I   THE VIBRATIONAL SPECTRUM OF WATER VAPOR

II   AN ANALYSIS OF THE VIBRATIONAL SPECTRUM

OF ETHYLENE

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The Vibrational Spectrum of Water Vapor

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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,

$$T = \tfrac{1}{2}(\mu_1 - A\mu_2^2 r_2^2 \sin^2 \alpha)\dot{r}_1^2 + \tfrac{1}{2}(\mu_1 - A\mu_2^2 r_1^2 \sin^2 \alpha)\dot{r}_2^2 + \tfrac{1}{2}A r_1^2 r_2^2(\mu_1^2 - \mu_2^2 \cos^2 \alpha)\dot{\alpha}^2$$

$$+ (-\mu_2 \cos \alpha + A\mu_2^2 r_1 r_2 \sin^2 \alpha)\dot{r}_1 \dot{r}_2 + A\mu_2 r_1 r_2 \sin \alpha(\mu_1 r_1 - \mu_2 r_2 \cos \alpha)\dot{r}_1 \dot{\alpha}$$

$$+ A\mu_2 r_1 r_2 \sin \alpha(\mu_1 r_2 - \mu_2 r_1 \cos \alpha)\dot{r}_2 \dot{\alpha}.$$

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

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.

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

If, in the coefficients of the dotted terms in T, the displacements in the coordinates may be considered neglibible compared with the equilibrium values, T takes the following form:

$$T = \tfrac{1}{2} B (\dot{\rho}^2 + \dot{\sigma}^2) + \tfrac{1}{2} C \dot{\phi}^2 + D \dot{\rho} \dot{\sigma} + E (\dot{\rho} \dot{\phi} + \dot{\sigma} \dot{\phi})$$

The coefficients B, C, D, and E are given by the following expressions:

$$B = \mu_1 - A \mu_2^2 R^2 \sin^2 \beta$$
$$C = \tfrac{1}{2} R^2 (\mu_1 + \mu_2 \cos \beta)$$
$$D = A \mu_2^2 R^2 \sin^2 \beta - \mu_2 \cos \beta$$
$$E = \tfrac{1}{2} R \mu_2 \sin \beta$$

In these displacement coordinates, the potential energy takes the form

$$V = \tfrac{1}{2} a (\rho^2 + \sigma^2) + \tfrac{1}{2} b \phi^2 + c \rho \sigma + d \phi (\rho + \sigma)$$

The customary normal coordinate derivation of the fundamental frequencies of a vibrating system may now be carried out. The procedure is first to apply the Lagrangian differerential equation of motion,

$$\frac{d}{dt} \frac{\partial T}{\partial \dot{q}} + \frac{\partial V}{\partial q} = 0$$

to the above expressions for T and V. This gives three equations containing the coordinates and their second derivatives with respect to the time. Next there is assumed a periodic solution in which the dependence of each coordinate upon the time is given by an expression of the form $q = A_q e^{i \lambda t}$. When this substitution is made the following set of

equations is obtained:

$$A_\rho(a - \lambda^2 B) + A_\sigma(c - \lambda^2 D) + A_\phi(d - \lambda^2 E) = 0$$

$$A_\rho(c - \lambda^2 D) + A_\sigma(a - \lambda^2 B) + A_\phi(d - \lambda^2 E) = 0$$

$$A_\rho(d - \lambda^2 E) + A_\sigma(d - \lambda^2 E) + A_\phi(b - \lambda^2 C) = 0$$

The condition that this set of linear homogeneous equations in the amplitudes, A_q, shall have a solution is, of course, that the determinant of the coefficients shall vanish. The solution of this third order determinant gives three values of λ^2. The λ's are related to the fundamental vibration frequencies of the system by the expression $\lambda^2 = 4\pi^2 \omega^2$. The λ's in terms of the fundamental constants of the molecule are given below.

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

$$\lambda_{2,\,3}^2 = 4\pi^2\omega_{2,\,3}^2 = R^{-2}(\mu_1^2 - \mu_2^2)^{-1}\{b(\mu_1 - \mu_2\cos\beta) + \tfrac{1}{2}R^2(\mu_1 + \mu_2\cos\beta)(a+c) - 2dR\mu_2\sin\beta\}$$

$$\pm R^{-2}(\mu_1^2 - \mu_2^2)^{-1}[\{b(\mu_1 - \mu_2\cos\beta) + \tfrac{1}{2}R^2(\mu_1 + \mu_2\cos\beta)(a+c) - 2dR\mu_2\sin\beta\}^2$$

$$- 2R^2(\mu_1^2 - \mu_2^2)\{b(a+c) - 2d^2\}]^{\frac{1}{2}}.$$

λ_2^2 is taken with the positive sign.

The general solution for each coordinate of the above set of differential equations will be a linear combination of the three separate solutions, i.e. of the form

$$\rho = A_{\rho_1} e^{i\lambda_1 t} + A_{\rho_2} e^{i\lambda_2 t} + A_{\rho_3} e^{i\lambda_3 t}$$

etc.

The amplitude ratios $\dfrac{A_{\rho_1}}{A_{\sigma_1}}$, etc. can be calculated from the initial set of linear equations by substituting the values for λ_1 , λ_2 , λ_3 . Using these ratios we get:

$$\rho = A_1 e^{i\lambda_1 t} + A_2 e^{i\lambda_2 t} + A_3 e^{i\lambda_3 t}$$

$$\sigma = -A_1 e^{i\lambda_1 t} + A_2 e^{i\lambda_2 t} + A_3 e^{i\lambda_3 t}$$

$$\phi = -2 \frac{d - \lambda_2^2 E}{b - \lambda_2^2 C} A_2 e^{i\lambda_2 t} - 2 \frac{d - \lambda_3^2 E}{b - \lambda_3^2 C} A_3 e^{i\lambda_3 t}$$

We have here three equations involving the three frequencies, λ_1 , λ_2 and λ_3 so we may eliminate them, two at a time, and find those combinations of the original coordinates which involve just one frequency. These combinations are, by definition, the normal coordinates of the system and are those substitution that reduce T and V to sums of squares.

ρ , σ , and ϕ in terms of the normal coordinates, y_1, y_2, y_3 are as follows:

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

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

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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

[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,

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.

observed and calculated, together with the designation of each in terms of the vibrational quantum numbers.

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:

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

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

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

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

[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

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

be noticed that due to the substitutions previously made the coefficients e–k of H' must be multiplied by terms of the order of $\omega^{\frac{1}{2}}$ 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

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

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.

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

Bartholomé and Clusius[11] have investigated the infrared spectrum of D_2O vapor in the region 2 - 10 μ and found the two fundamentals ν_1 and ν_3 to lie at 2775 and 1185 cm^{-1} with a probable error of 5 cm^{-1}. Rank, Larsen, and Bordner[12] found one line in the Raman spectrum of D_2O vapor at 2666 which is almost undoubtedly ν_2. Considering the crudeness of the above prediction the agreement between the theoretical and observed frequencies is quite satisfactory.

In conclusion a few remarks should be made concerning the Raman spectrum of H_2O. This spectrum has been carefully studied by Bender[13], by Rank, Larsen, and Bordner[12], and by others. It seems quite certain that H_2O vapor possesses just one line at about 3655 cm^{-1}, although all three frequencies are permitted in the Raman effect. It would seem most likely that this were the frequency ν_2^0, but it has been shown above from the combination relations of infrared bands that ν_2^0 lies at 3604.6 cm^{-1}. Furthermore, a frequency of 3655 cm^{-1} cannot be made to fit in with the infrared vibration analysis. As yet no satisfactory explanation of this state of affairs has been found although the fact that the fundamental frequency of the OH molecule lies at 3652 cm^{-1} may be significant. Some support of the 3605 cm^{-1} interpretation is given by the good agreement between the value of ν_2^0 for D_2O calculated from this frequency and the observed Raman lines of this molecule.

11. Bartholomé and Clusius, Naturwiss. 22, 420 (1934)
12. Rank, Larsen, and Bordner, J.Chem. Phys. 2, 464 (1934)
13. Bender, D., Phys. Rev. 47, 252 (1935)

II An Analysis of the Vibrational Spectrum of Ethylene

The first investigation of the infrared absorption spectrum of ethylene gas was made by Coblentz[1] in 1905. Using a prism spectrometer he was able to locate a number of absorption maxima but did not resolve any of the fine structure. In 1928, Levin and Meyer[2] reinvestigated the spectrum of this molecule, using higher dispersion instruments and taking greater care to obtain pure gas and to exclude atmospheric effects. In the region 2 - 15 μ they found a total of ten absorption bands, most of which were at least indicated on Coblentz[1] prism curve.

The spectrum of ethylene in the photographic region of the infrared has been investigated by Badger and Binder[3], who found only one band, at 8720 A.

The most recent work on the Raman spectrum of this molecule was carried out by Dickinson, Dillon, and Rassetti[4]. They used the gas at high pressure and mercury resonance excitation and found a total of six lines.

Any attempt to obtain a complete vibrational analysis of ethylene, for force constant evaluation, showed, however, that there were a good many gaps and inconsistencies in the experimental data. There has been made, then, in the present work, a complete reinvestigation of the photographic infrared and Raman spectra. The results of this work lead to a complete and quite satisfactory determination of all the fundamental frequencies of vibration of the ethylene molecule.

Ten new absorption bands have been found in the photographic infrared. Experiments using liquid ethylene have shown the presence of three new Raman lines, and have failed to show two of those reported by Dickinson, Dillon, and Rassetti[4].

EXPERIMENTAL

All infrared absorption experiments were done with the stainless steel absorption tube and twenty-one foot grating spectrograph recently constructed in this laboratory. The tube is approximately seven-eighths inches in diameter and has a maximum length of seventy feet. The full length was used in investigations of all regions of the spectrum except that beyond 10,000 A. For this region, due to the low sensitivity of all available plates, it was necessary to reduce the path length to twenty-eight feet. Pressures of gas used in the tube ranged from one to seven atmospheres and the entire spectral region investigated lay between 6,000 A and 12,000 A. Eastman spectroscopic plates were used for wave lengths below 10,300 A, but for longer wave lengths their sensitivity was too low, even with the reduced tube length. The Eastman plates were always hypersensitized before using by treating for one minute with a 4% ammonia solution at $10°C$. One series of measurements was made in the region 10,000 A - 12,000 A using special Agfa infrared plates very kindly supplied by Dr. T.J. Dunham, Jr. of the Mt. Wilson Observatory.

The ethylene used in these experiments was a commercial product, supplied for anaesthetic purposes, and guaranteed by the manufacturers to be better than 99% pure.

Raman scattering experiments were made on gaseous ethylene using λ = 2537 A excitation, but under these conditions only the three strong lines reported by Dickinson, Dillon, and Rassetti were found. Experiments were then made with the liquid in the hope of obtaining a larger number of shifts. Two types of experiment were made, one using glass apparatus and λ = 4358 A excitation, and the other with quartz and λ = 2537A. In each case liquid ethylene was confined in a tube about 15 mm. in diameter and 20 cm. long. This was then immersed in a Dewar flask filled with a mixture of alcohol and solid carbon dioxide. At this temperature, $-78°C$, the vapor pressure of ethylene is about 3.5 atmospheres. The Dewar was silvered on one side only, and the light from a mercury arc lamp was passed through the clear side. The scattered light was then focussed by means of a prism and lens on the slit of a prism spectrograph. For the glass apparatus, the dispersion of the spectrograph was about 50 A per mm., and for the quartz, 10 A per mm. Also, in the case of the visible excitation, an aqueous solution of quinine and $CoSO_4$ was placed between the lamp and the Dewar to serve as a filter, thereby restricting the exciting light as closely as possible to the line 4358 A. A total of seven lines was observed. Three quite strong ones were measured with frequency shifts of 3009, 1619, and 1341 cm^{-1}. Dickinson, Dillon, and Rassetti measured these same lines in the gas at 3019.3, 1623.3, and 1342.4 cm^{-1}, so it may be seen that, for the low frequency lines particularly, the shift in passing from the gas to the liquid is not large. However, gas values will be used wherever possible. In addition to the three strong lines there were four weak ones measured

at 3069, 2880, 1654, and 950 cm^{-1}. The last one in particular was extremely weak and diffuse, and in consequence the measurement may be in error by as much as 10 cm^{-1}. The line at 2880 cm^{-1} was observed by the previous investigators and was given by them as somewhat weaker than a pair, also observed by them, at 3240 and 3272 cm^{-1}. Since in these experiments the line at 2880 showed up quite definitely but no trace was obtained of the other two, they may probably be disregarded.
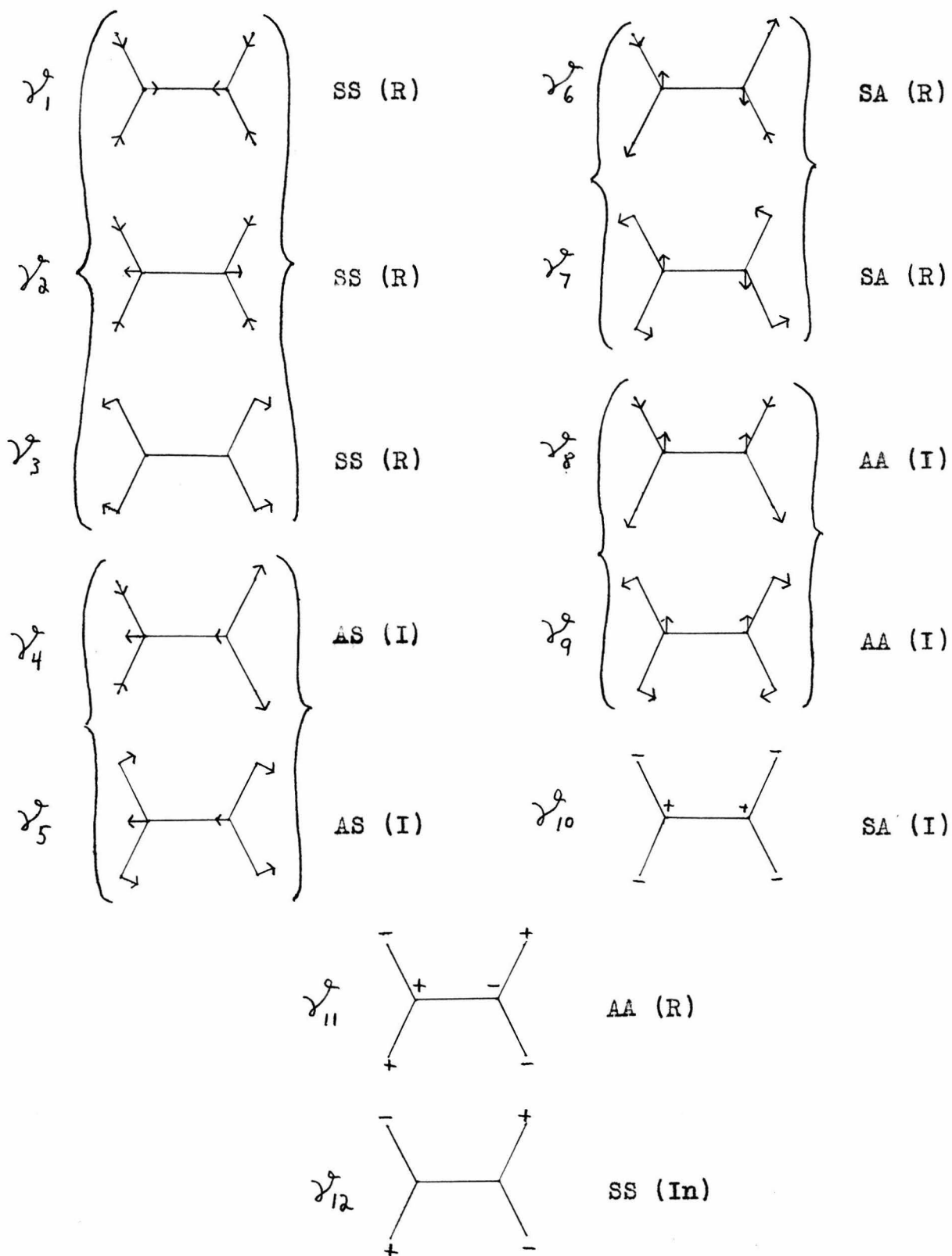
ASSIGNMENT OF FREQUENCIES

In Fig. I are shown diagrams of the twelve fundamental modes of vibration of ethylene as given by R. Mecke[5]. The first pair of letters following each mode gives its symmetry to rotations of π about the axes of greatest and least moment of inertia respectively. Thus mode 4 is antisymmetrical to a rotation of 180° about the axis of greatest moment of inertia (the axis perpendicular to the plane of the figure), but symmetrical to the same rotation about the axis of least moment of inertia (the figure axis). Of the letters in brackets, R indicates that the fundamental is active in the Raman spectrum, I that it is active in the infrared, and In that it is completely inactive. Since the molecule possesses a center of symmetry, no modes may be active in both Raman and infrared spectra. Linear combinations must be made of the bracketed modes to obtain the true vibration forms.

From the figure it may be seen that, on the basis of symmetry, there are three types of fundamental active in the infrared, and each of these is typified by its distinctive band envelope. The type AS is

Figure I

The Fundamental Modes of Vibration of Ethylene

γ_1 SS (R) γ_6 SA (R)

γ_2 SS (R) γ_7 SA (R)

γ_3 SS (R) γ_8 AA (I)

γ_4 AS (I) γ_9 AA (I)

γ_5 AS (I) γ_{10} SA (I)

γ_{11} AA (R)

γ_{12} SS (In)

recognized by its sharp central maximum, or Q branch. The type AA

has no central maximum and appears, under low resolution, as a widely

spaced doublet. The Type SA can have no real Q branch, but may appear to

have a small one due to piling up of lines near the center of the band.

These two last types are distinguished, under low resolution, by a series

of widely spaced maxima.

The three modes ν_1, ν_2, ν_3 are of the completely symmetrical

type, and should appear very strongly in the Raman effect, so to these

may be assigned at once the three strong observed Raman lines. The

assignment of frequencies to the remainder of the modes is not at all

such a clear cut case. Table I shows what seems at present to be the

most reasonable assignment of frequencies to the fundamental modes and

to the combinations and overtones appearing in the infrared and Raman

spectra.

In assigning the infrared frequencies the following principles

have been used. First, if two or more modes are excited simultaneously

the symmetry of the combination level is the product of the symmetries

of the individual modes. The multiplication of symmetries obeys the

same law as the multiplication of signs: S x S = S, A x A = S,

S x A = A. The type of the band resulting from a transition to this

combination level is that associated with the symmetry of the level.

Thus, if a mode of symmetry AA combines with one of symmetry SA the re-

sultant level is of symmetry AS and the band resulting from a combination

of this with the ground level is of the Q branch type. It follows from

this that any combination leading to the symmetry SS cannot appear in

the infrared. The second principle is that no two inactive fundamentals can combine to give an infrared active band.

In Table I the columns headed V_1, V_2, etc. give the quantum numbers of the upper level. The lower level is in all cases the ground level. The column headed "Type" tells whether the band possesses a Q branch (Q) or has a doublet structure (D).

The infrared band at 949.7 cm^{-1} is almost without a doubt not a single band but a superposition of two fundamentals. In fact, from the absorption curve published by Levin and Meyer[2], the maxima belonging to each may be picked out, and from this the spacing seems to be about 10 cm^{-1}. It is interesting that three fundamentals seem to fall in the region of 950 cm^{-1}, and this fact leads to some ambiguity in the assignments. It is in some cases impossible to tell whether a given band is an harmonic containing ν_7, ν_9 or ν_{10}. The frequency ν_{11} has not yet appeared in the spectrum although it should be active in the Raman effect. However, the infrared band at 2047 cm^{-1} is almost without a doubt a combination of this with one of the 950 cm^{-1} frequencies, thus fixing ν_{11} at about 1100 cm^{-1}. ν_{12} cannot appear alone in either the infrared or Raman spectra, but Eucken and Parts[6], from specific heat data, have estimated it to lie in the region 750 - 800 cm^{-1}. If the weak absorption reported by Coblentz[1] at 1724 cm^{-1} is real, it could be a combination of ν_{12} with one of the 950 cm^{-1} fundamentals, thereby locating ν_{12} at about 775 cm^{-1}, in good agreement with Eucken and Parts. Other possibilities are, however, that the weak Raman line observed in the present work at 1654 cm^{-1} is either the first overtone of this frequency, which

TABLE I

Assignment of Transition Frequencies

Frequency(cm^{-1})	Type	V_1	V_2	V_3	V_4	V_5	V_6	V_7	V_8	V_9	V_{10}	V_{11}	V_{12}
Infrared:													
950	D	0	0	0	0	0	0	0	0	1	0	0	0
940	D	0	0	0	0	0	0	0	0	0	1	0	0
1443.9	Q	0	0	0	0	1	0	0	0	0	0	0	0
1724	?	0	0	0	0	0	0	0	0	0	1	0	1
1889.7	Q	0	0	0	0	0	0	0	0	1	1	0	0
2047.0	Q	0	0	0	0	0	0	0	0	0	1	1	0
2988.2	Q	0	0	0	1	0	0	0	0	0	0	0	0
3107.4	D	0	0	0	0	0	0	0	1	0	0	0	0
4207.9	D	0	0	1	0	0	0	0	0	3	0	0	0
4324.3	D	0	0	0	0	1	0	1	0	2	0	0	0
4515.5	D	0	0	0	0	1	1	0	0	0	0	0	0
4729.0	D	1	0	0	0	0	0	0	1	0	0	0	0
8758 *	Q	0	0	0	3	0	0	0	0	0	0	0	0
8982 *	Q	0	0	0	1	0	0	0	2	0	0	0	0
9134 *	D	0	0	0	0	0	0	0	3	0	0	0	0
9776 *	Q	0	0	0	2	0	0	1	1	0	0	0	0
10119 *	D	0	0	0	1	0	0	0	2	0	0	1	0
10286 *	Q	0	0	1	1	0	0	0	2	0	0	0	0
10366 *	Q	1	0	0	3	0	0	0	0	0	0	0	0
11465	D	1	0	0	3	0	0	0	0	1	0	0	0
11724 *	Q	0	1	0	3	0	0	0	0	0	0	0	0
11780 *	D	0	0	0	3	0	1	0	0	0	0	0	0
14100 *	?	0	0	0	5	0	0	0	0	0	0	0	0
Raman:													
950 *		0	0	0	0	0	0	1	0	0	0	0	0
1342.4		0	0	1	0	0	0	0	0	0	0	0	0
1623.3		1	0	0	0	0	0	0	0	0	0	0	0
1654 *		0	0	0	0	0	0	0	0	0	0	0	2
2880.1		0	0	0	0	0	0	1	0	2	0	0	0
3019.3		0	1	0	0	0	0	0	0	0	0	0	0
3069 *		0	0	0	0	0	1	0	0	0	0	0	0

Frequencies marked * are reported for the first time in this paper.

would be permitted, or a combination of it with a 950 cm^{-1} band. This would give to ν_{12} the values 825 or 700 cm^{-1}. Considering the nature of the specific heat estimation either one of these would be in about as good agreement with experiment as the above value of 775 cm^{-1}. It is at present impossible to make a unique choice and to state definitely the value of the ν_{12} fundamental. However, the Raman line is certainly real, and there is considerable doubt as to the infrared band. Also the overtone would, in this case, be more likely to appear than the combination, thus giving some weight to the 825 cm^{-1} value.

In concluding this section, it might be to the point to give a table showing the frequencies at present assigned to all the fundamental vibrational modes of the ethylene molecule.

Table II

vibration	frequency	vibration	frequency
ν_1	1623.3	ν_7	950
ν_2	3019.3	ν_8	3107.4
ν_3	1342.4	ν_9	950
ν_4	2988.2	ν_{10}	940
ν_5	1443.9	ν_{11}	1100
ν_6	3069	ν_{12}	825

EVALUATION OF THE FORCE CONSTANTS

The most important results to be obtained from such an evalu-
ation of the fundamental vibration frequencies of a molecule as has been
made in the previous section, are the values of the force constants of
the bonds holding the atoms together. These force constants, together
with such constants for the interaction forces between bonds as may be
obtained are of interest for the deeper insight they give in to the
nature of intra-molecular forces. For a really accurate evaluation of
bond force constants the mechanical frequencies for infinitessimal am-
plitudes of vibration should be used, but for most molecules, particu-
larly the more complicated ones, the data are insufficient to bbtain
these, so the observed frequencies must be used. It is probable, though,
that for most types of vibration the deviations will not be so large
as to affect the calculated force constants greatly.

The expressions relating the fundamental frequencies with the
bond force contants and other constants of the ethylene molecule have
been derived by Dr. E.B. Wilson, Jr.

Figure II shows the assumed structure of the ethylene molecule.
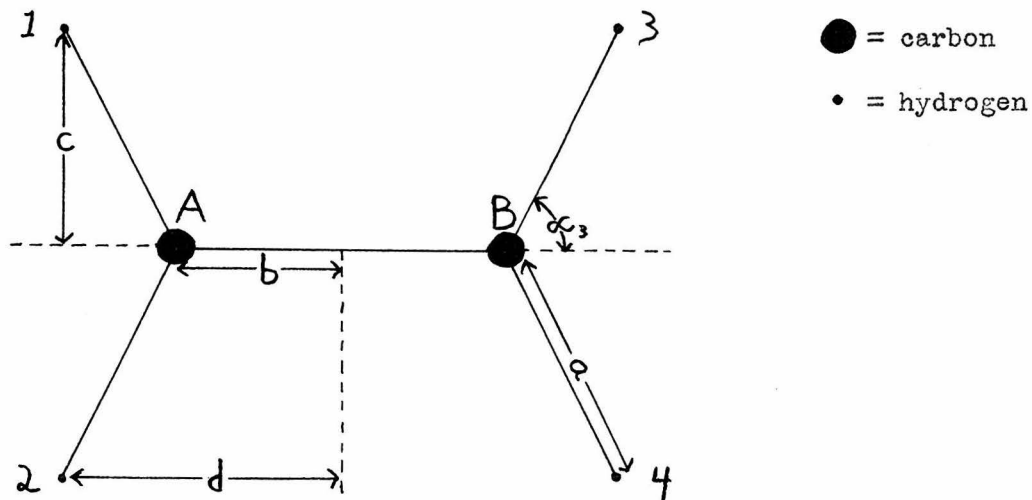
A somewhat simplified potential function containing eight constants may now be written down as follows:

$$2V = K(\Delta R)^2 + q\sum(\Delta S_i)^2 + H a^2 \sum(\Delta \alpha_i)^2 + h a^2 \sum \mu_i^2$$
$$+ 2L\{\Delta S_1 \Delta S_2 + \Delta S_3 \Delta S_4\} + 2\theta a^2\{\Delta \alpha_1 \Delta \alpha_2 + \Delta \alpha_3 \Delta \alpha_4\}$$
$$+ 2\Lambda a^2\{\Delta \alpha_1 \Delta \alpha_3 + \Delta \alpha_2 \Delta \alpha_4\} + 2\Omega a^2\{\mu_1 \mu_3 + \mu_2 \mu_4\}$$

Here ΔR refers to stretch of the C-C bond, ΔS_i to stretch of the C-H_i bond, $\Delta \alpha_i$ to bending of the C-H_i bond in the plane, and μ_i to bending of the C-H_i bond out of the plane.

The secular determinant in terms of the constants and of the frequency parameter λ factors into sub-determinants corresponding to the bracketed modes of Fig. I. These factors may now be written down for each of the sets of modes. The following abbreviations have been adopted:

m = mass of hydrogen $\qquad$ M = mass of carbon

$\beta = \cos \alpha$ $\qquad\qquad$ $\gamma = \sin \alpha$

$N = 1 + 2\dfrac{m}{M}\gamma^2$ $\qquad$ $E = 2\dfrac{m}{M}\dfrac{a + b\beta}{b}\gamma$

$F = 1 + 2\dfrac{m}{M}\left(\dfrac{a+b\beta}{b}\right)^2$ $\qquad$ $P = 2\dfrac{m}{M}\beta\gamma$

$Q = 1 + 2\dfrac{m}{M}\beta^2$

$\underline{\gamma_1, \gamma_2, \gamma_3}$

$$\begin{vmatrix} K + \beta^2(q+L) + \gamma^2(H+\theta+\Lambda) - \tfrac{1}{2}M\lambda & -\beta(q+L) & \gamma(H+\theta+\Lambda) \\ -\beta(q+L) & (q+L) - m\lambda & 0 \\ \gamma(H+\theta+\Lambda) & 0 & (H+\theta+\Lambda) - m\lambda \end{vmatrix} = 0$$

$\underline{\nu_4, \nu_5}$

$$\lambda = \frac{1}{2m}\left\{ Qq' + NH' \pm \left[(Qq' + NH')^2 - 4q'H'(NQ - P^2) \right]^{1/2} \right\}$$

$$q' = q + L \qquad H' = H + \theta - \Lambda$$

$\underline{\nu_6, \nu_7}$

$$\lambda = \frac{1}{2m}\left\{ Nq'' + FH'' \pm \left[(Nq'' + FH'')^2 - 4q''H''(NF - E^2) \right]^{1/2} \right\}$$

$$q'' = q - L \qquad H'' = H - \theta - \Lambda$$

$\underline{\nu_8, \nu_9}$

$$\lambda = \frac{1}{2m}\left\{ Nq'' + QH''' \pm \left[(Nq'' + QH''')^2 - 4q''H'''(NQ - P^2) \right]^{1/2} \right\}$$

$$q'' = q - L \qquad H''' = H - \theta + \Lambda$$

$\underline{\nu_{10}} \qquad \lambda = (h + \Omega)\frac{2m + M}{mM}$

$\underline{\nu_{11}} \qquad \lambda = (h - \Omega)\frac{2md^2 + Mb^2}{mMb^2}$

If we assume the dimensions of the ethylene molecule obtained by Badger[7] to be correct, viz: C-H = 1.04 A, C-C = 1.37 A, and $C\begin{smallmatrix}/H\\\backslash H\end{smallmatrix}$ angle = 126°, we are in a position to compute values for these constants. It is to be noted that the five constants q, L, H, θ and Λ occur in all the expressions for the first nine frequencies so there will be ample opportunity for checks on their values.

Due to approximations in choosing the potential function, the cubic factor $\gamma_1, \gamma_2, \gamma_3$ has no real solutions for the force constants. However, by a variation method, it has been possible to find the values of the force constants which give frequency values fitting most closely to the observed values. These are probably quite close to the true values. In Table III there are given the values of the force constants or force constant combinations occurring in the expressions for each frequency set.

TABLE III

$\gamma_1, \gamma_2, \gamma_3$	$K = 8.2 \times 10^5$ dynes/cm	$q + L = 5.09 \times 10^5$ dynes/cm
	$H + \theta + \Lambda = 1.18 \times 10^5$ "	
γ_4, γ_5	$q + L = 5.08 \times 10^5$ "	$H + \theta - \Lambda = 1.09 \times 10^5$ "
γ_6, γ_7	$q - L = 4.88 \times 10^5$ "	$H - \theta - \Lambda = 0.34 \times 10^5$ "
γ_8, γ_9	$q - L = 5.02 \times 10^5$ "	$H - \theta + \Lambda = 0.52 \times 10^5$ "
γ_{10}	$h + \Omega = 0.45 \times 10^5$ "	
γ_{11}	$h - \Omega = 0.37 \times 10^5$ "	

26.

It can be seen that the values of q + L and of q - L calculated from two different frequency sets check satisfactorily. Also, if the values of $H, \theta,$ and Λ be determined from the second, third, and fourth sets, the value of $H + \theta + \Lambda$ so obtained is 1.26 x 10^5 as compared with 1.18 obtained above, which is satisfactory when the nature of the solution obtained for the cubic factor is considered.

It is now possible to give a table of the values of all the individual force constants used in this work.

<div align="center">

TABLE IV

</div>

$K = 8.2 \times 10^5$	$\theta = 0.38 \times 10^5$
$q = 5.02$	$\Lambda = 0.09$
$L = 0.07$	$h = 0.41$
$H = 0.80$	$\Omega = 0.04$

The interaction constants are all quite small except for the constant θ. The size of this, comparable with the primary constant H, is a result of the definition in the potential function. The half angle in the CH_2 bond was used as the coordinate, and hence interactions between the two half angles of the same bond appear quite large. A different choice of coordinates, one in which the entire angle was used, would lead to a much smaller value of the apparent interaction.

<div align="center">

ACKNOWLEDGEMENTS

</div>

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