical Laboratory, California Institute of Technology*

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The nonlinear triatomic molecule of the type XY_2 has been treated and the expression for the energy of vibration has been obtained when second, third and fourth powers of the coordinates are considered in the potential function. The higher powers of the coordinates have been introduced by the use of first and second order perturbation theory. A method has also been outlined for treating the more complicated types of kinetic energy expressions by a perturbation method. Using the results of this treatment there have been evaluated for the water molecule, from the known spectrum, the primary binding constants and vibration frequencies for infinitesimal amplitudes. Finally, a prediction of the infrared vibration spectrum of the symmetrically substituted heavy water has been made.

Introduction

Recently Adel and Dennison[1] have published a quite thorough treatment of the linear triatomic molecule of the CO_2 type, and have obtained the energy expression when higher powers of the coordinates are considered in the potential function. In this paper it is proposed to discuss the nonlinear molecule of the H_2O type from a similar standpoint. Some of the results of this treatment have already been published.[2] In the present paper the method will be more completely presented and further results will be discussed.

The present case is somewhat complicated by the fact that the kinetic energy expression is of such a form that it cannot be treated rigorously. However, it is hoped that this difficulty has been successfully surmounted by using a perturbation method.

It is desired in this article to find the form of the energy expression when the deviation of the potential field from that of a harmonic oscillator is considered. Third and fourth powers of the coordinates will be included in the potential

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[1] A. Adel and D. M. Dennison, Phys. Rev. **43**, 716 (1933).

[2] L. Bonner, Phys. Rev. **45**, 496 (1934).

function. In addition, expressions will be found for the true mechanical frequencies of the molecule for infinitesimal amplitudes of vibration.

A brief outline of the method employed may now be given. First, the classical normal coordinates will be found, which, for infinitesimal amplitudes of vibration, reduce the kinetic and potential energies to sums of squares. The wave equation will then be written in terms of three coordinates having a simple significance in the molecule. The potential energy must, however, be expressed in terms of coordinates giving displacements from the equilibrium configuration, and a transformation to these displacement coordinates must be made. The normal coordinates will next be introduced and the Hamiltonian separated into three parts. The first of these will be solved rigorously, and the other two applied as perturbations.

This leads to the desired energy expression and to expressions for the mechanical frequencies of the molecule. The known spectrum of water vapor will then be used to evaluate certain of the constants of this molecule. Finally, a prediction will be made of the spectrum of the symmetrically substituted heavy water.

CLASSICAL TREATMENT

The kinetic energy expression for the nonlinear triatomic molecule has been given by Cross and Van Vleck;[3] and is, for the present case of a symmetric molecule,

$$\begin{aligned} T=&\tfrac{1}{2}(\mu_1-A\mu_2{}^2r_2{}^2\sin^2\alpha)\dot{r}_1{}^2+\tfrac{1}{2}(\mu_1-A\mu_2{}^2r_1{}^2\sin^2\alpha)\dot{r}_2{}^2+\tfrac{1}{2}Ar_1{}^2r_2{}^2(\mu_1{}^2-\mu_2{}^2\cos^2\alpha)\dot{\alpha}^2\\ &+(-\mu_2\cos\alpha+A\mu_2{}^2r_1r_2\sin^2\alpha)\dot{r}_1\dot{r}_2+A\mu_2r_1r_2\sin\alpha(\mu_1r_1-\mu_2r_2\cos\alpha)\dot{r}_1\dot{\alpha}\\ &+A\mu_2r_1r_2\sin\alpha(\mu_1r_2-\mu_2r_1\cos\alpha)\dot{r}_2\dot{\alpha}.\end{aligned}$$

$$1/A=\mu_1(r_1{}^2+r_2{}^2)-2\mu_2r_1r_2\cos\alpha,\qquad \mu_1=m(M+m)/(M+2m),\qquad \mu_2=m^2/(M+2m).$$

Here r_1 and r_2 represent the O−H distances, α is the angle between these two bonds, and m and M are, respectively, the masses of H and of O. For the present the potential energy expression may be taken to include all terms quadratic in the coordinates, and may be written

$$V^\circ=\tfrac{1}{2}a\{(\Delta r_1)^2+(\Delta r_2)^2\}+\tfrac{1}{2}b(\Delta\alpha)^2+c\Delta r_1\Delta r_2+d\Delta\alpha(\Delta r_1+\Delta r_2).$$

Displacement coordinates may now be substituted for the above r_1, r_2 and α, as follows

$$r_1=R+\rho,\qquad r_2=R+\sigma,\qquad \alpha=\beta+\varphi,$$

where R and β are the equilibrium values. If, in the coefficients of the dotted terms in T, the displacements in the coordinates may be considered negligible compared with the equilibrium values, the usual treatment by means of normal coordinates may be carried out. This gives expressions for the λ's, which are proportional to the fundamental frequencies, and also gives the substitutions which reduce T and V to sums of squares. These expressions are given below, where the ω's are the frequencies and the y's are the normal coordinates.

$$\lambda_1{}^2=4\pi^2\omega_1{}^2=(\mu_1-\mu_2\cos\beta)(a-c)/(\mu_1{}^2-\mu_2{}^2),$$

$$\begin{aligned}\lambda^2{}_{2,\,3}=4\pi^2\omega^2{}_{2,\,3}=&R^{-2}(\mu_1{}^2-\mu_2{}^2)^{-1}\{b(\mu_1-\mu_2\cos\beta)+\tfrac{1}{2}R^2(\mu_1+\mu_2\cos\beta)(a+c)-2dR\mu_2\sin\beta\}\\ &\pm R^{-2}(\mu_1{}^2-\mu_2{}^2)^{-1}[\{b(\mu_1-\mu_2\cos\beta)+\tfrac{1}{2}R^2(\mu_1+\mu_2\cos\beta)(a+c)-2dR\mu_2\sin\beta\}^2\\ &-2R^2(\mu_1{}^2-\mu_2{}^2)\{b(a+c)-2d^2\}]^{\frac{1}{2}}.\end{aligned}$$

$\lambda_2{}^2$ is taken with the positive sign.

$$\rho=y_1+y_2+y_3,\qquad \sigma=-y_1+y_2+y_3,$$

$$\varphi=\frac{-2d+\lambda_2{}^2R\mu_2\sin\beta}{b-\frac{1}{2}\lambda_2{}^2R^2(\mu_1+\mu_2\cos\beta)}y_2+\frac{-2d+\lambda_3{}^2R\mu_2\sin\beta}{b-\frac{1}{2}\lambda_3{}^2R^2(\mu_1+\mu_2\cos\beta)}y_3.$$

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[3] P. C. Cross and J. H. Van Vleck, J. Chem. Phys. 1, 350 (1933).

WAVE MECHANICAL

The assumption made above of constant coefficients in T introduces a certain amount of error, and it is desired to show here how this uncertainty may be considerably reduced, and a closer approximation obtained.

We may write the wave equation for the system under consideration in terms of the original coordinates, r_1, r_2 and α, following the method of Podolsky.[4] This gives:

$$\mu_1\left(\frac{\partial^2\psi}{\partial r_1^2}+\frac{\partial^2\psi}{\partial r_2^2}\right)+\frac{1}{Ar_1^2r_2^2}\frac{\partial^2\psi}{\partial\alpha^2}+2\mu_2\cos\alpha\frac{\partial^2\psi}{\partial r_1\partial r_2}-2\mu_2\sin\alpha\left(\frac{1}{r_2}\frac{\partial^2\psi}{\partial r_1\partial\alpha}+\frac{1}{r_1}\frac{\partial^2\psi}{\partial r_2\partial\alpha}\right)$$
$$+\frac{A}{r_1}(\mu_1^2r_2^2-2\mu_1\mu_2r_1r_2\cos\alpha+\mu_2^2r_1^2)\frac{\partial\psi}{\partial r_1}+\frac{A}{r_2}(\mu_1^2r_1^2-2\mu_1\mu_2r_1r_2\cos\alpha+\mu_2^2r_2^2)\frac{\partial\psi}{\partial r_2}$$
$$+\frac{8\pi^2(\mu_1^2-\mu_2^2)}{h^2}(W-V)\psi=0.$$

If, as before, we substitute in this expression the equilibrium positions plus the displacement coordinates, we obtain expressions involving $(R+\rho)^{-1}$, $\sin(\beta+\varphi)$, etc. Although a rigorous treatment of this wave equation is impossible, a sufficiently close approximation to the true solution may probably be obtained by expanding these expressions in powers of the displacement coordinates, and neglecting all powers higher than the second. The justification of this procedure is that, at least for moderately small values of the vibrational quantum numbers, these coordinates are small in comparison with the equilibrium distances. The expressions for the normal coordinates obtained above may now be substituted, and another transformation made to remove multiplying constants, after which the wave equation takes the form:

$$\left(\frac{4\pi^2\omega_1}{h}+\frac{\omega_1}{\omega_2}a_{12}x_2^2+\frac{\omega_1}{\omega_3}a_{13}x_3^2\right)\frac{\partial^2\psi}{\partial x_1^2}+\left(\frac{4\pi^2\omega_2}{h}+\frac{\omega_2}{\omega_1}a_{21}x_1^2+a_{22}x_2^2+\frac{\omega_2}{\omega_3}a_{23}x_3^2\right)\frac{\partial^2\psi}{\partial x_2^2}$$
$$+\left(\frac{4\pi^2\omega_3}{h}+\frac{\omega_3}{\omega_1}a_{31}x_1^2+\frac{\omega_3}{\omega_2}a_{32}x_2^2+a_{33}x_3^2\right)\frac{\partial^2\psi}{\partial x_3^2}+b_{12}x_1x_2\frac{\partial^2\psi}{\partial x_1\partial x_2}+b_{13}x_1x_3\frac{\partial^2\psi}{\partial x_1\partial x_3}+b_{23}x_2x_3\frac{\partial^2\psi}{\partial x_2\partial x_3}$$
$$+c_1x_1\frac{\partial\psi}{\partial x_1}+c_2x_2\frac{\partial\psi}{\partial x_2}+c_3x_3\frac{\partial\psi}{\partial x_3}+\frac{8\pi^2}{h^2}(W-V)\psi=0,$$

where the a's, b's, and c's are constants involving the equilibrium positions, the binding constants, and the ω's. Analytical expressions for these constants will not be given, since they are quite complicated and their contribution to the energy in the present case, is small. All other powers of the x's are rejected in the coefficients, and those given are the only ones which have nonvanishing diagonals in the Hermitian matrix. The advantage of the normal coordinate substitution is that this reduces to second order magnitude the contributions of terms such as $\partial^2\psi/\partial x_1\partial x_2$ which cannot be treated rigorously and must be applied as perturbations.

We will now assume that the Hamiltonian, H, may be expanded in a power series in γ, a parameter of smallness.

$$H=H^\circ+\gamma H'+\gamma^2H''$$

corresponding to the expansion

$$W=W^\circ+\gamma W'+\gamma^2W''.$$

In H° we will include V° and those terms from the wave equation which have constant coefficients. H' contains all possible terms of V cubic in the coordinates, and H'' contains, in addition to the

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[4] B. Podolsky, Phys. Rev. 32, 812 (1928).

quartic terms of V, the terms from the wave equation containing the coordinates explicitly. If we assume the potential function to possess the same symmetry as the molecule it follows that X_1, being an odd function of the r's, may appear in V only to even powers. The terms in the expansion of H may now be written:

$$H^\circ=-\frac{h}{2}\left\{\omega_1\frac{\partial^2}{\partial x_1^2}+\omega_2\frac{\partial^2}{\partial x_2^2}+\omega_3\frac{\partial^2}{\partial x_3^2}-\omega_1 x_1^2-\omega_2 x_2^2-\omega_3 x_3^2\right\},$$

$$\gamma H'=h\{ex_2^3+fx_3^3+gx_1^2x_2+ix_1^2x_3+jx_2^2x_3+kx_2x_3^2\},$$

$$\gamma^2 H''=-\frac{h^2}{8\pi^2}\left\{\left(\frac{\omega_1}{\omega_2}a_{12}x_2^2+\frac{\omega_1}{\omega_3}a_{13}x_3^2\right)\frac{\partial^2}{\partial x_1^2}+\left(\frac{\omega_2}{\omega_1}a_{21}x_1^2+a_{22}x_2^2+\frac{\omega_2}{\omega_3}a_{23}x_3^2\right)\frac{\partial^2}{\partial x_2^2}\right.$$
$$+\left(\frac{\omega_3}{\omega_1}a_{31}x_1^2+\frac{\omega_3}{\omega_2}a_{32}x_2^2+a_{33}x_3^2\right)\frac{\partial^2}{\partial x_3^2}+b_{12}x_1x_2\frac{\partial^2}{\partial x_1\partial x_2}+b_{13}x_1x_3\frac{\partial^2}{\partial x_1\partial x_3}+b_{23}x_2x_3\frac{\partial^2}{\partial x_2\partial x_3}$$
$$\left.+c_1x_1\frac{\partial}{\partial x_1}+c_2x_2\frac{\partial}{\partial x_2}+c_3x_3\frac{\partial}{\partial x_3}\right\}+h\{lx_1^4+mx_2^4+nx_3^4+px_1^2x_2^2+qx_1^2x_3^2+sx_2^2x_3^2\}.$$

The zeroth order equation separates, and may be solved at once, leading to the energy expression

$$W^\circ{}_{V_1V_2V_3}=h\omega_1(V_1+\tfrac{1}{2})+h\omega_2(V_2+\tfrac{1}{2})+h\omega_3(V_3+\tfrac{1}{2})$$

in which the V's are the vibration quantum numbers. The ψ's are then the regular Hermite functions of argument x_i. If W' is the first order perturbation energy, we have the expression

$$W'{}_{V_1V_2V_3}=\int H'\psi^2{}_{V_1V_2V_3}d\tau$$

and for the second order energy W''

$$W''{}_{V_1V_2V_3}=\int H''\psi^2{}_{V_1V_2V_3}d\tau+\sum{}'_{V_1'V_2'V_3'}\frac{\{\int\psi_{V_1V_2V_3}H'\psi_{V_1'V_2'V_3'}d\tau\}^2}{W^\circ{}_{V_1V_2V_3}-W^\circ{}_{V_1'V_2'V_3'}}.$$

Since the method of obtaining the necessary matrix elements of the Hermite functions is well known, it need not be gone into here and only the results will be given.

For the total energy of the system we obtain an expression of the form

$$W_{V_1V_2V_3}=h\{X_0+X_1V_1+X_2V_2+X_3V_3+X_{11}V_1^2+X_{22}V_2^2+X_{33}V_3^2+X_{12}V_1V_2+X_{13}V_1V_2+X_{23}V_2V_3\},$$

where the coefficients X_{ij} are given by the following equations:

$$X_0=\tfrac{1}{2}(\omega_1+\omega_2+\omega_3)+\frac{h}{16\pi^2}\left\{\frac{\omega_1}{\omega_2}\frac{a_{12}}{2}+\frac{\omega_1}{\omega_3}\frac{a_{13}}{2}+\frac{\omega_2}{\omega_1}\frac{a_{21}}{2}+\frac{\omega_2}{\omega_3}\frac{a_{23}}{2}+\frac{\omega_3}{\omega_1}\frac{a_{31}}{2}+\frac{\omega_3}{\omega_2}\frac{a_{32}}{2}-\frac{a_{22}}{4}-\frac{a_{33}}{4}\right.$$
$$\left.-\frac{b_{12}}{2}-\frac{b_{13}}{2}-\frac{b_{23}}{2}+c_1+c_2+c_3\right\}+\tfrac{1}{4}(3l+3m+3n+p+q+s)-\frac{11e^2+g^2+k^2+6eg+6ek+2gk}{8\omega_2}$$
$$-\frac{11f^2+i^2+j^2+6fi+6fj+2ij}{8\omega_3}-\frac{g^2}{4(2\omega_1+\omega_2)}-\frac{i^2}{4(2\omega_1+\omega_3)}-\frac{j^2}{4(2\omega_2+\omega_3)}-\frac{k^2}{4(2\omega_3+\omega_2)},$$

$$X_1=\omega_1+\frac{h}{16\pi^2}\left\{\frac{\omega_1}{\omega_2}a_{12}+\frac{\omega_1}{\omega_3}a_{13}+\frac{\omega_2}{\omega_1}a_{21}+\frac{\omega_3}{\omega_1}a_{31}\right\}+\tfrac{1}{2}(3l+p+q)-g\frac{g+3e+k}{2\omega_2}-i\frac{i+3f+j}{2\omega_3}$$
$$-\frac{3g^2}{8(2\omega_1+\omega_2)}-\frac{g^2}{8(2\omega_1-\omega_2)}-\frac{3i^2}{8(2\omega_1+\omega_3)}-\frac{i^2}{8(2\omega_1-\omega_3)},$$

$$X_2=\omega_2+\frac{h}{16\pi^2}\left\{\frac{\omega_1}{\omega_2}a_{12}+\frac{\omega_2}{\omega_1}a_{21}+\frac{\omega_2}{\omega_3}a_{23}+\frac{\omega_3}{\omega_2}a_{32}+a_{22}\right\}+\tfrac{1}{2}(3m+p+s)-\frac{15e^2+6eg+6ek}{4\omega_2}-\frac{j^2+3fj+ij}{2\omega_3}$$
$$-\frac{g^2}{4(2\omega_1+\omega_2)}-\frac{g^2}{4(2\omega_1-\omega_2)}-\frac{3j^2}{8(2\omega_2+\omega_3)}-\frac{j^2}{8(2\omega_2-\omega_3)}-\frac{k^2}{4(2\omega_3+\omega_2)}-\frac{k^2}{4(2\omega_3-\omega_2)},$$

$$X_3=\omega_3+\frac{h}{16\pi^2}\left\{\frac{\omega_1}{\omega_3}a_{13}+\frac{\omega_2}{\omega_3}a_{23}+\frac{\omega_3}{\omega_1}a_{31}+\frac{\omega_3}{\omega_2}a_{32}+a_{33}\right\}+\tfrac{1}{2}(3n+q+s)-\frac{15f^2+6fi+6fj}{4\omega_3}-\frac{k^2+3ek+gk}{2\omega_2}$$
$$-\frac{i^2}{4(2\omega_1+\omega_3)}-\frac{i^2}{4(2\omega_1-\omega_3)}-\frac{j^2}{4(2\omega_2+\omega_3)}-\frac{j^2}{4(2\omega_2-\omega_3)}-\frac{3k^2}{8(2\omega_3+\omega_2)}-\frac{k^2}{8(2\omega_3-\omega_2)},$$

$$X_{11}=\frac{3}{2}l-\frac{g^2}{2\omega_2}-\frac{i^2}{2\omega_3}-\frac{g^2}{8(2\omega_1+\omega_2)}+\frac{g^2}{8(2\omega_1-\omega_2)}-\frac{i^2}{8(2\omega_1+\omega_3)}+\frac{i^2}{8(2\omega_1-\omega_3)},$$

$$X_{22}=\frac{h}{16\pi^2}a_{22}+\frac{3}{2}m-\frac{15e^2}{4\omega_2}-\frac{j^2}{2\omega_3}-\frac{j^2}{8(2\omega_2+\omega_3)}+\frac{j^2}{8(2\omega_2-\omega_3)},$$

$$X_{33}=\frac{h}{16\pi^2}a_{33}+\frac{3}{2}n-\frac{15f^2}{4\omega_3}-\frac{k^2}{2\omega_2}-\frac{k^2}{8(2\omega_3+\omega_2)}+\frac{k^2}{8(2\omega_3-\omega_2)},$$

$$X_{12}=\frac{h}{8\pi^2}\left(\frac{\omega_1}{\omega_2}a_{12}+\frac{\omega_2}{\omega_1}a_{21}\right)+p-\frac{3eg}{\omega_2}-\frac{ij}{\omega_3}-\frac{g^2}{2(2\omega_1+\omega_2)}-\frac{g^2}{2(2\omega_1-\omega_2)},$$

$$X_{13}=\frac{h}{8\pi^2}\left(\frac{\omega_1}{\omega_3}a_{13}+\frac{\omega_3}{\omega_1}a_{31}\right)+q-\frac{gk}{\omega_2}-\frac{3fi}{\omega_3}-\frac{i^2}{2(2\omega_1+\omega_3)}-\frac{i^2}{2(2\omega_1-\omega_3)}.$$

$$X_{23}=\frac{h}{8\pi^2}\left(\frac{\omega_2}{\omega_3}a_{23}+\frac{\omega_3}{\omega_2}a_{32}\right)+s-\frac{3ek}{\omega_2}-\frac{3fj}{\omega_3}-\frac{j^2}{2(2\omega_2+\omega_3)}-\frac{j^2}{2(2\omega_2-\omega_3)}-\frac{k^2}{2(2\omega_3+\omega_2)}-\frac{k^2}{2(2\omega_3-\omega_2)}.$$

In spite of the apparent complexity of these expressions, they are readily solved for the ω's, leading to the result

$$\omega_1=X_1-X_{11}-\tfrac{1}{2}X_{12}-\tfrac{1}{2}X_{13},\qquad \omega_2=X_2-X_{22}-\tfrac{1}{2}X_{12}-\tfrac{1}{2}X_{23},\qquad \omega_3=X_3-X_{33}-\tfrac{1}{2}X_{13}-\tfrac{1}{2}X_{23}.$$

These equations for the ω's in terms of experimentally determinable quantities are perhaps the most important result of this analysis, since it is from these that the zeroth order binding constants in the potential energy expression are evaluated, and it is about these constants that the greatest interest centers.

APPLICATION TO THE SPECTRUM OF WATER VAPOR

We have now obtained an expression which should fit the known vibrational energy levels of triatomic molecules to a fair degree of accuracy. We have also obtained expressions giving the true mechanical frequencies of the molecule in terms of the coefficients in this energy expression. It is desirable to check the validity of the energy formula over as wide a range as possible in order to determine its general usefulness and the degree of reliability to be attached to the results. For this purpose the spectrum of water vapor is at present most favorable. In the case of water seventeen infrared and visible vibration-rotation bands are known, and have been measured with great care. In addition the recent work of R. Mecke,[5] Baumann and Mecke,[6] and Freudenberg and Mecke[7] on the rotational analysis of these bands should give the positions of the band centers with considerable accuracy.

The figures for the band centers have been taken from Mecke's paper, and nine of the best known bands, distributed throughout the spectrum, have been selected to determine the coefficients X_{ij}. X_0 cannot, of course, be determined in this way, since the given band positions are differences between the given energy level and the ground level.

In Table I are given the positions of the bands, observed and calculated, together with the designation of each in terms of the vibrational quantum numbers.

TABLE I. *Positions of vibrational bands.*

Designation V_1	V_2	V_3	Position (cm^{-1}) obs.	calc.	Designation V_1	V_2	V_3	Position (cm^{-1}) obs.	calc.
0	0	1	1595.5	1595.5*	1	2	1	12151.22	12149.8
0	0	2	3152.0	3152.0*	3	0	1	12565.01	12565.0*
0	1	0	(3600)	3604.6	1	3	0	13830.92	13830.8*
1	0	0	3756.5	3756.5*	3	1	0	14318.77	14318.8*
1	0	1	5332.3	5331.0	1	3	1	15347.91	15348.6
1	1	0	7253.0	7255.0	3	1	1	15832.47	15832.4*
1	1	1	8807.05	8810.6	1	3	2	16821.61	16827.4
1	2	0	10613.12	10613.1*	1	4	0	16899.01	16908.1
3	0	0	11032.36	11032.5*	3	2	0	17495.48	17464.7

* Indicates the band centers used in evaluating the constants.

The fundamental (0, 1, 0) is not observed due to heavy overlying of that region by neighboring stronger bands, but is predicted at about 3600 cm^{-1} from combination relations. The value given above of 3604.6 cm^{-1} confirms this, and gives a more reliable figure for the actual frequency.

The check here is satisfactory, within experimental error for all cases but the last two. There is considerable doubt as to the complete correctness of the rotational analysis of these two bands, which appear very weakly in the solar spectrum. This agreement between the observed and calculated values of the band centers justifies the use of the coefficients X_{ij} in further calculation. The values of the X's which have been calculated are:

$$X_1 = 3796.0\ cm^{-1},\quad X_{11} = -39.5\ cm^{-1},$$
$$X_2 = 3674.8\ cm^{-1},\quad X_{22} = -70.2\ cm^{-1},$$
$$X_3 = 1615.0\ cm^{-1},\quad X_{33} = -19.5\ cm^{-1},$$
$$X_{12} = -106.1\ cm^{-1},$$
$$X_{13} = -21.0\ cm^{-1},$$
$$X_{23} = -18.9\ cm^{-1}.$$

If these quantities are substituted in the formulae of the previous section, we obtain for the ω's

$$\omega_1 = 3899.0\ cm^{-1},\quad \omega_2 = 3807.5\ cm^{-1},$$
$$\omega_3 = 1654.5\ cm^{-1}.$$

We are now in a position to calculate the zeroth order force constants in the potential function, from the normal coordinate expressions given earlier. However, we have only three relations from which to calculate the four constants therein assumed. The reasonable assumption may therefore be made that the constant d is small in comparison with a, b and c, and has, in this case, been taken equal to zero. The values for the equilibrium positions of the molecule have been obtained from Freudenberg and Mecke's[7] extrapolation to the vibrationless state, and were

$$\beta = 104°\ 36' \quad \text{and} \quad R = 0.9558\text{A}.$$

The equations may now be solved and we obtain

$$a = 8.233 \times 10^5\ \text{dynes/cm},$$
$$b/2R^2 = 0.376 \times 10^5\ \text{dynes/cm},$$
$$c = -0.0757 \times 10^5\ \text{dynes/cm}.$$

b is divided by $2R^2$ to give dimensional similarity.

The above values of the force constants are in fair agreement with those obtained by Van Vleck and Cross[8] by an entirely different, and somewhat less accurate method. It is also of interest to note that the constants a and b may be obtained with fair accuracy from the relation

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[5] R. Mecke, Zeits. f. Physik **81**, 313 (1933).

[6] Baumann and Mecke, Zeits. f. Physik **81**, 445 (1933).

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

[8] J. H. Van Vleck and P. C. Cross, J. Chem. Phys. **1**, 357 (1933).

proposed by Badger[9] between force constant and internuclear distance.

Three of the nine relations given by the X's have now been used, and it should be possible to calculate six higher order constants in the potential expression. However, it seems scarcely worth while to do this, since the additional information concerning the nature of the function would be small. It seems desirable to leave this until the nature of the interaction between rotation and vibration has been studied.

Prediction of the Spectrum of Heavy Water

It may be assumed for the present that the equilibrium positions and force constants of the water molecule are unchanged by the introduction of the hydrogen isotope of mass two. If this assumption be made we may calculate the mechanical frequencies and convergence factors of the symmetrical heavy water. Putting the changed masses in the normal coordinate expressions for the ω's given above, we find the following values

$$\omega_1 = 2865.4 \text{ cm}^{-1}, \qquad \omega_2 = 2764.7 \text{ cm}^{-1},$$
$$\omega_3 = 1209.7 \text{ cm}^{-1}.$$

The ratios of these three frequencies to the corresponding frequencies for ordinary water are rather close to 1.37. Making use of this fact, it is possible to calculate approximate values for the X_{ij}. It will be assumed that the force constants l–s appearing in H'' are small compared with the higher order constants, and that the contributions of the terms from the kinetic energy perturbation are negligible. Further, it should be noticed that due to the substitutions previously made the coefficients e–k of H' must be multiplied by terms of the order of $\omega^{\frac{3}{2}}$ before the real force constants are obtained. These assumptions, then, make the factors X_{11}, X_{22}, etc., but not X_1, X_2, X_3, homogeneous functions of the order ω^2. Using the average value of the ratio of ω's given above, we see that we may expect these X's for ordinary water to be approximately $(1.37)^2$ or 1.78 times the same constants for heavy water. From these six values, and the values of the ω's, X_1, X_2 and X_3 may be readily calculated. This gives

$$X_1 = 2810 \text{ cm}^{-1}, \qquad X_{11} = -21.2 \text{ cm}^{-1},$$
$$X_2 = 2694 \text{ cm}^{-1}, \qquad X_{22} = -37.7 \text{ cm}^{-1},$$
$$X_3 = 1188 \text{ cm}^{-1}, \qquad X_{33} = -10.5 \text{ cm}^{-1},$$
$$X_{12} = -56.9 \text{ cm}^{-1},$$
$$X_{13} = -11.3 \text{ cm}^{-1},$$
$$X_{23} = -10.1 \text{ cm}^{-1}.$$

The positions of the three fundamentals so calculated are 2790, 2655 and 1180 cm^{-1}, respectively. These figures fit the band observed by Casselman[10] at 4.2μ very closely as being the first overtone of ν_3. It should be observed that there has been as yet no completely satisfactory proof that the potential function for a bond involving heavy hydrogen is the same as that for the same bond with ordinary hydrogen. In consequence, any prediction of the spectrum of heavy water is a risky procedure, and the above values are to be taken as merely provisional.

In conclusion I wish to express my thanks to Professor Richard M. Badger who proposed this problem and who has assisted in its prosecution with valuable aid and advice.

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[9] R. M. Badger, J. Chem. Phys. **2**, 128 (1934).

[10] A. L. Casselman, Phys. Rev. **45**, 221 (1934).