Estimation of Anharmonic Potential Constants. II. Bent XY_2 Molecules

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In the preceding paper, Part I,[1] the anharmonic potential constants of the linear XY_2 molecules have been estimated on the basis of a simple potential function. That procedure will here be extended to the bent XY_2 molecules, for which previous theoretical studies of the anharmonic constants[2-5] have been limited to H_2O and D_2O. The purpose of the present study is to set up a convenient method for a quantitative or at least a semi-quantitative prediction of the anharmonic constants in order to achieve a better understanding of the physical significance of these constants. It is also intended to seek for a simple and plausible representation of the anharmonic force field of polyatomic molecules.

The estimation of anharmonic constants is more complicated in this case than in the case of the linear XY_2 molecule, because the coordinate transformation depends on the off-diagonal elements of the $\boldsymbol{L}$ matrix (two-dimensional in this case); moreover, the potential constants which depend on the odd power of the angular displacement do not vanish by symmetry requirement, while they do in the case of linear XY_2. These circumstances, however, do not seriously disturb the present analysis; in addition, the quadratic force constants for most of the bent XY_2 molecules are generally much better known than those for more complex molecules.

The importance of the bent XY_2 molecules for the study of anharmonicity is twofold. First, relatively abundant, although far from complete, experimental data have been reported concerning their α and x values, especially for those of H_2O, D_2O, and SO_2, and further information will be obtained in the near future. Secondly, the bent XY_2 molecule is one of the few simple systems for which the cubic and most of the quartic potential constants can be determined uniquely, provided all α and x values are known. The following sections will, therefore, present a general formulation necessary for the analysis, a formulation by means of which the "anharmonic constants" of the potential function expressed in the normal-coordinate system can be transformed into the "higher-order constants" in the internal-coordinate system. A simple method for estimating the anharmonic constants will then be presented on the basis of an examination of the physical significance of these higher-order potential constants.

Expansion of Internal Coordinates

The internal coordinates are expanded in terms of the normal coordinates by the method discussed in Ref. 5. The displacements of the X-Y_i $(i=1,2)$ bond length, Δr_i, and that of the Y_1-X-Y_2 angle, $\Delta\alpha$, from their equilibrium values are first expanded in terms of the Cartesian displacement coordinates shown in Fig. 1; Δz_i and Δx_i are taken to be the projections of the instantaneous displacement of the Y_i atom with respect to the X atom along and perpendicular to the equilibrium direction of the X-Y_i bond respectively. The out-of-plane displacements, Δy_i, are of course zero. It is shown in Eq. 14 of Ref. 5 that:

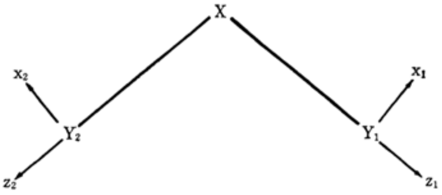

Fig. 1. Cartesian coordinates for the bent XY_2 molecule. The z_i axis ($i=1$ or 2) is taken in the direction of the bond X-Y_i at their equilibrium positions, and the x_i axis is taken on the molecular plane and perpendicular to the z_i axis outwards. The displacement of the Y_i atom relative to the X atom is described in the x_i, z_i coordinates.

$$\left.\begin{aligned} \Delta r_i &= \Delta z_i + \Delta x_i^2/2r_e - \Delta z_i \Delta x_i^2/2r_e^2 + \cdots \\ r_e\Delta\alpha &= \Delta x_1 + \Delta x_2 - (\Delta x_1\Delta z_1 + \Delta x_2\Delta z_2)/r_e \\ &\quad + [\Delta x_1\Delta z_1^2 + \Delta x_2\Delta z_2^2 \\ &\quad - \frac{1}{3}(\Delta x_1^3 + \Delta x_2^3)]/r_e^2 + \cdots \end{aligned}\right\} \qquad (1)$$

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[1] K. Kuchitsu and Y. Morino, This Bulletin, **38**, 805 (1965).

[2] O. Redlich, *J. Chem. Phys.*, **9**, 298 (1941).

[3] J. Pliva, *Collection Czechoslov. Chem. Communs.*, **23**, 777 (1958).

[4] D. R. Herschbach and V. W. Laurie, *J. Chem. Phys.*, **35**, 458 (1961).

[5] K. Kuchitsu and L. S. Bartell, ibid., **36**, 2460 (1962).

TABLE I. MATRIX REPRESENTATION OF CUBIC POTENTIAL CONSTANTS

$$\begin{bmatrix} k_{111}/h_{111} \\ k_{122}/h_{122} \\ k_{133}/h_{133} \\ k_{211}/h_{211} \\ k_{222}/h_{222} \\ k_{233}/h_{233} \end{bmatrix} = \begin{bmatrix} \alpha^2\lambda & \alpha^2\lambda & \alpha(\alpha^2-2\lambda^2) & \alpha^2\lambda \\ \beta(2\alpha\mu+\beta\lambda) & \beta(2\alpha\mu+\beta\lambda) & 3\alpha\beta^2-2\alpha\mu^2-4\beta\lambda\mu & \beta(2\alpha\mu+\beta\lambda) \\ \gamma(\gamma\lambda+2\alpha\nu) & \gamma(\gamma\lambda-2\alpha\nu) & \gamma(\alpha\gamma-2\lambda\nu) & \alpha\gamma\nu \\ \alpha(\alpha\mu+2\beta\lambda) & \alpha(\alpha\mu+2\beta\lambda) & 3\alpha^2\beta-2\beta\lambda^2-4\alpha\lambda\mu & \alpha(\alpha\mu+2\beta\lambda) \\ \beta^2\mu & \beta^2\mu & \beta(\beta^2-2\mu^2) & \beta^2\mu \\ \gamma(\gamma\mu+2\beta\nu) & \gamma(\gamma\mu-2\beta\nu) & \gamma(\beta\gamma-2\mu\nu) & \beta\gamma\nu \end{bmatrix} \begin{bmatrix} f_r/r_e \\ f_{r'}/r_e \\ 2f_{r\alpha}/r_e \\ -4f_\alpha/r_e \end{bmatrix}$$

$$+ \begin{bmatrix} \lambda^3 & \lambda^3 & \alpha\lambda^2 & \alpha\lambda^2 & \alpha^2\lambda & \alpha^3 \\ 3\lambda\mu^2 & 3\lambda\mu^2 & \mu(\alpha\mu+2\beta\lambda) & \mu(\alpha\mu+2\beta\lambda) & \beta(2\alpha\mu+\beta\lambda) & 3\alpha\beta^2 \\ 3\lambda\nu^2 & -\lambda\nu^2 & \alpha\nu^2 & -\alpha\nu^2 & 0 & 0 \\ 3\lambda^2\mu & 3\lambda^2\mu & \lambda(2\alpha\mu+\beta\lambda) & \lambda(2\alpha\mu+\beta\lambda) & \alpha(\alpha\mu+2\beta\lambda) & 3\alpha^2\beta \\ \mu^3 & \mu^3 & \beta\mu^2 & \beta\mu^2 & \beta^2\mu & \beta^3 \\ 3\mu\nu^2 & -\mu\nu^2 & \beta\nu^2 & -\beta\nu^2 & 0 & 0 \end{bmatrix} \begin{bmatrix} 2f_{rrr}/r_e \\ 2f_{rrr'}/r_e \\ 4f_{rr\alpha}/r_e \\ 2f_{rr'\alpha}/r_e \\ 8f_{r\alpha\alpha}/r_e \\ 8f_{\alpha\alpha\alpha}/r_e \end{bmatrix}$$

Units: k : cm^{-1}; $h_{ijj}=N^{3/2}h^{1/2}/8\pi^3c^{5/2}\omega_i^{1/2}\omega_j$; α, β, γ, λ, μ, ν : a. m. u.
f : dyne/cm.; r_e : cm.

On the other hand, the following linear relations exist between the Cartesian and normal coordinates, Q:

$$\left.\begin{aligned} \Delta x_i &= \alpha Q_1+\beta Q_2\pm\gamma Q_3 \\ \Delta z_i &= \lambda Q_1+\mu Q_2\pm\nu Q_3 \end{aligned}\right\} \quad (2)$$

where the positive and negative signs of γ and ν apply to $i=1$ and 2 respectively, and where the coefficients are related to the $\boldsymbol{L}$ and the $\boldsymbol{G}$ matrices as follows:

$$\left.\begin{aligned} \alpha&=\frac{1}{2}L_{21}, \quad \beta=\frac{1}{2}L_{22}, \quad \gamma=-G_{12}/2L_{33} \\ \lambda&=\frac{1}{\sqrt{2}}L_{11}, \quad \mu=\frac{1}{\sqrt{2}}L_{12}, \quad \nu=\frac{1}{\sqrt{2}}L_{33} \end{aligned}\right\} \quad (3)$$

The desired expansion of the internal coordinates is, therefore, straightforward.

Potential Function

The vibrational potential function of the bent XY_2 molecule can be expanded in terms of the internal coordinates in the following way:

$$\begin{aligned} V=&\frac{1}{2}f_r(\Delta r_1^2+\Delta r_2^2)+f_{r'}\Delta r_1\Delta r_2 \\ &+f_{r\alpha}(\Delta r_1+\Delta r_2)r_e\Delta\alpha+\frac{1}{2}f_\alpha r_e^2\Delta\alpha^2 \\ &+\frac{1}{r_e}[f_{rrr}(\Delta r_1^3+\Delta r_2^3)+f_{rrr'}(\Delta r_1+\Delta r_2) \\ &\times\Delta r_1\Delta r_2+f_{rr\alpha}(\Delta r_1^2+\Delta r_2^2)r_e\Delta\alpha \\ &+f_{rr'\alpha}\Delta r_1\Delta r_2 r_e\Delta\alpha+f_{r\alpha\alpha}(\Delta r_1+\Delta r_2) \\ &\times r_e^2\Delta\alpha^2+f_{\alpha\alpha\alpha}r_e^3\Delta\alpha^3] \\ &+\frac{1}{r_e^2}[f_{rrrr}(\Delta r_1^4+\Delta r_2^4)+f_{rrrr'} \\ &\times(\Delta r_1^2+\Delta r_2^2)\Delta r_1\Delta r_2+f_{rrr'r'}\Delta r_1^2\Delta r_2^2 \\ &+f_{rrr\alpha}(\Delta r_1^3+\Delta r_2^3)r_e\Delta\alpha \\ &+f_{rrr'\alpha}(\Delta r_1+\Delta r_2)\Delta r_1\Delta r_2 r_e\Delta\alpha \\ &+f_{rr\alpha\alpha}(\Delta r_1^2+\Delta r_2^2)r_e^2\Delta\alpha^2 \\ &+f_{rr'\alpha\alpha}\Delta r_1\Delta r_2 r_e^2\Delta\alpha^2 \\ &+f_{r\alpha\alpha\alpha}(\Delta r_1+\Delta r_2)r_e^3\Delta\alpha^3+f_{\alpha\alpha\alpha\alpha}r_e^4\Delta\alpha^4] \\ &+\cdots \end{aligned} \quad (4)$$

The quadratic force constants, f_r, $f_{r'}$, $f_{r\alpha}$, and f_α, can be determined uniquely if the elements of the $\boldsymbol{F}$ matrix,

$$\left.\begin{aligned} &f_r=\frac{1}{2}(F_{11}+F_{33}) \qquad f_{r'}=\frac{1}{2}(F_{11}-F_{33}) \\ &f_{r\alpha}=\frac{1}{\sqrt{2}}F_{12} \quad \text{and} \quad f_\alpha=F_{22} \end{aligned}\right\} \quad (5)$$

are known.

Upon replacing Δr_i and $r_e\Delta\alpha$ by Δz_i and Δx_i and the latter by Q, by the use of Eqs. 1 and 2, the cubic and quartic constants of the potential function in terms of the dimensionless normal coordinates⁶⁾:

$$\left.\begin{aligned} V/hc=&\frac{1}{2}(\omega_1q_1^2+\omega_2q_2^2+\omega_3q_3^2) \\ &+k_{111}q_1^3+k_{122}q_1q_2^2+k_{133}q_1q_3^2 \\ &+k_{211}q_2q_1^2+k_{222}q_2^3+k_{233}q_2q_3^2 \\ &+k_{1111}q_1^4+k_{1122}q_1^2q_2^2+k_{1133}q_1^2q_3^2 \\ &k_{2222}q_2^4+k_{2233}q_2^2q_3^2+k_{3333}q_3^4 \end{aligned}\right\} \quad (6)$$

where

$$q_s=2\pi(c\omega_s/h)^{1/2}Q_s$$

can be expressed in the matrix form shown in Tables I and II.*¹ On the other hand, the

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*¹ Similar expressions for other nonvanishing quartic constants, k_{1112}, k_{1222}, and k_{1233}, are not listed in Table II, since they are not included in x as far as the ordinary second-order perturbation theory is concerned⁶⁻⁸⁾ and, hence, remain unknown. The orders of magnitude of k_{1112}, k_{1222}, and k_{1233} may, however, be estimated by an extension of the method given below, if such an estimate is necessary for a discussion of higher-order interactions.

TABLE II. MATRIX REPRESENTATION OF QUARTIC POTENTIAL CONSTANTS

$$
\begin{pmatrix} k_{1111}/h_{1111} \\ k_{1122}/h_{1122} \\ k_{1133}/h_{1133} \\ k_{2222}/h_{2222} \\ k_{2233}/h_{2233} \\ k_{3333}/h_{3333} \end{pmatrix}
=
\begin{pmatrix}
\alpha^2(\alpha^2-4\lambda^2) & \alpha^2(\alpha^2-4\lambda^2) & 2\alpha\lambda(\lambda^2-\frac{4}{3}\alpha^2) & \alpha^2(3\lambda^2-\frac{2}{3}\alpha^2) \\
\begin{array}{l}6\alpha^2\beta^2-4\alpha^2\mu^2\\-4\beta^2\lambda^2-16\alpha\beta\lambda\mu\end{array} & \begin{array}{l}6\alpha^2\beta^2-4\alpha^2\mu^2\\-4\beta^2\lambda^2-16\alpha\beta\lambda\mu\end{array} & 2(3\lambda\mu-4\alpha\beta)(\alpha\mu+\beta\lambda) & \begin{array}{l}3\alpha^2\mu^2+3\beta^2\lambda^2\\+12\alpha\beta\lambda\mu-4\alpha^2\beta^2\end{array} \\
\begin{array}{l}6\alpha^2\gamma^2-4\alpha^2\nu^2\\-4\gamma^2\lambda^2-16\alpha\gamma\lambda\nu\end{array} & \begin{array}{l}4\alpha^2\nu^2-4\gamma^2\lambda^2\\-2\alpha^2\gamma^2\end{array} & \begin{array}{l}2\alpha\lambda\nu^2-3\alpha^2\gamma\nu\\+4\gamma\lambda^2\nu-4\alpha\gamma^2\lambda\end{array} & \begin{array}{l}2\alpha^2(\nu^2-\gamma^2)\\+6\alpha\gamma\lambda\nu\end{array} \\
\beta^2(\beta^2-4\mu^2) & \beta^2(\beta^2-4\mu^2) & 2\beta\mu(\mu^2-\frac{4}{3}\beta^2) & \beta^2(3\mu^2-\frac{2}{3}\beta^2) \\
\begin{array}{l}6\beta^2\gamma^2-4\beta^2\nu^2\\-4\gamma^2\mu^2-16\beta\gamma\mu\nu\end{array} & \begin{array}{l}4\beta^2\nu^2-4\gamma^2\mu^2\\-2\beta^2\gamma^2\end{array} & \begin{array}{l}2\beta\mu\nu^2-3\beta^2\gamma\nu\\+4\gamma\mu^2\nu-4\beta\gamma^2\mu\end{array} & \begin{array}{l}2\beta^2(\nu^2-\gamma^2)\\+6\beta\gamma\mu\nu\end{array} \\
\gamma^2(\gamma^2-4\nu^2) & \gamma^2(\gamma^2+4\nu^2) & -\gamma^3\nu & \gamma^2\nu^2
\end{pmatrix}
\begin{pmatrix} f_r/4r_e^2 \\ f_{r'}/4r_e^2 \\ 2f_{r\alpha}/r_e^2 \\ 2f_\alpha/r_e^2 \end{pmatrix}
$$

$$
+\begin{pmatrix}
\alpha^2\lambda^2 & 3\alpha^2\lambda^2 & \alpha\lambda(\alpha^2-\lambda^2) & \alpha\lambda(\alpha^2-\lambda^2) & \alpha^2(\alpha^2-4\lambda^2) & \alpha^3\lambda \\
\alpha^2\mu^2+\beta^2\lambda^2+4\alpha\beta\lambda\mu & \begin{array}{l}3\alpha^2\mu^2+3\beta^2\lambda^2\\+12\alpha\beta\lambda\mu\end{array} & \begin{array}{l}3(\alpha\beta-\lambda\mu)\\(\alpha\mu+\beta\lambda)\end{array} & \begin{array}{l}3(\alpha\beta-\lambda\mu)\\(\alpha\mu+\beta\lambda)\end{array} & \begin{array}{l}6\alpha^2\beta^2-4\alpha^2\mu^2\\-4\beta^2\lambda^2-16\alpha\beta\lambda\mu\end{array} & 3\alpha\beta(\alpha\mu+\beta\lambda) \\
\alpha^2\nu^2+\gamma^2\lambda^2+4\alpha\gamma\lambda\nu & \begin{array}{l}3\gamma^2\lambda^2-\alpha^2\nu^2\\-4\alpha\gamma\lambda\nu\end{array} & \begin{array}{l}\alpha\gamma(\gamma\lambda+2\alpha\nu)\\-\gamma\nu(\gamma\lambda+\alpha\nu)\end{array} & \begin{array}{l}\alpha\gamma(\gamma\lambda-2\alpha\nu)\\-\lambda\nu(\gamma\lambda-\alpha\nu)\end{array} & \alpha^2\gamma^2-4\alpha\gamma\lambda\nu & \alpha^2\gamma\nu \\
\beta^2\mu^2 & 3\beta^2\mu^2 & \beta\mu(\beta^2-\mu^2) & \beta\mu(\beta^2-\mu^2) & \beta^2(\beta^2-4\mu^2) & \beta^3\mu \\
\beta^2\nu^2+\gamma^2\mu^2+4\beta\gamma\mu\nu & \begin{array}{l}3\gamma^2\mu^2-\beta^2\nu^2\\-4\beta\gamma\mu\nu\end{array} & \begin{array}{l}\beta\gamma(\gamma\mu+2\beta\nu)\\-\mu\nu(\gamma\mu+\beta\nu)\end{array} & \begin{array}{l}\beta\gamma(\gamma\mu-2\beta\nu)\\-\mu\nu(\gamma\mu-\beta\nu)\end{array} & \beta^2\gamma^2-4\beta\gamma\mu\nu & \beta^2\gamma\nu \\
\gamma^2\nu^2 & -\gamma^2\nu^2 & -\gamma\nu^3 & \gamma\nu^3 & 0 & 0
\end{pmatrix}
\begin{pmatrix} 3f_{rrr}/r_e^2 \\ f_{rrr'}/r_e^2 \\ 4f_{rr\alpha}/r_e^2 \\ 2f_{rr'\alpha}/r_e^2 \\ 4f_{r\alpha\alpha}/r_e^2 \\ -24f_{\alpha\alpha\alpha}/r_e^2 \end{pmatrix}
$$

$$
+\begin{pmatrix}
\lambda^4 & \lambda^4 & \lambda^4 & \alpha^2\lambda^2 & \alpha^2\lambda^2 & \alpha^4 & \alpha\lambda^3 & \alpha\lambda^3 & \alpha^3\lambda \\
6\lambda^2\mu^2 & 6\lambda^2\mu^2 & 6\lambda^2\mu^2 & \begin{array}{l}\alpha^2\mu^2+\beta^2\lambda^2\\+4\alpha\beta\lambda\mu\end{array} & \begin{array}{l}\alpha^2\mu^2+\beta^2\lambda^2\\+4\alpha\beta\lambda\mu\end{array} & 6\alpha^2\beta^2 & 3\lambda\mu(\alpha\mu+\beta\lambda) & 3\lambda\mu(\alpha\mu+\beta\lambda) & 3\alpha\beta(\alpha\mu+\beta\lambda) \\
6\lambda^2\nu^2 & 0 & -2\lambda^2\nu^2 & \alpha^2\nu^2 & -\alpha^2\nu^2 & 0 & 3\alpha\lambda\nu^2 & -\alpha\lambda\nu^2 & 0 \\
\mu^4 & \mu^4 & \mu^4 & \beta^2\mu^2 & \beta^2\mu^2 & \beta^4 & \beta\mu^3 & \beta\mu^3 & \beta^3\mu \\
6\mu^2\nu^2 & 0 & -2\mu^2\nu^2 & \beta^2\nu^2 & -\beta^2\nu^2 & 0 & 3\beta\mu\nu^2 & -\beta\mu\nu^2 & 0 \\
\nu^4 & -\nu^4 & \nu^4 & 0 & 0 & 0 & 0 & 0 & 0
\end{pmatrix}
\begin{pmatrix} 2f_{rrrr}/r_e^2 \\ 2f_{rrrr'}/r_e^2 \\ 2f_{rrr'r'}/r_e^2 \\ 8f_{rr\alpha\alpha}/r_e^2 \\ 4f_{rr'\alpha\alpha}/r_e^2 \\ 16f_{\alpha\alpha\alpha\alpha}/r_e^2 \\ 4f_{rrr\alpha}/r_e^2 \\ 4f_{rrr'\alpha}/r_e^2 \\ 16f_{r\alpha\alpha\alpha}/r_e^2 \end{pmatrix}
$$

Unit: k: cm^{-1}; $h_{iijj}=N^2h/16\pi^4c^3\omega_i\omega_j$; α, β, γ, λ, μ, ν: a. m. u.; f: dyne/cm.; r_e: cm.

TABLE III. VIBRATIONAL FREQUENCIES OF BENT XY_2 (in cm^{-1})

	H_2O	D_2O	H_2S	D_2S[a]	H_2Se[a]	D_2Se[a]	SO_2	ClO_2	$^{14}NO_2$	$^{15}NO_2$
ω_1	3832.17	2763.80	2721.92	1950	2435	1732	1167.60	962.8	1357.8	1342.5
ω_2	1648.47	1206.39	1214.51	874	1054	750	526.27	455.4	756.8	747.1
ω_3	3942.53	2888.78	2733.36	1964	2448	1743	1380.91	1128.2	1665.5	1628.0
Ref.	9	9	10	11	12	12	13	14	15	15

a) Normal frequencies estimated in the present study on the basis of the fundamental frequencies listed in the references.

TABLE IV. QUADRATIC FORCE CONSTANTS (in md./Å) AND EQUILIBRIUM STRUCTURE OF BENT XY_2

	f_r	$f_{r'}$	$f_{r\alpha}$	f_α	r_e (Å)	α_e	Ref.
H_2O D_2O	8.454	−0.101	0.228	0.761	0.9572_1	104°31.$_3$′	5, 9
H_2S[a] D_2S	4.284	−0.012	0.101	0.429	1.336[b]	92°12′	10
H_2Se[a] D_2Se	3.493	−0.020	0.055	0.327	1.460_5	90°55′	16
SO_2	10.332	0.081	0.227	0.815	1.4308	119°19′	8
ClO_2	7.018	−0.170	0.006	0.651	1.473 (r_s)	117°36′ (α_s)	17, 18
NO_2	11.043	2.140	0.481	1.109	1.1934 (r_s)	134°4′ (α_s)	19

a) Calculated in the present study from the data given in Table III.

b) Calculated from the equilibrium moments of inertia listed in Eq. 14 of Allen and Plyler's paper.[10] The r_e distance of H–S given in their paper, 1.328 Å, seems to be in error.

relations between the anharmonic constants and the α and x values have been derived by Darling and Dennison[6−8] as follows:

$$\left.\begin{aligned}
\alpha_1^A&=A_1+3a_1k_{111}+a_2k_{211}\\
\alpha_2^A&=A_2+a_1k_{122}+3a_2k_{222}\\
\alpha_3^A&=A_3+a_1k_{133}+a_2k_{233}\\
\alpha_1^B&=B_1+3b_1k_{111}+b_2k_{211}\\
\alpha_2^B&=B_2+b_1k_{122}+3b_2k_{222}\\
\alpha_3^B&=B_3+b_1k_{133}+b_2k_{233}\\
\alpha_1^C&=C_1+3c_1k_{111}+c_2k_{211}\\
\alpha_2^C&=C_2+c_1k_{122}+3c_2k_{222}\\
\alpha_3^C&=C_3+c_1k_{133}+c_2k_{233}
\end{aligned}\right\}\qquad(7)$$

and:

$$\left.\begin{aligned}
x_{11}&=\frac{3}{2}k_{1111}-\frac{15k_{111}^2}{4\omega_1}-\frac{k_{211}^2(8\omega_1^2-3\omega_2^2)}{4\omega_2(4\omega_1^2-\omega_2^2)}\\
x_{22}&=\frac{3}{2}k_{2222}-\frac{15k_{222}^2}{4\omega_2}-\frac{k_{122}^2(8\omega_2^2-3\omega_1^2)}{4\omega_1(4\omega_2^2-\omega_1^2)}\\
x_{33}&=\frac{3}{2}k_{3333}-\frac{k_{133}^2(8\omega_3^2-3\omega_1^2)}{4\omega_1(4\omega_3^2-\omega_1^2)}\\
&\quad-\frac{k_{233}^2(8\omega_3^2-3\omega_2^2)}{4\omega_2(4\omega_3^2-\omega_2^2)}\\
x_{12}&=k_{1122}-\frac{3k_{111}k_{122}}{\omega_1}-\frac{3k_{211}k_{222}}{\omega_2}\\
&\quad-\frac{2k_{211}^2\omega_1}{4\omega_1^2-\omega_2^2}-\frac{2k_{122}^2\omega_2}{4\omega_2^2-\omega_1^2}\\
x_{13}&=k_{1133}-\frac{3k_{111}k_{133}}{\omega_1}-\frac{k_{211}k_{233}}{\omega_2}\\
&\quad-\frac{2k_{133}^2\omega_3}{4\omega_3^2-\omega_1^2}+C_e\zeta_{13}^2\left(\frac{\omega_3}{\omega_1}+\frac{\omega_1}{\omega_3}\right)\\
x_{23}&=k_{2233}-\frac{k_{122}k_{133}}{\omega_1}-\frac{3k_{222}k_{233}}{\omega_2}\\
&\quad-\frac{2k_{233}^2\omega_3}{4\omega_3^2-\omega_2^2}+C_e\zeta_{23}^2\left(\frac{\omega_3}{\omega_2}+\frac{\omega_2}{\omega_3}\right)
\end{aligned}\right\}\qquad(8)$$

where[*2]

$$A_1=-\frac{6A_e^2}{\omega_1}\sin^2\Gamma,\quad a_1=-\left(\frac{2A_e}{\omega_1}\right)^{3/2}\sin\Gamma$$

$$A_2=-\frac{6A_e^2}{\omega_2}\cos^2\Gamma,\quad a_2=-\left(\frac{2A_e}{\omega_2}\right)^{3/2}\cos\Gamma$$

$$A_3=-\frac{6A_eC_e}{\omega_3}$$

$$B_1=-\frac{6B_e^2}{\omega_1}\cos^2\Gamma,\quad b_1=-\left(\frac{2B_e}{\omega_1}\right)^{3/2}\cos\Gamma$$

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6) H. H. Nielsen, *Revs. Mod. Phys.*, 23, 90 (1951).

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

8) Y. Morino, Y. Kikuchi, S. Saito and E. Hirota, *J. Mol. Spectry.*, 13, 95 (1964).

[*2] In Refs. 7 and 8, $\sin\Gamma$ is denoted as $\sin\gamma$ and $\cos\Gamma$ as $\cos\gamma$. The symbol Γ is used here in order to avoid confusion.

TABLE V. COEFFICIENTS OF THE CARTESIAN DISPLACEMENT COORDINATES[a] (in a.m.u.)

	α	β	γ	λ	μ	ν	$\sin\Gamma$	ζ_{23}^2
H_2O	−0.0019	0.7316	0.0414	0.7197	−0.0395	0.7316	0.5913	1.0000
D_2O	−0.0348	0.5349	0.0564	0.5207	−0.0227	0.5360	0.6210	0.9958
H_2S	0.0149	0.7155	0.0218	0.7139	−0.0366	0.7156	0.6670	0.9996
D_2S	−0.0077	0.5141	0.0303	0.5125	−0.0227	0.5142	0.6828	0.9998
H_2Se	0.0168	0.7086	0.0089	0.7082	−0.0257	0.7088	0.6797	0.9994
D_2Se	0.0043	0.5046	0.0125	0.5041	−0.0169	0.5046	0.6863	0.9999
SO_2	−0.0717	0.2228	0.0577	0.1974	0.0030	0.2340	0.6463	0.9061
ClO_2	−0.0824	0.2130	0.0555	0.1966	0.0166	0.2284	0.7046	0.8697
$^{14}NO_2$	−0.1410	0.2681	0.0847	0.2049	0.0121	0.3029	0.6548	0.7833
$^{15}NO_2$	−0.1307	0.2658	0.0808	0.2032	0.0098	0.2962	0.6379	0.8054

a) See Eqs. 3 and 7.

TABLE VI. ANHARMONIC POTENTIAL CONSTANTS[a] (in cm⁻¹)

cubic[b]	k_{111}	k_{122}	k_{133}	k_{211}	k_{222}	k_{233}
H_2O	−319.4±3.3	255.4±31.4	−921.7± 1.5	39.6±2.4	−61.9±2.5	147.3±0.4
D_2O	−193.3±2.1	191.1±24.8	−632.1±18.0	7.6±1.6	−33.4±2.1	93.7±2.1
H_2S	−194.9±3.6	102.7±13.2	−587.5± 2.7	−18.3±3.3	−1.0±1.4	13.9±0.8
H_2Se	−165.4±0.3	79.2± 1.5	−478.4±17.8	10.9±0.3	1.1±0.2	32.5±5.3
D_2Se	−100.8±2.6	28.3± 2.7	−279.2±14.1	1.8±2.3	−4.6±0.3	21.5±4.2
SO_2	−44.3±0.4	12.0± 0.8	−159.2± 0.1	−19.0±0.3	−6.9±0.1	4.6±0.1
quartic[c]	k_{1111}	k_{1122}	k_{1133}	k_{2222}	k_{2233}	k_{3333}
H_2O	38.5±1.4	−140.4±15.9	209.2±2.5	11.2±4.1	−122.2±7.6	35.0±0.2
D_2O	18.8±0.7	−96.8±13.6	135.7±6.5	9.9±3.6	−74.3±5.8	26.0±2.3
H_2S	18.2±1.3	−58.6± 5.2	115.2±2.5	0.7±1.2	−56.3±2.9	19.4±0.3
SO_2	1.77±0.08	−3.09±0.12	15.36±0.17	−1.62±0.02	−6.51±0.11	3.01±0.01

a) Derived from the observed α and x values listed in Tables XII and XIII by using Eqs. 7 and 8.

b) Quoted uncertainties represent the standard errors estimated by a least-squares fit of the observed α values to Eq. 7 (with equal statistical weights for α^A, α^B, and α^C). Because of the inconsistencies among α^A, α^B, and α^C, larger uncertainties have to be assigned to some of the k_{122} and k_{133} constants.

c) The standard errors, which are propagated from those of the cubic constants by the application of Eq. 8, are taken as uncertainties. They are probably somewhat underestimated, because the errors involved in the experimental x values, which are not given in the original references, are left out of consideration.

TABLE VII. HIGHER-ORDER POTENTIAL CONSTANTS[a] (in md./Å)

	f_{rrr}	$f_{rrr'}$	$f_{rr\alpha}$	$f_{rr'\alpha}$	$f_{r\alpha\alpha}$	$f_{\alpha\alpha\alpha}$
H_2O	−9.55±0.06	−0.32±0.16	0.16±0.03	−0.66±0.01	0.15±0.20	−0.14±0.01
D_2O	−10.18±0.45	0.48±0.47	0.22±0.06	−0.46±0.04	0.31±0.26	−0.13±0.02
H_2S	−5.16±0.06	0.03±0.15	−0.40±0.03	−0.15±0.02	−0.04±0.08	−0.01±0.01
H_2Se	−4.04±0.22	−0.09±0.22	−0.03±0.05	−0.13±0.02	−0.06±0.01	−0.00±0.01
D_2Se	−3.97±0.30	−0·23±0.34	−0.04±0.07	−0.20±0.03	−0.14±0.03	−0.02±0.01
SO_2	−16.95±0.08	−0.82±0.23	−0.68±0.05	−0.76±0.03	−0.63±0.05	−0.20±0.01
	f_{rrrr}	$f_{rrrr'}$	$f_{rrr'r'}$	$f_{rr\alpha\alpha}$	$f_{rr'\alpha\alpha}$	$f_{\alpha\alpha\alpha\alpha}$
H_2O	15.4±0.3	0.8±0.6	1.3±1.1	−1.7±0.8	−0.5±1.7	0.0±0.2
D_2O	18.5±1.5	−2.8±2.0	0.1±4.0	−2.7±1.4	−1.5±2.8	0.0±0.2
H_2S	8.5±0.3	−0.2±0.6	−0.3±1.1	−0.7±0.4	−0.3±0.8	−0.0±0.2
SO_2	33.8±1.2	−2.2±2.6	−0.3±4.3	0.7±3.2	2.8±6.2	−0.3±0.1

a) Calculated from Table VI by the matrix equations given in Tables I and II with the assumption that the contributions from the $f_{rrr\alpha}$, $f_{rr'r'\alpha}$, and $f_{r\alpha\alpha\alpha}$ constants to the quartic constants listed in Table VI are zero. The uncertainties are represented somewhat arbitrarily by twice the standard errors estimated from those of the anharmonic constants given in Table VI. The uncertainties introduced by the above assumption are included in the uncertainties of the fourth-order constants.

TABLE VIII. ANALYSIS OF THE CUBIC CONSTANTS INTO COMPONENT TERMS (in cm^{-1})

H_2O	k_{111}	k_{122}	k_{133}	k_{211}	k_{222}	k_{233}
f_r	0	328.8	0.4	−1.1	−27.5	24.0
$f_{r'}$	0	−3.9	0	0	0.3	0.3
$f_{r\alpha}$	0	3.7	−0.8	−22.8	27.3	0.1
f_α	0	−118.3	0	0	9.9	−4.3
f_{rrr}	−309.2	−6.5	−931.5	77.6	0.2	77.9
$f_{rrr'}$	−10.3	−0.2	10.3	2.6	0	−0.9
$f_{rr\alpha}$	0	−2.8	0	16.5	0.1	16.6
$f_{rr'\alpha}$	0.1	5.6	−0.1	−33.4	−0.2	33.5
$f_{r\alpha\alpha}$	0	48.7	0	−0.2	−4.1	0
$f_{\alpha\alpha\alpha}$	0	0.3	0	0	−67.8	0
Total	−319.4	255.4	−921.7	39.6	−61.9	147.3
SO_2	k_{111}	k_{122}	k_{133}	k_{211}	k_{222}	k_{233}
f_r	1.81	38.43	−1.93	−16.73	0.88	13.54
$f_{r'}$	0.01	0.30	0.03	−0.13	0.01	−0.11
$f_{r\alpha}$	0.41	−1.95	−0.37	−1.61	2.87	0.07
f_α	−0.57	−12.12	0.46	5.28	−0.28	−2.13
f_{rrr}	−45.07	−0.07	−160.64	−3.05	0	−3.62
$f_{rrr'}$	−2.17	0	2.58	−0.15	0	0.06
$f_{rr\alpha}$	1.31	−0.27	1.56	−6.02	0	−7.22
$f_{rr'\alpha}$	0.73	−0.15	−0.87	−3.36	0	4.03
$f_{r\alpha\alpha}$	−0.88	−18.66	0	8.13	−0.42	0
$f_{\alpha\alpha\alpha}$	0.10	6.46	0	−1.40	−9.96	0
Total	−44.31	11.96	−159.18	−19.04	−6.92	4.62

$$B_2=-\frac{6B_e^2}{\omega_2}\sin^2\Gamma,\quad b_2=-\left(\frac{2B_e}{\omega_2}\right)^{3/2}\sin\Gamma$$

$$B_3=-\frac{6B_eC_e}{\omega_3}$$

$$C_1=-\frac{6C_e^2}{\omega_1}+\frac{8C_e^2\omega_3^2}{\omega_1(\omega_3^2-\omega_1^2)}\zeta_{13}^2$$

$$C_2=-\frac{6C_e^2}{\omega_2}+\frac{8C_e^2\omega_3^2}{\omega_2(\omega_3^2-\omega_2^2)}\zeta_{23}^2$$

$$C_3=\frac{2C_e^2}{\omega_3}-8C_e^2\omega_3\left(\frac{\zeta_{13}^2}{\omega_3^2-\omega_1^2}+\frac{\zeta_{23}^2}{\omega_3^2-\omega_2^2}\right)$$

$$c_1=C_e^2(a_1/A_e^2+b_1/B_e^2)$$

$$c_2=C_e^2(a_2/A_e^2+b_2/B_e^2)$$

and A_e, B_e, C_e are the equilibrium rotational constants. It is easily shown that:

$$\sin\Gamma=(c\lambda-s\alpha)(1/m_X+1/2m_Y)^{1/2}$$

$$\cos\Gamma=(s\beta-c\mu)(1/m_X+1/2m_Y)^{1/2}$$

$$\zeta_{13}^2=(\beta\gamma+\mu\nu)^2/(\beta\lambda-\alpha\mu)^2$$

and

$$\zeta_{23}^2=1-\zeta_{13}^2=(\alpha\gamma+\lambda\nu)^2/(\beta\lambda-\alpha\mu)^2$$

where

$$c=\cos\frac{1}{2}(Y_1\text{-}X\text{-}Y_2)\ \text{and}\ s=\sin\frac{1}{2}(Y_1\text{-}X\text{-}Y_2)$$

Determination of the Higher-Order Potential Constants

The vibrational frequencies, the quadratic force constants, and the coefficients of Eq. 3 used in the following analysis[8-20] are summarized in Tables III—V. Since the normal frequencies for D_2S, H_2Se, and D_2Se are not available in the literature, they are estimated from the fundamental frequencies by the method described in a previous paper,[21] by

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TABLE IX. ANALYSIS OF THE QUARTIC CONSTANTS INTO COMPONENT TERMS[a] (in cm^{-1})

H_2O	k_{1111}	k_{1122}	k_{1133}	k_{2222}	k_{2233}	k_{3333}
f_r	0	−23.2	0	13.8	−22.9	0
$f_{r'}$	0	0.3	0	−0.2	−0.3	0
$f_{r\alpha}$	0	−0.4	0.1	0.4	−0.3	0
f_α	0	12.5	0	−6.6	8.3	0
f_{rrr}	0	−78.6	−0.1	−0.6	−77.9	−0.1
$f_{rrr'}$	0	−2.6	0	0	0.9	0
$f_{rr\alpha}$	0	0.3	0	−0.2	0.3	0
$f_{rr'\alpha}$	0	−0.6	0.1	0.5	0.6	−0.1
$f_{r\alpha\alpha}$	0	−6.9	0	4.1	0	0
$f_{\alpha\alpha\alpha}$	0	−0.1	0	−1.2	0.5	0
f_{rrrr}	35.2	1.5	212.2	0	1.5	35.5
$f_{rrrr'}$	1.7	0.1	0	0	0	−1.8
$f_{rrr'r'}$	1.5	0.1	−3.1	0	0	1.5
$f_{rr\alpha\alpha}$	0	−37.7	0	−0.3	−37.9	0
$f_{rr'\alpha\alpha}$	0	−5.0	0	0	5.0	0
$f_{\alpha\alpha\alpha\alpha}$	0	0	0	1.5	0	0
Total	38.5	−140.4	209.2	11.2	−122.2	35.0
SO_2	k_{1111}	k_{1122}	k_{1133}	k_{2222}	k_{2233}	k_{3333}
f_r	−0.04	−0.71	0.07	0.64	−1.00	−0.03
$f_{r'}$	0	−0.01	0	0.01	0.01	0
$f_{r\alpha}$	−0.01	0.12	0	0	−0.03	0
f_α	0.02	0.35	−0.02	−0.27	0.32	0
f_{rrr}	−0.21	−4.39	0.31	0	−5.39	−0.14
$f_{rrr'}$	−0.01	−0.21	−0.01	0	0.09	0
$f_{rr\alpha}$	−0.03	0.27	−0.02	−0.01	−0.14	0.03
$f_{rr'\alpha}$	−0.01	0.15	0.04	−0.01	0.08	−0.02
$f_{r\alpha\alpha}$	0.04	0.69	−0.03	−0.62	−0.01	0
$f_{\alpha\alpha\alpha}$	−0.01	−0.45	0.01	0.02	0.12	0
f_{rrrr}	2.11	0.01	15.02	0	0.01	2.97
$f_{rrrr'}$	−0.14	0	0	0	0	0.20
$f_{rrr'r'}$	−0.01	0	0.02	0	0	−0.01
$f_{rr\alpha\alpha}$	0.02	0.51	0.03	0	0.62	0
$f_{rr'\alpha\alpha}$	0.05	0.98	−0.06	0	−1.18	0
$f_{\alpha\alpha\alpha\alpha}$	0	−0.38	0	−1.37	0	0
Total	1.77	−3.09	15.36	−1.62	−6.51	3.01

a) Contributions from the $f_{rrr\alpha}$, $f_{rrr'\alpha}$, and $f_{r\alpha\alpha\alpha}$ constants are assumed to be zero.

the product rule, and by the x values estimated in the present study. The cubic and the quartic constants listed in Table VI are calculated, by using Eqs. 7 and 8, from the observed α and x values. They are then transformed into the constants in the internal-coordinate system by solving the simultaneous equations based on Tables I and II.[*3] The results, with

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[*3] The solution of the simultaneous equations is unique for the six third-order constants, whereas for the fourth-order constants the number of unknowns (nine) exceeds that of the observed quartic constants (six), since the k_{1112}, k_{1222}, and k_{1233} constants have not been observed. As Tables II and V indicate, all the matrix elements of Table II related to the $f_{rrr\alpha}$, $f_{rrr'\alpha}$, and $f_{r\alpha\alpha\alpha}$ constants have at least one α or μ parameter and, hence, are relatively small. The contributions from these constants are, accordingly, assumed to be zero in the course of determining the rest of the fourth-order constants from the simultaneous equations. This assumption, however, does not necessarily mean that these constants are negligibly small; as Table VII shows, the order of magnitude of these constants may be as much as ± 2md./Å. In that case, the three constants may contribute as much as $\pm 10\,cm^{-1}$ to the k_{1122} of D_2O and H_2S and to the k_{2222} of H_2O and H_2S, $\pm 5\,cm^{-1}$ to the k_{1122} of H_2O and to the k_{2222} of D_2O, and $\pm 3\,cm^{-1}$ to the k_{1122} of SO_2. All other contributions are negligible. The effect of this indeterminacy on the determination of the rest of the constants, which is found to be important only in the case of SO_2, is, therefore, included in their final uncertainties. The $f_{rrr\alpha}$, $f_{rrr'\alpha}$, and $f_{r\alpha\alpha\alpha}$ constants of H_2O and D_2O can be determined if at least six fourth-order constants of H_2O are assumed to be equal to the corresponding constants of D_2O. It is not likely, however, that more definite values of these constants can be obtained by this process because of the smallness of the matrix elements related to these constants and because of the errors involved in the original quartic constants.

TABLE X. COMPARISON OF THE a_3 AND a_4 PARAMETERS (in Å^{-1})

	a_3		a_4	
	Diatomic[a]	Bond[b]	Diatomic[a]	Bond[b]
O–H	2.36	2.36±0.02	2.56	2.61±0.03
S–H	1.84	1.80±0.02	1.81	1.95±0.02
Se–H	(1.65)	1.58±0.09	(1.74)	—
S–O	2.072	2.29±0.01	2.297	2.34±0.04

a) Taken from Table VI of Ref. 1. The parameters of Se–H are estimated by the Lippincott function, Ref. 24.

b) The parameters pertaining to the bond calculated from the experimental constants given in Table VII by using Eq. 9.

TABLE XI. PARAMETERS OF BOND-STRETCHING ANHARMONICITY (in Å^{-1})

		D.[a]	L. S.[b]	H. L.[c]	Add.[d]	Ass.[e]
H_2O	a_3	2.305(OH) 2.406(OD)	2.33	2.44	2.31	2.35_5
	a_4	2.464(OH) 2.654(OD)	2.47	2.37	2.47	2.56
H_2S	a_3	1.84	1.76	1.59	1.92	1.84
	a_4	1.81	1.86	1.76	2.06	1.86
H_2Se	a_3	—	1.63	1.57	1.79	1.65
	a_4	—	1.70	1.15	1.79	1.74
SO_2	a_3	2.072	2.16	1.92	2.07	2.07
	a_4	2.186	2.26	2.13	2.15	2.19
ClO_2	a_3	—	2.19	1.88	2.06	2.13
	a_4	—	2.30	2.07	2.14	2.23
NO_2	a_3	2.549	2.46	2.30	2.46	2.55
	a_4	2.618	2.56	2.52	2.51	2.62

a) Experimental a_3 and a_4 for the corresponding diatomic radical, Ref. 1.

b) Estimation according to the Lippincott function, Ref. 24.

c) Estimation according to the function of Herschbach and Laurie, Ref. 3.

d) Estimation according to the rule of additivity. See Ref. 1.

e) Values assumed in the present analysis.

TABLE XII. ESTIMATION OF THE CUBIC CONSTANTS OF BENT XY_2 (in cm^{-1})

		k_{111}	k_{122}	k_{133}	k_{211}	k_{222}	k_{233}
H_2O	obs.[a]	−319.4	255.4	−921.7	39.6	−61.9	147.3
	calc.[b]	−308.4	203.8	−929.9	53.9	10.2	97.9
D_2O	obs.	−193.3	191.1	−632.1	7.6	−33.4	93.7
	calc.	−189.9	126.4	−581.2	12.6	8.6	61.8
H_2S	obs.	−194.9	102.7	−587.5	−18.3	−1.0	13.9
	calc.	−199.3	107.4	−597.9	37.5	4.5	51.9
D_2S	calc.	−121.4	65.5	−364.4	15.8	3.4	31.1
H_2Se	obs.	−165.4	79.2	−478.4	10.9	1.1	32.5
	calc.	−168.2	99.3	−502.3	24.2	2.3	29.9
D_2Se	obs.	−100.8	28.3	−279.2	1.8	−4.6	21.5
	calc.	−101.0	59.7	−301.8	12.1	1.6	17.9
SO_2	obs.	−44.3	12.0	−159.2	−19.0	−6.9	4.6
	calc.	−39.1	24.6	−147.1	−16.0	3.5	8.1
ClO_2	calc.	−36.2	15.0	−131.1	−23.2	2.2	−7.0
$^{14}NO_2$	calc.	−40.4	25.5	−260.5	−41.9	10.3	−3.1
$^{15}NO_2$	calc.	−40.9	26.9	−253.7	−38.3	9.7	0.1

a) Taken from Table VI.

b) Calculated by a simple method, which takes into account the quadratic force constants and the principal third-order potential constant f_{rrr} estimated from the a_3 parameter given in Table XI.

TABLE XIII. ESTIMATION OF THE QUARTIC CONSTANTS of BENT XY_2 (in cm^{-1})

		k_{1111}	k_{1122}	k_{1133}	k_{2222}	k_{2233}	k_{3333}
H_2O	obs.[a]	38.5	−140.4	209.2	11.2	−122.2	35.0
	calc.[b]	33.8	−87.8	203.6	6.9	−91.6	33.9
D_2O	obs.	18.8	−96.8	135.7	9.9	−74.3	26.0
	calc.	17.7	−46.9	108.6	3.8	−49.0	18.1
H_2S	obs.	18.2	−58.6	115.2	0.7	−56.3	19.4
	calc.	17.4	−43.7	104.2	2.7	−45.7	17.4
D_2S	calc.	9.0	−22.8	53.9	1.4	−23.6	8.9
H_2Se	calc.	15.0	−37.0	89.6	2.6	−38.6	14.9
D_2Se	calc.	7.6	−18.8	45.4	1.3	−19.6	7.5
SO_2	obs.	1.8	−3.1	15.4	−1.6	−6.5	3.0
	calc.	1.6	−4.2	13.5	0.4	−5.6	2.5
ClO_2	calc.	1.6	−3.0	13.3	0.2	−4.7	2.4
$^{14}NO_2$	calc.	1.3	−4.6	26.8	0.6	−12.0	7.1
$^{15}NO_2$	calc.	1.5	−4.9	26.1	0.6	−11.6	6.9

a) Taken from Table VI.

b) Calculated by a simple method, which takes into account the quadratic force constants and the principal third- and fourth-order potential constants, f_{rrr} and f_{rrrr}, estimated from the a_3 and a_4 parameters given in Table XI.

TABLE XIV. ESTIMATION OF THE α PARAMETERS OF BENT XY_2 (in cm^{-1})

		$\alpha_1{}^A$	$\alpha_2{}^A$	$\alpha_3{}^A$	$\alpha_1{}^B$	$\alpha_2{}^B$	$\alpha_3{}^B$	$\alpha_1{}^C$	$\alpha_2{}^C$	$\alpha_2{}^C$	Ref.
H_2O	obs.	0.750	−2.941	1.253	0.238	−0.160	0.078	0.2018	0.1392	0.1445	9
	calc.	0.787	−1.831	1.020	0.204	−0.422	0.150	0.182	0.132	0.149	
D_2O	obs.	0.246	−1.161	0.593	0.0958	−0.0823	0.0418	0.0768	0.0495	0.0538	9
	calc.	0.255	−0.717	0.455	0.090	−0.162	0.049	0.071	0.046	0.053	
H_2S	obs.	0.125	−0.346	0.173	0.159	−0.219	0.123	0.069	0.062	0.055	10
	calc.	0.222	−0.319	0.241	0.095	−0.238	0.082	0.079	0.054	0.056	
D_2S	obs.	(0.066)	(−0.071)	(0.013)	(0.039)	(−0.061)	(0.030)	(0.022)	(0.027)	(0.012)	11
	calc.	0.078	−0.118	0.095	0.039	−0.087	0.027	0.028	0.019	0.021	
H_2Se	obs.	0.125	−0.230	0.145	0.092	−0.190	0.062	0.055	0.040	0.045	12
	calc.	0.147	−0.232	0.152	0.079	−0.202	0.076	0.056	0.037	0.040	
D_2Se	obs.	0.043	−0.092	0.053	0.038	−0.052	0.018	0.017	0.016	0.017	12
	calc.	0.052	−0.084	0.057	0.030	−0.073	0.026	0.020	0.014	0.015	
SO_2[b]	obs.	−1.036	−39.224	20.682	1.673	−0.073	1.163	1.429	0.534	1.097	8
	calc.	−1.51	−24.9	20.9	1.42	−1.16	0.92	1.20	0.02	0.92	
ClO_2[b]	calc.	−3.75	−19.2	14.2	1.96	−1.17	1.47	1.59	0.10	1.11	
$^{14}NO_2$[b]	obs.	—	−360	—	2.8	—	2.4	—	—	—	15
	calc.	−117	−239	199	2.07	−1.74	2.62	2.18	−0.43	2.35	
$^{15}NO_2$[b]	obs.[c]	—	−335	—	2.6	—	2.1	—	—	—	15
	calc.	−97	−232	185	2.02	−1.69	2.55	2.13	−0.35	2.29	

a) Rough estimates from the rotational constants given in Ref. 11.

b) Multiplied by 10^3.

c) The α values in Table II of Ref. 15 are given in opposite signs. The present revision of the signs is made with reference to the data given in their Table I.

estimated uncertainties, are given in Table VII.

Tables VIII and IX analyze the anharmonic constants into the contributions from various quadratic and higher-order constants on the basis of Tables I and II, expressing which potential constants are the principal contributors to a particular anharmonic constant. For example, k_{111} and k_{133} depend almost exclusively on the f_{rrr} term, and k_{1111}, k_{1133}, and k_{3333}, on the f_{rrrr} term. The rest of the anharmonic constants, on the other hand, are hybrids to a greater or lesser extent. For example, the k_{122} and k_{1122} constants depend strongly on the quadratic force constants. The dependence of f_r on k_{122} originates from the second term of the expansion of Δr^2 in Eq. 1 and represents the effect of the perpendicular (arc) motion of the X–Y bond. The physical

TABLE XV. ESTIMATION OF THE x PARAMETERS OF BENT XY_2 (in cm^{-1})

		x_{11}	x_{22}	x_{33}	x_{12}	x_{13}	x_{23}	Ref.
H_2O	obs.	−42.576	−16.813	−47.566	−15.933	−165.824	−20.322	9
	calc.	−43.29	−5.75	−47.30	−4.12	−167.74	−18.46	
D_2O	obs.	−22.58	−9.18	(−26.15)	−7.58	−87.15	−10.61	9
	calc.	−22.49	−3.57	−26.52	0.06	−87.65	−10.60	
H_2S	obs.	−25.09	−5.72	−24.00	−19.69	−94.68	−21.09	10
	calc.	−29.23	−3.29	−29.88	−2.28	−115.71	−10.24	
D_2S	calc.	−15.00	−1.76	−15.60	−0.93	−59.59	−5.32	
H_2Se	calc.	−21.34	−2.22	−21.41	−2.65	−83.60	−7.76	
D_2Se	calc.	−10.79	−1.14	−10.89	−1.30	−42.36	−3.91	
SO_2	obs.	−3.99	−3.00	−5.17	−2.05	−13.71	−3.90	13
	calc.	−2.71	−0.48	−4.63	0.95	−10.54	−1.85	
ClO_2	obs.	−4.4	0.0	−2.0	−3.0	−14.4	−13(?)	14
	calc.	−3.26	−0.46	−4.44	0.79	−11.07	−1.86	
$^{14}NO_2$	obs.	−9.0	−0.5	−16.4	−9.7	−28.7	−2.7	15
	obs.	−7.1	−7.5	−15.9	−16.0	−33.4	−8.2	20
	calc.	−3.59	0.59	−11.80	−3.46	−20.88	−6.10	
$^{15}NO_2$	obs.	−8.8	−0.4	−15.6	−9.5	−27.7	−2.6	15
	obs.	−7.0	−7.3	−15.1	−15.6	−32.3	−7.9	20
	calc.	−3.41	0.71	−11.24	−4.00	−20.78	−5.65	

significance of this term has been discussed in Part I in connection with a similar situation involving the k_{122} constant of linear XY_2.

Table VII indicates that the f_{rrr} and f_{rrrr} constants are more than ten times as great as the rest of the higher-order constants, and that they are determined with accuracies of about two significant figures. As has been discussed in Part I, these constants originate from the anharmonic stretching vibrations of the X-Y_1 and X-Y_2 bonds, and they may be expressed in terms of the a_3 and a_4 parameters, introduced in Part I, as follows:

$$f_{rrr}=-\frac{1}{2}a_3f_rr_e \quad \text{and} \quad f_{rrrr}=\frac{7}{24}a_4^2f_rr_e^2 \tag{9}$$

As is shown in Table X, the a_3 and a_4 parameters of the X-Y bond agree closely (to within 12%) with those of the X-Y diatomic molecule taken from Table VI of Part I. This affords direct support to similar statements presented in previous studies.[1-5)]

Table VII further shows that some of the other third-order constants listed in the table are determined significantly. For example, all the $f_{rr'\alpha}$ and $f_{\alpha\alpha\alpha}$ constants are negative, as are all the third-order constants of SO_2[*4]. The third-order constants of H_2O and H_2Se agree with those of the corresponding deuterides within the listed uncertainties (except for the $f_{rr'\alpha}$ constants of H_2O and D_2O). The fourth-order constants (except for f_{rrrr}), on the other hand, are indeterminate.

It is more difficult to put forward an intuitive model for interpreting the physical significance of the third-order potential constants other than f_{rrr}. They are, nevertheless, important, since previous discussions of the molecular potential field have almost always been based on the quadratic part of the potential, and, consequently, an examination of the higher-order constants may give a novel insight into the nature of the potential field. Some discussion of the physical significance of these constants will be given as a separate paper.[23),*5]

Estimation of Anharmonic Constants

The above findings for the f_{rrr} and f_{rrrr} constants suggest that the simple "diatomic approximation" discussed in Part I may also be used in this case for predicting the anharmonic constants. This method approximates the total potential function (Eq. 4) by the

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[*4] The same trend has been observed for the OF_2 molecule recently studied in our laboratory.[22)] All the third-order constants are found to be negative, and they are of an order of magnitude very similar to that of the corresponding constants of the SO_2 molecule.[23)]

22) Y. Morino and S. Saito, *J. Mol. Spectry*, to be published.

23) K. Kuchitsu and Y. Morino, *Spectrochim. Acta*, to be published.

[*5] Note added in proof: The experimental values of ω, α and x of H_2Se have recently been published: R. A. Hill and T. H. Edwards, *J. Chem. Phys.* **42**, 1391 (1965). Some of their ω and x values of $H_2{}^{80}Se$ ($\omega_1=2438.66$, $\omega_3=2453.77$, $x_{11}=-21.43$, $x_{33}=-21.71$, and $x_{13}=-84.90\,cm^{-1}$) are in good agreement with the corresponding estimates given in Tables III and XV respectively, while their x_{12}($-17.69\,cm^{-1}$) and x_{23}($-20.20\,cm^{-1}$) are not, in line with the discussion in the text. Their α values differ from Palik's α values[12)]; the third-order constants and the cubic constants based on their α values are accordingly different from those based on Palik's values given in Tables VI, VII and XII by as much as the uncertainties listed in the tables. See Ref. 23.

four quadratic terms plus the f_{rrr} and f_{rrrr} terms and ignores all the other higher-order terms. The constants f_{rrr} and f_{rrrr} are estimated by Eq. 9 with the a_3 and a_4 parameters transferred from those of the corresponding diatomic radical. The use of the matrices given in Tables I and II then gives approximate values of the cubic and quartic constants and those of α and x. It can be expected from Tables VIII and IX that this method will be effective for predicting k_{111}, k_{133}, k_{1111}, k_{1133}, and k_{3333} provided the a_3 and a_4 parameters are estimated properly, while it will give somewhat poorer results for the other constants except when the contributions from the disregarded higher-order constants accidentally cancel one another.

Calculations by means of this method have been made for ten bent XY_2 molecules. The estimations of a_3 and a_4 by the various methods[1,3,24] discussed in Part I are given in Table XI. A comparison of the results with the corresponding observed values in Tables XII–XV verifies the above expectation; the agreement is particularly good for the above five anharmonic constants and for x_{11}, x_{13}, and x_{33}, which almost exclusively depend on these constants. It is shown in the tables that at least the signs and the orders of magnitude are correctly estimated by this method, even for the rest of the constants of all the molecules, except for k_{222}, x_{22}, and x_{12}. It seems that it will be necessary to introduce higher-order cross terms, which are here ignored, in order to make quantitative estimates for these three constants.

This method may be regarded as a primitive but practical representation of the anharmonic potential field. The role of this model may be compared with that of the "valence-force" representation of the quadratic field which prevailed in the early stage of the studies of molecular normal vibrations.

Application of the Method

The present method for estimating anharmonic constants has been applied in this laboratory to the microwave studies of the SO_2 and OF_2 molecules in their excited vibrational states. The prediction of the k_{133} and k_{233} constants of the SO_2 molecule made it easier to discover and assign the relatively weak absorption lines which belong to the ν_3 state of this molecule, as was reported in a previous paper.[8] In a similar way, the detection and analysis of the lines which belong to the ν_1 and ν_3 states of the OF_2 molecule would have been more difficult without the preliminary but approximately correct estimates of the k_{111}, k_{133}, k_{211}, and k_{233} constants obtained by the present method. The details of the analysis will be published as a forthcoming paper.[22]

Summary

The vibrational potential function of the bent XY_2 molecule has been expanded in terms of the internal coordinates to the fourth order, and a general formulation which relates the coefficients of this expansion (second-, third-, and fourth-order potential constants) to the cubic and quartic constants in the normal-coordinate system has been derived. The third- and fourth-order constants in the internal-coordinate system for H_2O, D_2O, H_2Se, D_2Se, and SO_2 have been determined by using the experimental α and x values taken from the literature. It has been shown that the third- and fourth-order constants which represent the anharmonic bond-stretching vibration, f_{rrr} and f_{rrrr}, are much larger than the other higher-order constants and that they are nearly equal (to within 12 per cent) to the anharmonic potential constants of the corresponding diatomic radicals. The method presented in Part I of this paper, which makes use of the "diatomic approximation" for estimating the anharmonic constants and the α and x values, has been applied to the bent XY_2 molecules. A comparison of the results with currently available experimental data has shown that the signs and the orders of magnitude are in most cases correctly predicted by this approximation. This method has been further applied as an aid for the detection and analysis of the microwave absorption lines in the case of the SO_2 and OF_2 molecules in their excited vibrational states.

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[24] E. R. Lippincott and R. Schroeder, *J. Chem. Phys.*, 23, 1131 (1955); D. Steele and E. R. Lippincott, ibid., 35, 2065 (1961).