

Valence and Central Forces in Bent Symmetrical XY₂ Molecules

W. H. Shaffer and R. R. Newton

Citation: *The Journal of Chemical Physics* **10**, 405 (1942); doi: 10.1063/1.1723741

View online: <http://dx.doi.org/10.1063/1.1723741>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/10/7?ver=pdfcov>

Published by the AIP Publishing

Articles you may be interested in

[The application of an effective nuclear charge model to the prediction of valence force constants in tetrahedral XY₄ molecules. III](#)

J. Chem. Phys. **73**, 5459 (1980); 10.1063/1.440090

[The application of an effective nuclear charge model to the prediction of valence force constants in planar and pyramidal XY₃ molecules. II.](#)

J. Chem. Phys. **72**, 3663 (1980); 10.1063/1.439575

[Molecular constants of some bent symmetrical XY₂ molecules](#)

J. Chem. Phys. **61**, 470 (1974); 10.1063/1.1681920

[Comment on "On the Force Constants of the XY₂ Molecule"](#)

J. Chem. Phys. **14**, 294 (1946); 10.1063/1.1724135

[On the Force Constants of the XY₂ Molecule](#)

J. Chem. Phys. **14**, 294 (1946); 10.1063/1.1724134



THE JOURNAL OF CHEMICAL PHYSICS

VOLUME 10

JULY, 1942

NUMBER 7

Valence and Central Forces in Bent Symmetrical XY_2 Molecules

W. H. SHAFFER AND R. R. NEWTON

Mendenhall Laboratory of Physics, Ohio State University, Columbus, Ohio

(Received April 1, 1942)

Appropriate generalized coordinates and potential functions are set up for studying the zero- and first-order vibration problem of the bent symmetrical XY_2 molecular model under the assumption of valence and central forces. The force constants in the quadratic and cubic parts of the potential function of the water vapor molecule are evaluated for these two types of forces by using the data of Darling and Dennison.

I. INTRODUCTION

THE data obtained from experiment on the normal frequencies of vibration of polyatomic molecules are usually insufficient to allow evaluation of all the force constants in the most general form of the harmonic potential function consistent with the symmetry of a molecule. Consequently it is necessary to adopt simplified potential functions, such as those based on valence- or central-forces, involving a number of force constants not greater than the number of independent data available. These approximations often lead to consistent results and appear to give fairly good interpretation of experimental data. However, their validity should be tested in cases where it is possible to evaluate all the constants in the most general form of the harmonic potential function and it would be desirable to investigate the possibility of extending the same types of approximations to higher order parts of the potential function.

In this paper the vibrations of the bent symmetrical XY_2 molecular model are discussed for valence- and central-forces. Appropriate generalized coordinates are selected for describing these two types of forces and the most general zero-

(harmonic) and first-order (cubic) parts of the potential function are set up in terms of these coordinates. Relations are derived giving the force constants in the valence- and central-force expressions in terms of those occurring in the normal coordinate form of potential function. The results are applied to the interpretation of the data on the vibrations of the water vapor molecule which Darling and Dennison¹ obtained from a study of the vibration-rotation spectra of H_2O and D_2O . This is the first case in which sufficient data have been available on the vibrations of a polyatomic molecule to make it feasible to extend the valence- and central-force types of potential function to include the cubic terms.

II. NORMAL MODES OF OSCILLATION

Several writers¹⁻⁵ have discussed the normal modes and frequencies of vibration of the bent symmetrical XY_2 molecular model. A brief sum-

¹ B. T. Darling and D. M. Dennison, *Phys. Rev.* **57**, 128 (1940).

² N. Bjerrum, *Verh. d. D. Phys. Ges.* **16**, 737 (1914).

³ D. M. Dennison, *Phil. Mag.* **1**, 195 (1926).

⁴ E. O. Salant and J. E. Rosenthal, *Phys. Rev.* **42**, 812 (1932).

⁵ W. H. Shaffer and H. H. Nielsen, *Phys. Rev.* **56**, 188 (1939).

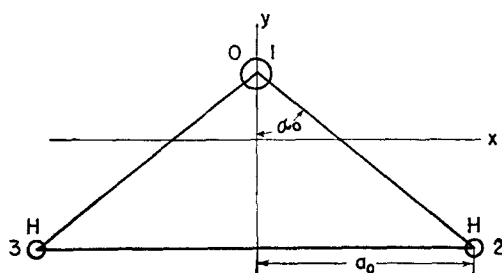


FIG. 1a.

mary of the problem is given here in order to clarify the notation used in this paper.

The equilibrium configuration of the model is shown in Fig. 1a. The positions of the particles are referred to a right-handed coordinate system, xyz , so oriented that its origin lies at the center of gravity, its xy plane coincides with the plane of the molecule, and its z axis points upward from the xy plane. In the equilibrium configuration the coordinate axes coincide with the principal axes of inertia as shown in Fig. 1a and the equilibrium coordinates are $x^0_1=0$, $x^0_2=-x^0_3=a_0$, $y^0_1=(\mu/M)a_0 \cot \alpha_0$, $y^0_2=y^0_3=-(\mu/2m)a_0 \cot \alpha_0$, $z^0_1=z^0_2=z^0_3=0$, where m is the mass of a Y-particle, M the mass of the X-particle and $\mu=2mM/(2m+M)$.

When the system is oscillating, the components of displacement of the i th particle ($i=1, 2, 3$) from equilibrium are denoted by x'_i , y'_i , z'_i as illustrated in Fig. 1b, where the z'_i vanish because the molecule lies in the xy plane. It has been shown^{4, 5} that appropriate symmetry coordinates for studying the small oscillations of the XY_2 model are

$$\begin{aligned} u &= x'_1 - (1/2)(x'_2 + x'_3), \\ v &= y'_1 - (1/2)(y'_2 + y'_3), \\ w &= x'_2 - x'_3. \end{aligned} \quad (1a)$$

These coordinates are also suitable for studying the interactions between rotation and vibration since they are consistent with the Eckart^{6, 7} conditions:

$$\begin{aligned} Mx'_1 + m(x'_2 + x'_3) &= 0, \\ My'_1 + m(y'_2 + y'_3) &= 0, \end{aligned}$$

⁶ C. Eckart, Phys. Rev. **47**, 552 (1932).

⁷ E. B. Wilson and J. B. Howard, J. Chem. Phys. **4**, 260 (1936).

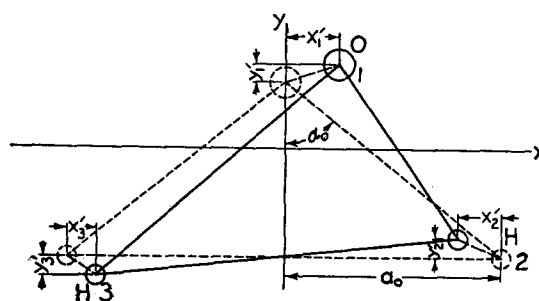


FIG. 1b.

and

$$M(x^0_1 y'_1 - y^0_1 x'_1) + m(x^0_2 y'_2 - y^0_2 x'_2 + x^0_3 y'_3 - y^0_3 x'_3) = 0. \quad (1b)$$

It can readily be shown from Eqs. (1a) and (1b) that

$$\begin{aligned} x'_1 &= (\mu/M)u, & x'_2 &= -(\mu/2m)u + (w/2), \\ x'_3 &= -(\mu/2m)u - (w/2), \\ y'_1 &= (\mu/M)v, & y'_2 &= (\mu/2m)(-v + u \cot \alpha_0), \\ y'_3 &= (\mu/2m)(-v - u \cot \alpha_0). \end{aligned} \quad (2)$$

The kinetic energy of oscillation (see reference 5) is

$$T_v = (1/2)\{\mu_1 \dot{u}^2 + \mu \dot{v}^2 + (m/2)\dot{w}^2\},$$

where $\mu_1 = \mu[1 + (\mu/2m) \cot^2 \alpha_0]$, and the most general quadratic potential energy function* consistent with the symmetry of the molecule is

$$U_0 = (1/2)\{Aw^2 + Bu^2 + Cv^2 + 2Dvw\}.$$

The normal frequencies of oscillation ω_j (in cm^{-1}) are given by the relations $\omega_j = (2\pi c)^{-1} \lambda_j^{1/2}$, ($j=1, 2, 3$), where c is the velocity of light in cm/sec . and the λ_j are roots of Lagrange's secular determinant, $|\lambda T_v - U_0| = 0$. The λ_i satisfy the following relations:

$$\begin{aligned} (\lambda_1 + \lambda_2) &= [(2A/m) + (C/\mu)], \\ (\lambda_1 - \lambda_2)^2 &= [(2A/m) - (C/\mu)]^2 + (8D^2/\mu m), \\ \lambda_1 \lambda_2 &= (2/\mu m)(AC - D^2), \quad \lambda_3 = (B/\mu_1). \end{aligned}$$

The three constants A , C , and D which are related to the two roots λ_1 and λ_2 can be determined if the roots, λ'_1 and λ'_2 , of the isotopic molecule $X'Y'_2$ are known. If m' denotes the mass of Y' , M' the mass of X' , and $\mu' = 2m'M'/(2m' + M')$,

* For comparison with reference 5 where the generalized force constants are $k'_1 \dots k'_4$, note that $A = k'_1$, $B = k'_3$, $C = k'_2$, $2D = k'_4$.

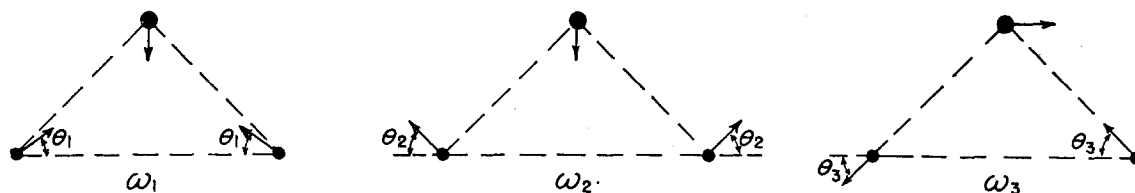


FIG. 2.

the following relations hold:

$$A = [\mu(\lambda_1 + \lambda_2) - \mu'(\lambda'_1 + \lambda'_2)] / [(2\mu/m) - (2\mu'/m')];$$

$$C = [m(\lambda_1 + \lambda_2) - m'(\lambda'_1 + \lambda'_2)] / [(m/\mu) - (m'/\mu')]; \quad (3)$$

$$D^2 = AC - (\mu m/2)\lambda_1\lambda_2;$$

$$(\mu^2/\mu_1)\lambda_3 = (\mu'^2/\mu'_1)\lambda'_3, \quad (\lambda_1\lambda_2/\lambda'_1\lambda'_2) = (\mu'm'/\mu m).$$

The following relations give the symmetry coordinates u , v , and w , in terms of the normal coordinates $q_i = A_i \cos(\lambda_i t - \epsilon_i)$ associated with the normal frequencies, ω_i :

$$w = (m/2)^{-1/2}(\sigma_1 q_1 - \sigma_2 q_2), \quad (4)$$

$$v = \mu^{-1/2}(\sigma_2 q_1 + \sigma_1 q_2), \quad u = \mu_1^{-1/2} q_3,$$

where

$$\sigma_1 = 2^{-1/2}(1+K)^{1/2}, \quad \sigma_2 = 2^{-1/2}(1-K)^{1/2}$$

and

$$K = +\{1 - 8(\mu m)^{-1}(\lambda_1 - \lambda_2)^{-2} D^2\}^{1/2}.$$

It follows from Eqs. (3) and (4) that the displacement coordinates x'_i and y'_i are related to the normal coordinates q_i in the following manner:

$$x'_i = \sum_j l_{ij} q_j, \quad y'_i = \sum_j m_{ij} q_j, \quad (5)$$

where

$$l_{11} = l_{12} = m_{13} = 0, \quad l_{13} = (\mu/M)\mu_1^{-1/2},$$

$$l_{21} = -l_{31} = (2m)^{-1/2}\sigma_1, \quad -l_{22} = l_{32} = (2m)^{-1/2}\sigma_2,$$

$$l_{23} = -l_{33} = -(\mu/2m)\mu_1^{-1/2}, \quad m_{11} = (\mu/M)\mu^{-1/2}\sigma_2,$$

$$m_{12} = (\mu/M)\mu^{-1/2}\sigma_1, \quad m_{21} = m_{31} = -(\mu/2m)\mu^{-1/2}\sigma_2,$$

$$m_{22} = m_{32} = -(\mu/2m)\mu^{-1/2}\sigma_1,$$

$$m_{23} = -m_{33} = (\mu/2m)\mu_1^{-1/2} \cot \alpha_0.$$

The normal modes of oscillation are illustrated in Fig. 2 where $\tan \theta_1 = (\sigma_2/\sigma_1)(\mu/2m)^{1/2}$ and $\tan \theta_2 = (\sigma_1/\sigma_2)(\mu/2m)^{1/2}$.

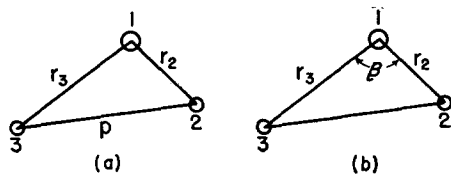


FIG. 3.

III. VALENCE- AND CENTRAL-FORCE COORDINATES

Two common types of force fields which are used in discussions of molecular vibrations are (a) the central-force field in which it is assumed that there are restoring forces acting essentially along the lines connecting the atomic nuclei and (b) the valence-force field in which it is assumed that there are restoring forces acting along the valence bonds and restoring torques tending to maintain the angles between valence bonds. Suitable coordinates for describing the central- and valence-force fields are illustrated in Figs. 3a and 3b, respectively, where $r_2 = r_0 + \delta r_2$, $r_3 = r_0 + \delta r_3$, $p = p_0 + \delta p$, and $\beta = \beta_0 + \delta \beta$, if r_0 , p_0 , and β_0 denote equilibrium values of the respective coordinates and δr_2 , δr_3 , δp , and $\delta \beta$ denote changes in the coordinates occurring during oscillation. Assuming small oscillations and using Eqs. (1) and (3), one can show that

$$\delta p = w, \quad \delta r_2 + \delta r_3 = w \sin \alpha_0 + 2v \cos \alpha_0,$$

$$\delta r_3 - \delta r_2 = 2u(\mu_1/\mu) \sin \alpha_0, \quad (6)$$

$$\delta \beta = (1/r_0)(w \cos \alpha_0 - 2v \sin \alpha_0).$$

It follows from Eqs. (4) and (6) that the normal coordinates are related to the central- and valence-force coordinates in the following manner:

$$q_1 = \beta_1(\delta r_2 + \delta r_3) + \beta_2 \delta p,$$

$$q_2 = \beta_3(\delta r_2 + \delta r_3) + \beta_4 \delta p, \quad (7)$$

$$q_3 = \beta_5(\delta r_3 - \delta r_2),$$

and

$$q_1 = \gamma_1(\delta r_2 + \delta r_3) + \gamma_2 r_0 \cos \alpha_0 \delta \beta,$$

$$q_2 = \gamma_3(\delta r_2 + \delta r_3) + \gamma_4 r_0 \cos \alpha_0 \delta \beta, \quad (8)$$

$$q_3 = \gamma_5(\delta r_3 - \delta r_2),$$

where

$$\beta_1 = [\mu^3 \sigma_2 / 2 \cos \alpha_0], \quad \beta_3 = [\mu^3 \sigma_1 / 2 \cos \alpha_0],$$

$$\gamma_2 = \beta_2 = (1/2)[(2m)^{1/2} \sigma_1 - \mu^{1/2} \sigma_2 \tan \alpha_0],$$

$$\gamma_4 = \beta_4 = (1/2)[-(2m)^{1/2} \sigma_2 - \mu^{1/2} \sigma_1 \tan \alpha_0],$$

$$\gamma_5 = \beta_5 = [\mu \mu_1^{-1/2} / 2 \sin \alpha_0],$$

$$\gamma_1 = \beta_1 + \beta_2 \sin \alpha_0, \quad \gamma_3 = \beta_3 + \beta_4 \sin \alpha_0.$$

It follows from (7) and (8) that the zero-order or harmonic potential function U_0 can be expressed in terms of the central-force coordinates as

$$U_0 = (1/2) \{ K_1(\delta r_2^2 + \delta r_3^2) + K_2 \delta p^2 + 2K_3 \delta p(\delta r_2 + \delta r_3) + 2K_4 \delta r_2 \delta r_3 \} \quad (9)$$

and in terms of the valence-force coordinates as

$$U_0 = (1/2) \{ c_1(\delta r_2^2 + \delta r_3^2) + c_2 r_0^2 \cos^2 \alpha_0 \delta \beta^2 + 2c_3 r_0 \cos \alpha_0 \delta \beta(\delta r_2 + \delta r_3) + 2c_4 \delta r_2 \delta r_3 \} \quad (10)$$

where

$$\begin{aligned} K_1 &= [(C/4 \cos^2 \alpha_0) + (\mu/\mu_1)^2 (B/4 \sin^2 \alpha_0)], \\ K_2 &= [A + (C/4) \tan^2 \alpha_0 - D \tan \alpha_0], \\ 2K_3 &= [- (C/2) \tan \alpha_0 + D] / \cos \alpha_0, \\ 2K_4 &= [(C/2 \cos^2 \alpha_0) - (\mu^2/\mu_1) (B/2 \sin^2 \alpha_0)]; \end{aligned}$$

and

$$\begin{aligned} c_1 &= A \sin^2 \alpha_0 + (C/4) \cos^2 \alpha_0 \\ &\quad + (\mu/\mu_1)^2 (B/4 \sin^2 \alpha_0) + D \sin \alpha_0 \cos \alpha_0, \\ c_2 &= K_2, \\ c_3 &= A \sin \alpha_0 - (C/4) \sin \alpha_0 \\ &\quad + (D/2 \cos \alpha_0) \cos 2\alpha_0, \\ c_4 &= A \sin^2 \alpha_0 + (C/4) \cos^2 \alpha_0 \\ &\quad - (\mu/\mu_1)^2 (B/4 \sin^2 \alpha_0) + D \sin \alpha_0 \cos \alpha_0. \end{aligned} \quad (11)$$

IV. CUBIC POTENTIAL FUNCTION

It can be shown^{1,5,8} from consideration of the symmetry properties of the normal modes that the first-order part of the anharmonic potential energy function contains the following terms cubic in the normal coordinates q_1 , q_2 , and q_3 :

$$U_1 = a_1 q_1^3 + a_2 q_2^3 + a_3 q_1^2 q_2 + a_4 q_1 q_2^2 + a_5 q_1 q_3^2 + a_6 q_2 q_3^2. \quad (12)$$

It follows from Eqs. (7), (8), and (12) that U_1 can be expressed in terms of the central-force coordinates as

$$\begin{aligned} U_1 &= L_1(\delta r_2^3 + \delta r_3^3) + L_2 \delta p^3 \\ &\quad + 3L_3(\delta r_2^2 \delta r_3 + \delta r_2 \delta r_3^2) + 6L_4 \delta r_2 \delta r_3 \delta p \\ &\quad + 3L_5(\delta r_2 + \delta r_3) \delta p^2 \\ &\quad + 3L_6(\delta r_2^2 + \delta r_3^2) \delta p, \end{aligned} \quad (13)$$

⁸ L. G. Bonner, Phys. Rev. **46**, 458 (1934).

and in terms of the valence-force coordinates as

$$\begin{aligned} U_1 &= l_1(\delta r_2^3 + \delta r_3^3) + l_2 r_0^3 \cos^3 \alpha_0 \delta \beta^3 \\ &\quad + 3l_3(\delta r_2^2 \delta r_3 + \delta r_2 \delta r_3^2) \\ &\quad + 6l_4 r_0 \cos \alpha_0 \delta r_2 \delta r_3 \delta \beta \\ &\quad + 3l_5 r_0^2 \cos^2 \alpha_0 (\delta r_2 + \delta r_3) \delta \beta^2 \\ &\quad + 3l_6 r_0 \cos \alpha_0 (\delta r_2^2 + \delta r_3^2) \delta \beta, \end{aligned} \quad (14)$$

where the L 's are defined as

$$\begin{aligned} L_1 &= (a_1 \beta_1 + a_3 \beta_3) \beta_1^2 + (a_2 \beta_3 + a_4 \beta_1) \beta_3^2 \\ &\quad + (a_5 \beta_1 + a_6 \beta_3) \beta_5^2, \\ L_2 &= (a_1 \beta_2 + a_3 \beta_4) \beta_2^2 + (a_2 \beta_4 + a_4 \beta_2) \beta_4^2, \\ L_3 &= L_1 - (4/3)(a_5 \beta_1 + a_6 \beta_3) \beta_5^2, \\ L_4 &= (a_1 \beta_1 + a_3 \beta_3) \beta_1 \beta_2 + (a_2 \beta_3 + a_4 \beta_1) \beta_3 \beta_4 \\ &\quad + (1/3)[(\beta_1 \beta_4 - \beta_2 \beta_3)(a_3 \beta_1 - a_4 \beta_3) \\ &\quad - (a_5 \beta_2 + a_6 \beta_4) \beta_5^2], \\ L_5 &= (a_1 \beta_1 + a_3 \beta_3) \beta_2^2 + (a_2 \beta_3 + a_4 \beta_1) \beta_4^2 \\ &\quad + (2/3)(a_3 \beta_2 - a_4 \beta_4)(\beta_1 \beta_4 - \beta_2 \beta_3), \\ L_6 &= L_4 + (2/3)(a_5 \beta_2 + a_6 \beta_4) \beta_5^2, \end{aligned}$$

and the definitions of the l 's can be obtained from those of the corresponding L 's simply by replacing the β 's by γ 's.

V. APPLICATION TO WATER VAPOR MOLECULE

The expressions developed in the preceding sections for the valence- and central-force coordinates are now applied to the case of the water vapor molecule. For this purpose we use the following data obtained by Darling and Dennison:¹

- Normal frequencies of H_2O :
 $\omega_1 = 3825.32 \text{ cm}^{-1}$, $\omega_2 = 1653.91 \text{ cm}^{-1}$,
 $\omega_3 = 3935.59 \text{ cm}^{-1}$.
- Normal frequencies of D_2O :
 $\omega'_1 = 2758.06 \text{ cm}^{-1}$, $\omega'_2 = 1210.25 \text{ cm}^{-1}$,
 $\omega'_3 = 2883.79 \text{ cm}^{-1}$.
- Equilibrium coordinates:
 $\beta_0 = 2\alpha_0 = 104^\circ 31'$, $r_0 = 0.9508 \text{ \AA}$.
- Cubic constants[†] in the potential energy:
 $a_1 = -3.615 \times 10^{49}$, $a_2 = 1.500 \times 10^{48}$,
 $a_3 = -7.391 \times 10^{46}$, $a_4 = 1.049 \times 10^{49}$,
 $a_5 = -1.050 \times 10^{50}$,
 $a_6 = -1.217 \times 10^{49} \text{ dynes per cm}^2 \text{ per g}^{\frac{1}{2}}$.

[†] The constants a_1 , a_2 , etc., of Eq. (12) can readily be obtained from the α_1 , α_2 , etc., of Darling and Dennison by means of the relations $a_1 = C\omega_1^{\frac{1}{2}}\alpha_1$, $a_2 = -C\omega_2^{\frac{1}{2}}\alpha_2$, $a_3 = -C\omega_1\omega_2^{\frac{1}{2}}\alpha_3$, $a_4 = C\omega_1^{\frac{1}{2}}\omega_2\alpha_4$, $a_5 = C\omega_1^{\frac{1}{2}}\omega_3\alpha_5$, $a_6 = -C\omega_2^{\frac{1}{2}}\omega_3\alpha_6$.

The above values for the normal frequencies of H_2O and D_2O lead to the following values of the generalized force constants defined in (3): $A=3.129 \times 10^5$, $C=7.197 \times 10^5$, and $D=3.161 \times 10^5$ dynes per cm. The coefficients σ_1 and σ_2 of (4) have for H_2O the values $\sigma_1=0.8101$, $\sigma_2=0.5863$, and for D_2O the values $\sigma_1'=0.7876$, $\sigma_2'=0.6161$. The angles describing the normal modes in Fig. 2 are for H_2O , $\theta_1=34^\circ 17' 30''$, $\theta_2=46^\circ 2'$ and for D_2O , $\theta_1'=34^\circ 57' 30''$, $\theta_2'=48^\circ 48' 30''$; if the vibrations of the hydrogen atoms were exactly parallel and perpendicular to the OH bonds in modes ω_1 and ω_2 , respectively, it would be true that $\theta_1=\theta_1'=37^\circ 44' 30''$ and $\theta_2=\theta_2'=52^\circ 15' 30''$.

The constants defined in (11) for the valence- and central-force forms of the zero-order potential function have the following values in units of 10^5 dynes per cm:

$$\begin{aligned} \text{Central, } K_1 &= 9.064, \quad K_2 = 2.049, \\ &K_3 = -1.215, \quad K_4 = 0.5398; \\ \text{Valence, } c_1 &= 8.423, \quad c_2 = 2.049, \quad c_3 = 0.4047, \\ &c_4 = -0.1015. \end{aligned}$$

It is interesting to compare the above values of the valence-force constants with the corresponding ones obtained by Ta-You Wu⁹ from earlier values of the normal frequencies: $c_1=8.23$, $c_2=2.00$, $c_3=0$, $c_4=-0.076$.

The constants occurring in the valence- and central-force forms of the first-order potential function given in (13) and (14) have the fol-

lowing values in units of 10^{13} dynes per cm per cm:

$$\begin{aligned} \text{Central, } L_1 &= -8.48, \quad L_2 = -0.258, \quad L_3 = 1.91, \\ &L_4 = -1.61, \quad L_5 = 0.825, \quad L_6 = -1.19; \\ \text{Valence, } l_1 &= -9.89, \quad l_2 = -0.258, \quad l_3 = -0.163, \\ &l_4 = -0.510, \quad l_5 = 0.624, \quad l_6 = -0.084. \end{aligned}$$

The constants in the valence- or central-force forms of the second-order or quartic part of the anharmonic potential function cannot be computed from the data available. It can easily be shown that such a calculation would require knowledge of all the constants in the normal-coordinate form of the second-order potential function. The study of Darling and Dennison, which was based on a second-order calculation of the vibration-rotation energies of the bent XY_2 molecule, yielded the values of only six of the nine constants in the second-order function.

VI. CONCLUSIONS

These results show that the cross-product terms in the generalized valence-force form of both the zero-order and the first-order potential function are smaller than in the generalized central-force form, and hence the usual simplified valence-force potential function should give a better approximation to the true potential of the water vapor molecule than would the simplified central-force form. A very good three-term approximation to the zero-order potential can be obtained by neglecting the constant c_4 in the valence-force form.

A possible type of approximation to the first-order potential function for water vapor is suggested by the values of the constants in the valence-force form. This approximation would be

$$\begin{aligned} U_1 &= l_1(\delta r_2^3 + \delta r_3^3) + 6l_4 r_0 \cos \alpha_0 \delta r_2 \delta r_3 \delta \beta \\ &\quad + 3l_5 r_0^2 \cos^2 \alpha_0 (\delta r_2 + \delta r_3) \delta \beta^2. \end{aligned}$$

⁹ Ta-You Wu, *Vibrational Spectra and Structure of Polyatomic Molecules* (Prentice-Hall, New York, 1940).