Estimation of Anharmonic Potential Constants. I. Linear XY_2 Molecules

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(Received October 10, 1964)

Within the framework of the Born-Oppenheimer approximation, the motions of the nuclei in a molecule can be fully understood if the potential function, *iuclnding the anharmonicity*, of the molecule is known. The fundamental importance of the anharmonic (usually cubic and quartic) potential constants for molecular spectroscopy is, as is well recognized,[1] that they are closely related to the dependence, α_i, of the rotational constants on the vibrational quantum numbers; to the vibrational anharmonic constants, x_{ij}; to the anharmonic resonance, and to the effects of vibrations on the molecular structure.[2,3]

Potential functions, including anharmonicity, have been the subject of extensive studies concerning diatomic molecules,[4-6] whereas little information has yet been obtained concerning polyatomic molecules; no parameters α and x have been determined by spectroscopic studies under high resolution except for only a few of the simplest molecules. Nor has the physical significance of cubic and quartic potential constants been fully explored, in contrast to the case of the quadratic force constants,[7] which have been studied in relation to the intramolecular force field. In view of the recent development of rotation and rotation-vibration spectroscopy, it seems of practical utility for spectroscopic analyses to investigate the basic relations which exist among the anharmonic potential constants; by means of such relations, one may make quantitative, or at least semiquantitative, estimates of the magnitude of anharmonic constants and those of the α and x parameters for which sufficient experimental data have not been determined.

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[1] H. H. Nielsen, *Revs. Mod. Phys.*, **23**, 90 (1951).

[2] D. R. Herschbach and V. W. Laurie, *J. Chem. Phys.*, **37**, 1668 (1962); V. W. Laurie and D. R. Herschbach, ibid., **37**, 1687 (1962).

[3] M. Toyama, T. Oka and Y. Morino, *J. Mol. Spectry.*, **13**, 193 (1964).

[4] G. Herzberg "Spectra of Diatomic Molecules," D. Van Nostrand, New York (1950).

[5] Y. P. Varshni, *Revs. Mod. Phys.*, **29**, 664 (1957).

[6] D. Steele, E. R. Lippincott and J. T. Vanderslice, ibid., **34**, 239 (1962).

[7] E. B. Wilson, Jr., J. C. Decius and P. C. Cross, "Molecular Vibrations," McGraw-Hill, New York (1955).

Studies in this direction were originated by Adel and Dennison[8] and by Redlich,[9] and after a long intermission their idea was successfully extended by Pliva.[10] He suggested a potential function of internal coordinates based on the general valence-force field and determined the values of adjustable parameters by using observed spectroscopic constants. The results of the application to CO_2, H_2O, and HCN show that the function reproduces the vibrational constants very well and may serve for the prediction of the rotation-vibration coupling constants. Kuchitsu and Bartell[11] developed a method by which cubic constants were estimated by using the elements of the $\boldsymbol{L}$ matrix and force constants derivable even in the absence of complete spectroscopic analyses, and they applied their method to H_2O and D_2O. Herschbach and Laurie's empirical study[12] of the anharmonic force constants of diatomic molecules led to reasonable predictions of the available cubic constants for bond stretching in polyatomic molecules. Suzuki, Pariseau, and Overend[13] have recently made extensive least-squares calculations for the determination of anharmonic constants from the observed band origins and rotational constants of fundamentals, overtones and combination tones for CO_2, H_2O, HCN, and C_2H_2.

In the present series of papers, a systematic study will be made of the physical significance of the cubic and quartic constants of simple polyatomic molecules in order to set up a simple model for predicting these constants. The linear XY_2 molecules may be the most suitable for starting the investigation of this problem. Precise experimental values have been reported for CO_2 and CS_2, and transformations among the coordinate systems are simple and unique, since the elements of the L matrix depend only on the masses of the component atoms. Accordingly, although CO_2[8-10] and CS_2[14] have been the subject of previous studies for similar purposes, the anharmonic constants of these molecules will be further examined in the present paper.

The potential function will be expanded in terms of internal coordinates. It has often been pointed out[8-11] that this expansion allows one to use chemical intuition in handling the problem and to correlate the anharmonic constants of isotopic molecules. Even for more complex molecules, it is not difficult, at least in principle, to relate the coefficients of this expansion by appropriate transformation of coordinates to the anharmonic potential constants (in the normal-coordinate system), which are most conveniently applied to theoretical problems.[1]

Expansion of Internal Coordinates

If the z axis is taken along the equilibrium molecular axis of the XY_2 molecule, the displacements of the $X\text{-}Y_i$ bond ($i=1, 2$) in the directions parallel and perpendicular to the z_i axis, Δz_i and $\Delta\rho$ respectively, are shown to be expanded in terms of the normal coordinates, of which Q_1 denotes the totally symmetric stretching vibration; Q_3, the antisymmetric stretching, and Q_{2a} and Q_{2b}, the degenerate bending vibrations:

$$\left.\begin{aligned}\Delta z_1&=g_1Q_1+g_2Q_3\\ \Delta z_2&=g_1Q_1-g_2Q_3\\ \Delta\rho^2&=g_2^2Q_2^2\end{aligned}\right\}\qquad(1)$$

where $g_1=(1/2m_Y)^{1/2}$, $g_2=(1/2m_Y+1/m_X)^{1/2}$

and $Q_2^2=Q_{2a}^2+Q_{2b}^2$

Since the instantaneous changes in the $X\text{-}Y_i$ bond length, Δr_i, and in the $Y_1\text{-}X\text{-}Y_2$ angle, $\Delta\alpha$, are given by:

$$\left.\begin{aligned}\Delta r_i&=\Delta z_i+\Delta\rho^2/2r_e-\Delta z_i\Delta\rho^2/2r_e^2+\cdots\\ r_e\Delta\alpha&=2\Delta\rho-\Delta\rho(\Delta z_1+\Delta z_2)/r_e\\ &\quad+\Delta\rho(\Delta z_1^2+\Delta z_2^2)/r_e^2-2\Delta\rho^3/3r_e^2+\cdots\end{aligned}\right\}\qquad(2)$$

where $r_e=r_e(\text{X-Y})$, they may also be expanded in terms of the normal coordinates. The internal symmetry coordinates are shown to be:

$$\left.\begin{aligned}S_1&=\frac{1}{\sqrt{2}}(\Delta r_1+\Delta r_2)=\sqrt{2}g_1Q_1\\ &\quad+\frac{1}{\sqrt{2}r_e}g_2^2Q_2^2-\frac{g_1g_2^2}{\sqrt{2}r_e^2}Q_1Q_2^2+\cdots\\ S_2^2&=(r_e\Delta\alpha)^2=4g_2^2Q_2^2-\frac{8}{r_e}g_1g_2^2Q_1Q_2^2\\ &\quad+\frac{1}{r_e^2}(12g_1^2g_2^2Q_1^2Q_2^2\\ &\quad-\frac{8}{3}g_2^4Q_2^4+8g_2^4Q_2^2Q_3^2)+\cdots\\ S_3&=\frac{1}{\sqrt{2}}(\Delta r_1-\Delta r_2)=\sqrt{2}g_2Q_3\\ &\quad-\frac{1}{\sqrt{2}r_e^2}g_2^3Q_2^2Q_3+\cdots\end{aligned}\right\}\qquad(3)$$

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[8] A. Adel and D. M. Dennison, *Phys. Rev.*, **44**, 99 (1933).

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

[10] J. Pliva, *Collection Czechoslow. Chem. Communs.*, **23**, 777 (1958).

[11] K. Kuchitsu and L. S. Bartell, *J. Chem. Phys.*, **36**, 2460 (1962).

[12] D. R. Herschbach and V. W. Laurie, ibid., **35**, 458 (1961).

[13] I. Suzuki, M. A. Pariseau and J. Overend, Symposium on Molecular Structure and Spectroscopy, S7, Columbus, Ohio, June, 1964.

[14] J. Pliva, Symposium on Molecular Structure and Spectroscopy, R5, Columbus, Ohio, June, 1960.

It is important to note that higher-order terms of the normal coordinates must be included in the above expressions in order to discuss anharmonic terms.

Anharmonic Constants

The potential function of the molecule, expanded in terms of the internal coordinates, is given by:

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

In terms of the internal symmetry coordinates, on the other hand, it is shown to be:

$$\begin{aligned} V=&\frac{1}{2}(f_1S_1^2+f_2S_2^2+f_3S_3^2) \\ &+\frac{1}{r_e}(f_{111}S_1^3+f_{122}S_1S_2^2+f_{133}S_1S_3^2) \\ &+\frac{1}{r_e^2}(f_{1111}S_1^4+f_{1122}S_1^2S_2^2+f_{1133}S_1^2S_3^2 \\ &+f_{2222}S_2^4+f_{2233}S_2^2S_3^2+f_{3333}S_3^4)+\cdots \end{aligned} \tag{5}$$

where the interrelations among the coefficients of Eq. 4 and Eq. 5 are given in Eq. A-1. From Eqs. 3 and 4, it is easy to derive the cubic and quartic potential constants in the expression of the potential function in terms of the dimensionless normal coordinates,[1] q_i:

$$\begin{aligned} V/hc=&\frac{1}{2}(\omega_1q_1^2+\omega_2q_2^2+\omega_3q_3^2)+k_{111}q_1^3 \\ &+k_{122}q_1q_2^2+k_{133}q_1q_3^2+k_{1111}q_1^4+k_{1122}q_1^2q_2^2 \\ &+k_{1133}q_1^2q_3^2+k_{2222}q_2^4+k_{2233}q_2^2q_3^2 \\ &+k_{3333}q_3^4+\cdots \end{aligned} \tag{6}$$

as is given in the Appendix. These potential constants are related to the α and x in Eq. A-3 of the Appendix, as has been shown by Dennison.[8,15]

Since there are twelve observables and twelve constants, the anharmonic constants, k, and the force constants, f, can be determined uniquely from the observed values of ω, α, and x.

The experimental values of α and x, reported by Courtoy for CO_2,[16] and by Agar et al.[17] and by Stoicheff[18] for CS_2, are taken for calculating the anharmonic constants, k (shown in Table I) by using Eq. A-2. The k values for CO_2 are in agreement with those calculated by Pliva[10] except for k_{1122} and k_{2222}, which are here obtained from $x_{12}+4x_{22}$ and $x_{22}+x_{ll}$ instead of from x_{12} and x_{22} in order to eliminate the effect of the Fermi resonance. The higher-order constants are obtained from the k constants by Eqs. A-1 and A-2; they are listed in Table II. The contributions to k from individual terms in Eq. A-2 are listed in Table III.

It is shown in Eq. A-2 and in Table III that the anharmonic constants which are related to the bending vibration, ν_2, namely, k_{122}, k_{1122}, k_{2222}, and k_{2233}, depend on both the quadratic and the higher-order constants. For k_{122} and k_{2222}, in particular, the contribution from the quadratic constant, f_r, is predominant. The dependence of the k on the quadratic force constants originates from the nonlinear dependence of the internal coordinates, Δr and $\Delta\alpha$, on the Cartesian coordinates, Δz and $\Delta\rho$, which, on the contrary, transform linearly into the normal coordinates.[10,11] A simple illustration of this situation is given in Fig. 1. Suppose the atom Y is displaced to the position P by a pure bending displacement. An increase in the total potential energy will not depend on f_r, since Δr is zero. The quadratic part of the potential energy, however, has a finite term, $(1/2)f_r(\Delta z)^2$, since the projection of the bond on the z axis, Δz, is finite ($\Delta z<0$). This positive contribution must be compensated for by the negative contributions from the anharmonic

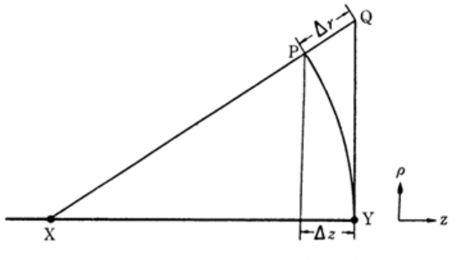

Fig. 1 A model representing the displacement of the Y atom in the X-Y bond relative to the X atom.
Y: Equilibrium position
Y→P: A pure bending displacement
Y→Q: A perpendicular displacement

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[15] D. M. Dennison, *Revs. Mod. Phys.*, **12**, 175 (1940).

[16] C. P. Courtoy, *Can. J. Phys.*, **35**, 608 (1957); *Ann. Soc. Sci. Bruxelles*, I **73**, 5 (1959).

[17] D. Agar, E. K. Plyler and E. D. Tidwell, *J. Res. Natl. Bur. Std. (U. S.)*, **66A**, 259 (1962).

[18] B. P. Stoicheff, *Can. J. Phys.*, **36**, 218 (1958); his ω^0 and x values have been revised according to his private communication to Y. Morino (1959).

TABLE I. ANHARMONIC POTENTIAL CONSTANTS DERIVED FROM OBSERVED α AND x VALUES (in cm^{-1})

	k_{111}	k_{122}	k_{133}	k_{1111}	k_{1122}	k_{1133}	k_{2222}	k_{2233}	k_{3333}	Ref.
$^{12}C^{16}O_2$	−45.07	73.81	−252.91	1.25	−9.11	20.37	2.16	−27.81	6.63	a
$^{13}C^{16}O_2$	−45.07	73.02	−245.36	1.25	−9.18	19.72	2.12	−26.48	6.23	a
$^{12}C^{32}S_2$	−14.89	41.55	−129.97	0.11	−7.48	6.45	2.06	−14.93	3.80	b
CS_2	−14.71	49.40	−127.84	0.16	18.36	5.93	−1.89	−16.39	3.55	c

a), b), c) Calculated from the α and x values listed in Refs. 16, 17 and 18, respectively, by using Eq. A-3.

TABLE II. POTENTIAL CONSTANTS IN THE INTERNAL-COORDINATE SYSTEM[a)] (in md./Å)

	f_r	$f_{r'}$	f_α	f_{rrr}	$f_{rrr'}$	$f_{r\alpha\alpha}$
$^{12}C^{16}O_2$	16.030	1.268	0.582	−22.18	−1.75	−0.54
$^{13}C^{16}O_2$	16.030	1.268	0.582	−22.16	−1.77	−0.52
CO_2(D)[b)]	(16.030)	(1.268)	(0.582)	−22.2	0	0
$^{12}C^{32}S_2$	7.880	0.648	0.236	−10.98	0.51	−0.26
CS_2	7.789	0.552	0.240	−10.73	0.56	−0.11
CS_2(D)	(7.880)	(0.648)	(0.236)	−11.9	0	0

	f_{rrrr}	$f_{rrrr'}$	$f_{rrr'r'}$	$f_{rr\alpha\alpha}$	$f_{rr'\alpha\alpha}$	$f_{\alpha\alpha\alpha\alpha}$
$^{12}C^{16}O_2$	34.84	−3.28	−8.03	1.21	3.18	0.02
$^{13}C^{16}O_2$	34.72	−3.14	−7.92	1.16	2.88	0.02
CO_2(D)	38.1	0	0	0	0	0
$^{12}C^{32}S_2$	14.53	−7.80	−4.89	−1.28	−2.52	0.04
CS_2	12.54	−2.25	−8.44	10.26	21.80	−0.17
CS_2(D)	23.6	0	0	0	0	0

a) Calculated from Table I by using Eqs. A-1 and A-2.
b) Diatomic approximation. See Eq. 9.

terms, k_{122}, etc.; these terms must, therefore, depend on f_r. If, on the other hand, the atom Y is displaced to the point Q, a part of the increase in the potential energy will come from $(1/2)f_r(\Delta r)^2$, since the X–Y bond is stretched ($\Delta r>0$). Since Δz is zero, the quadratic part which depends on f_r is zero. The above increase in the potential energy must, therefore, come from the anharmonic terms, mainly from k_{2222} in this case. The physical significance of this problem in relation to the mean bond displacement has been discussed in more detail by Bartell.[19)]

A problem to be explored by the valence theory is presented by the observation that the force constant $f_{r\alpha\alpha}$ is negative in the case of CO_2 and CS_2. This implies that the X–Y bond is likely to be stretched when the molecule is bent. At the root-mean-square angle of the zero-point bending vibration, $\langle\Delta\alpha^2\rangle^{1/2}$, the average lengthening of the bond for this reason, $-f_{r\alpha\alpha}r_e\langle\Delta\alpha^2\rangle/(f_r+f_{r'})$, is about 0.0003 Å for CO_2 and CS_2.[*1]

The potential function for the bending vibration is found to be very nearly harmonic, since the fourth-order constant $f_{\alpha\alpha\alpha\alpha}$ is small. At the angle of $\langle\Delta\alpha^2\rangle^{1/2}$, the quartic part of the potential energy, $f_{\alpha\alpha\alpha\alpha}r_e^2\Delta\alpha^4$, is less than 1% of the quadratic contribution, $(1/2)f_\alpha r_e^2\Delta\alpha^2$.

The constants k which are not related to the ν_2 vibration originate exclusively from the higher-order constants, f_{rrr} or f_{rrrr}. As is shown in Table II, the constants f_{rrr} and f_{rrrr} are much larger than the others. This can be understood by a model in which each bond executes a stretching vibration with little interaction (higher than the quadratic) with the other bond. The magnitudes of f_{rrr} and f_{rrrr} are found to be approximately equal to those of the corresponding constants of a diatomic X–Y molecule; this confirms similar statements given in previous papers.[9−12)] Since a method for predicting the anharmonic constants based on as simple a potential function as possible is aimed at, an approximate potential function based on the diatomic potential constants will be studied in some detail in the next section.

An Approximate Potential Function

The potential function of a diatomic molecule is in general expanded around the equilibrium distance as:

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19) L. S. Bartell, *J. Chem. Phys.*, **38**, 1827 (1963).

[*1] In another expression, the force constant of the bending vibration, f_α, is apparently decreased (or increased) as the bonds are symmetrically stretched (or compressed). For the displacement of the root-mean-square amplitude of the bond, ±0.035 Å for CO_2 and ±0.039 Å for CS_2, the increase in f_α is about 11%.

TABLE III. CONTRIBUTIONS TO THE ANHARMONIC CONSTANTS FROM POTENTIAL CONSTANTS IN THE INTERNAL-COORDINATE SYSTEM[a] (in cm^{-1})

Molecule		f_r	$f_{r'}$	f_α	f_{rrr}	$f_{rrr'}$	$f_{r\alpha\alpha}$	f_{rrrr}	$f_{rrrr'}$	$f_{rrr'r'}$	$f_{rr\alpha\alpha}$	$f_{rr'\alpha\alpha}$	$f_{\alpha\alpha\alpha\alpha}$	Total
$^{12}C^{16}O_2$	k_{111}	0	0	0	−41.78	−3.29	0	0	0	0	0	0	0	−45.07
	k_{122}	111.40	8.81	−16.18	0	0	−30.22	0	0	0	0	0	0	73.81
	k_{133}	0	0	0	−259.74	6.83	0	0	0	0	0	0	0	−252.91
	k_{1111}	0	0	0	0	0	0	1.58	−0.15	−0.18	0	0	0	1.25
	k_{1122}	−2.68	−0.21	0.58	−11.11	−0.88	1.45	0	0	0	1.61	2.13	0	−9.11
	k_{1133}	0	0	0	0	0	0	19.62	0	0.75	0	0	0	20.37
	k_{2222}	4.95	0.39	−0.96	0	0	−2.68	0	0	0	0	0	0.46	2.16
	k_{2233}	−5.55	0.44	0.81	−23.05	0.61	0	0	0	0	3.35	−4.42	0	−27.81
	k_{3333}	0	0	0	0	0	0	6.78	0.63	−0.78	0	0	0	6.63
$^{12}C^{32}S_2$	k_{111}	0	0	0	−15.62	0.73	0	0	0	0	0	0	0	−14.89
	k_{122}	59.88	4.92	−7.18	0	0	−16.07	0	0	0	0	0	0	41.55
	k_{133}	0	0	0	−127.98	−1.99	0	0	0	0	0	0	0	−129.55
	k_{1111}	0	0	0	0	0	0	0.37	−0.20	−0.06	0	0	0	0.11
	k_{1122}	−1.08	−0.09	0.19	−4.51	0.21	0.58	0	0	0	−1.40	−1.38	0	−7.48
	k_{1133}	0	0	0	0	0	0	6.11	0	0.34	0	0	0	6.45
	k_{2222}	2.88	0.24	−0.46	0	0	−1.55	0	0	0	0	0	0.95	2.06
	k_{2233}	−2.95	0.24	0.36	−12.33	−0.19	0	0	0	0	−3.83	3.77	0	−14.93
	k_{3333}	0	0	0	0	0	0	2.78	1.49	−0.47	0	0	0	3.80

a) Calculated from Table II and Eqs. A-1 and A-2.

TABLE IV. ESTIMATION OF THE ANHARMONIC CONSTANTS OF CO_2 AND CS_2 BY USE OF THE SIMPLE POTENTIAL FUNCTION (in cm^{-1})

		k_{111}	k_{122}	k_{133}	k_{1111}	k_{1122}	k_{1133}	k_{2222}	k_{2233}	k_{3333}	$\alpha_1\times10^3$	$\alpha_2\times10^3$	$\alpha_3\times10^3$	x_{11}	x_{33}	x_{13}	x_{23}	$x_{22}+x_{ll}$	$x_{12}+4x_{22}$
$^{12}C^{16}O_2$	obs.	−45.1	73.8	−252.9	1.25	−9.11	20.37	2.16	−27.81	6.63	1.20	−0.72	3.09	−3.75	−12.63	−19.37	−12.53	0.15	1.13
	est. I[a]	−41.9	104.0	−260.2	1.73	−13.45	21.47	4.38	−27.39	7.42	1.07	−1.14	3.19	−2.26	−12.77	−17.99	−5.91	0.38	2.47
	est. II	−41.9	(73.8)	−260.2	1.73	−11.99	21.47	1.69	−27.39	7.42	1.07	(−0.72)	3.19	−2.26	−12.77	−17.99	−11.71	−0.32	−5.05
$^{12}C^{32}S_2$	obs.	−14.9	41.5	−130.0	0.11	−7.48	6.45	2.07	−14.93	3.80	0.155	−0.205	0.711	−1.07	−6.54	−7.86	−6.45	0.78	1.36
	est. I	−16.9	57.6	−138.7	0.61	−5.87	9.93	2.66	−15.71	4.52	0.19	−0.30	0.76	−0.69	−7.17	−7.01	−3.38	0.19	2.31
	est. II	−16.9	(41.5)	−138.7	0.61	−5.29	9.93	1.11	−15.71	4.52	0.19	(−0.205)	0.76	−0.69	−7.17	−7.01	−6.69	−0.17	−1.79

a) Case I: Estimated by using the constants (D) listed in Table II. Case II: Estimated by using the constants (D) plus $f_{r\alpha\alpha}=-0.544$ md./Å (CO_2) and -0.264 md./Å (CS_2) in order to make α_2 agree with the observed values.

$$V(\Delta r)=\frac{1}{2}f_r\Delta r^2-\frac{1}{2}a_3f_r\Delta r^3+\frac{7}{24}a_4^2f_r\Delta r^4+\cdots \tag{7}$$

An advantage of taking a_3 and a_4 as independent parameters lies in the approximate equality of a_3 and a_4; the above expression (Eq. 7) is taken by analogy to the Morse function:[20]

$$V(\Delta r)=D_e[\exp(-2a\Delta r)-2\exp(-a\Delta r)] \tag{8}$$

in which case it follows that $a_3=a_4=a$.

As a natural extension to the XY_2 molecule, the following expression of the anharmonic force constants of Eq. 4 are derived by taking the higher-order terms of Eq. 7, other cross-interaction terms simply being ignored:

$$\left.\begin{aligned} &f_{rrr}=-\frac{1}{2}a_3f_rr_e, \quad f_{rrrr}=\frac{7}{24}a_4^2f_rr_e^2 \\ &f_{rrr'}\sim 0 \quad f_{rrrr'}\sim 0 \quad \text{and} \quad f_{rrr'r'}\sim 0 \end{aligned}\right\} \tag{9}$$

In order to estimate f_{rrr} and $f_{rrrr'}$, f_r and r_e may be taken to be equal to those of the $CO_2(CS_2)$ molecule,[*2] and the parameters a_3 and a_4 may be approximated by those of the CO(CS) molecule, while the parameters a_3 and a_4 may be approximated by those of the CO (CS) molecule, which are determined by the method to be described in the next section. The constants obtained from Eq. 9 in this way are listed in Table II as a "Diatomic Approximation (D)". The constants k, α, and x calculated from Eqs. A-2 and A-3 by using the approximate potential constants (D) of Table II are compared in Table IV with the corresponding observed values. The agreement in the order of magnitude is good except for α_2 and x_{23}. This indicates the practical usefulness of this simple potential function. A better agreement for x_{23} may result, as shown in Table IV, by the introduction of a negative $f_{r\alpha\alpha}$ to make α_2 agree with the experimental α_2; this adjustment, however, makes the agreement of $x_{22}+x_{ll}$ and $x_{12}+4x_{22}$ somewhat worse.

There is no analogous principle at present for estimating the constants which are left undetermined in the "diatomic approximation": $f_{rrr'}$, $f_{r\alpha\alpha}$, $f_{rrrr'}$, $f_{rrr'r'}$ $f_{rr\alpha\alpha}$, $f_{rr'\alpha\alpha}$, and $f_{\alpha\alpha\alpha\alpha}$. It is an important problem for future studies to establish a scheme by which plausible estimates may be made for the higher-order terms of the stretching-stretching, stretching-bending, and bending-bending interactions.

The Parameters a_3 and a_4

It was shown in the preceding section that the estimation of a_3 and a_4 is a key step in predicting the anharmonic constants of the stretching vibrations. Some characteristic features of these parameters will, therefore, be discussed in the present section.

The parameters a_3 and a_4 of a diatomic molecule are readily determined by the following equations, if the constants ω_e, α_e, and ω_ex_e are known by spectroscopic measurements;

$$\left.\begin{aligned} &a_3=\frac{2}{3}\pi\omega_e(c\mu/2hB_e^3)^{1/2}(\alpha_e+6B_e^2/\omega_e) \\ &a_4=(15a_3^2/7-64\pi^2c\mu\omega_ex_e/7h)^{1/2} \end{aligned}\right\} \tag{10}$$

where μ is the reduced mass.

From the parameters for various diatomic molecules determined in this way (Tables V and VI), the following general features of a_3 and a_4 may be observed.

First, the magnitude of a_3 is about $2\,\text{Å}^{-1}$; for most diatomic molecules for which spectroscopic values are available,[4,6,21] a_3 is in the range 1.6—$2.4\,\text{Å}^{-1}$, the largest and the smallest values being $2.55\,\text{Å}^{-1}$ (NO) and $1.34\,\text{Å}^{-1}$ (Si_2) respectively. The only exceptions[*3] are those molecules which contain alkali atoms as one or both of their components; their a_3 values are much smaller, in many cases less than $1\,\text{Å}^{-1}$. Second, a_4 is equal to, or slightly larger than, a_3. For the diatomic molecules studied here, the ratio a_4/a_3 is 1.03, with an average deviation of 0.03. Third, an additivity rule, $a_i(\text{X-Y})=(1/2)[a_i(\text{X-X})+a_i(\text{Y-Y})]$ ($i=3$ or 4), is applicable to molecules X-Y, except for alkali hydrides. As for the ratio $[a_i(\text{X-X})+a_i(\text{Y-Y})]/2a_i(\text{X-Y})$, the following average values and average deviations are obtained:

	a_3	a_4
Nonhydrides	1.00±0.04	0.98±0.04
Hydrides	1.05±0.06	1.04±0.07

These rules may be useful for a simple order-of-magnitude estimation of these parameters.

For estimating the a_3 and a_4 values of a bond X-Y for which no spectroscopic values of the corresponding diatomic molecules are known, probably a more reliable method than the above additivity rule is the use of an analytical function obtained by a systematic fit to various spectroscopic data of diatomic molecules. For example, for the function proposed by Steele

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20) P. M. Morse, *Phys. Rev.*, **34**, 57 (1929).

[*2] An alternative process is to take f_r and r_e, as well as the a_3 and a_4 parameters, to be equal to those of the CO(CS) molecule; the constants, f_r and r_e, of CO(CS) are appreciably different from those of the $CO_2(CS_2)$ molecule. There is no definite physical reason for choosing whether we should transfer a_3 and a_4 or $a_3f_rr_e$ and $a_4^2f_rr_e^2$ from the corresponding diatomic molecule. According to our experience, however, a better agreement is usually obtained by transfering a_3 and a_4.

21) E. R. Lippincott and R. Schroeder, *J. Chem. Phys.*, **23**, 1131 (1955).

[*3] Other peculiar exceptions are BrF, SnO, ZrO, and PbS, for which $a_3\sim 3\,\text{Å}^{-1}$ and $a_4\sim 4\,\text{Å}^{-1}$.

TABLE V. PARAMETERS a_3 AND a_4 OF CO AND CS (in Å^{-1})

	CO		CS	
	a_3	a_4	a_3	a_4
obs.[a)]	2.390	2.462	1.945	2.065
S. L.[b)]	2.40	2.48	1.89	1.96
H. L.[c)]	2.46	2.65	1.83	1.99
Morse[d)]	2.32	2.32	1.83	1.83
Add.[e)]	2.30	2.32	1.92	1.92

a) Calculated by using observed values of ω_e, α_e, and $\omega_e x_e$.
b) Steele-Lippincott function, Ref. 21.
c) Herschbach-Laurie function, Ref. 12.
d) Morse function, Ref. 20.
e) Additivity rule, $[a(C_2)+a(O_2)]/2$, $[a(C_2)+a(S_2)]/2$.

TABLE VI. PARAMETERS a_3 AND a_4 FOR DIATOMIC MOLECULES[a)] (in Å^{-1})

	a_3	a_4		a_3	a_4		a_3	a_4		a_3	a_4		a_3	a_4
H_2	2.155	2.413	K_2	0.528	0.359	NaH	1.113	1.167	BF	2.16	2.15	OSi	1.982	2.081
D_2	2.142	2.336	Se_2	1.46	1.30	SH[f)]	1.84	1.81	BCl	1.709	1.832	OP	2.03	2.05
Li_2	0.715	0.692	Br_2[d)]	1.382	1.158	SD[f)]	1.84	1.80	BBr	1.41	1.40	OS	2.072	2.186
B_2	1.68	1.59	I_2[e)]	1.536	1.563	ClH[g)]	1.855	1.966	CN	2.268	2.294	OTi	1.74	1.65
C_2[b)]	2.131	2.074	LiH	1.181	1.267	ClD[g)]	1.855	1.966	CO	2.390	2.462	OGe	1.91	2.00
N_2	2.443	2.461	LiD	1.193	1.282	KH	0.870	0.803	CF[j)]	2.406	2.643	CI	1.952	2.008
O_2	2.476	2.568	BH	1.724	1.82	BrH[h)]	1.719	1.806	CP	1.878	1.881	OBa	1.34	1.36
F_2	(2.418	2.560)	CH	1.981	2.087	BrD	1.720	1.812	CS	1.945	2.065	OPb	1.78	1.75
Na_2	0.61	0.48	CD	1.982	2.088	IH[i)]	1.589	1.643	CSe[k)]	1.83	1.93	FP[l)]	1.891	2.019
Si_2	1.344	1.413	OH	2.305	2.464	ID[i)]	1.589	1.643	NO	2.549	2.618	FCl	1.919	2.13
P_2	1.630	1.652	OD	2.406	2.654	BeO	2.050	2.093	NSi	1.932	1.961	AlBr	1.360	1.490
S_2	1.702	1.766	FH	2.457	2.659	BeF	1.914	2.017	NP	2.018	2.039	SiS	1.565	1.631
Cl_2[c)]	1.709	1.748	FD	2.458	2.650	BO	2.186	2.244	OMg	1.71	1.69	ClI	1.562	1.561

a) Calculated by Eq. 13 from experimental values of ω_e, α_e, and $\omega_e x_e$ listed in Refs. 4 and 22.
b) E. A. Ballik and D. A. Ramsay, *Astrophys. J.*, **137**, 84 (1963).
c) A. E. Douglas, C. K. Møller and B. P. Stoicheff, *Can. J. Phys.*, **41**, 1174 (1963).
d) Y. V. Rao and P. Venkateswarlu, *J. Mol. Spectry.*, **13**, 288 (1964).
e) D. H. Rank and B. S. Rao, ibid., **13**, 34 (1964).
f) D. A. Ramsay, *J. Chem. Phys.*, **20**, 1920 (1952).
g) D. H. Rank, D. P. Eastman, B. S. Rao and T. A. Wiggins, *J. Opt. Soc. Am.*, **52**, 1 (1962).
h) E. K. Plyler, *J. Res. Natl. Bur. Std.* (*U. S.*), **64**, 377 (1960).
i) L. H. Jones, *J. Mol. Spectry.*, **1**, 179 (1957).
j) E. B. Andrews and R. F. Barrow, *Proc. Phys. Soc.*, **64A**, 481 (1951).
k) R. K. Laird and R. F. Barrow, ibid., **66A**, 836 (1953).
l) A. E. Douglas and M. Frackowiak, *Can. J. Phys.*, **40**, 832 (1962).

and Lippincott[21,22] (Eq. 5b of their paper[22]), it follows that:

$$\left.\begin{aligned} a_3 &= 1/r_e + ab(n/2r_e)^{1/2} \\ a_4 &= \{(3/7r_e)\,[6a_3 - 2/r_e + n(2ab^2-1)]\}^{1/2} \end{aligned}\right\} \quad (11)$$

where the parameters a, b, and n for any molecule may be evaluated by the method described in their papers. On the other hand, by the use of the exponential function proposed by Herschbach and Laurie,[12] a_3 and a_4 (in Å^{-1} units) can be estimated from the $a_{ij}(n)$ and $b_{ij}(n)$ values listed in their Table II:

$$\left.\begin{aligned} \log_{10} a_3 &= [a_{ij}(3) - r_e]/b_{ij}(3) \\ &\quad - [a_{ij}(2) - r_e]/b_{ij}(2) \\ \log_{10} a_4 &= 0.1170 + \frac{1}{2}\{[a_{ij}(4) - r_e]/b_{ij}(4) \\ &\quad - [a_{ij}(2) - r_e]/b_{ij}(2)\} \end{aligned}\right\} \quad (12)$$

The a_3 and a_4 values of CO and CS estimated by various methods are listed in Table V; they are in substantial agreements with one another.

Anharmonicity of NH_2, ND_2, and BO_2

Among the linear XY_2 radicals which have recently been identified by spectroscopic studies,[23] NH_2, ND_2 and BO_2 have been the

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[22] D. Steele and E. R. Lippincott, ibid., 35, 2065 (1961).
[23] G. Herzberg, *ICSU Review*, 4, 179 (1962).

TABLE VII. APPROXIMATE ESTIMATION OF THE ANHARMONIC COSTANTS OF NH_2, ND_2, AND BO_2 (in cm^{-1})

	k_{111}	k_{122}	k_{133}	k_{1111}	k_{1122}	k_{1133}	k_{2222}	k_{2233}	k_{3333}
NH_2 est.[a]	−264	457	−847	25	−122	163	39	−216	29
ND_2 est.	−157	289	−536	13	−65	87	22	−122	16
BO_2 est.	−45	60	−214	2	−14	19	2	−26	5

	α_1	α_2	α_3	x_{11}	x_{22}	x_{33}	x_{12}	x_{13}	x_{23}	x_{ll}
NH_2 est.	0.15	(−0.017)	0.18	−37	(11)	−45	(5)	−153	−46	−3
obs.[b]	0.12	−0.024	—	—	11.4	—	5	—	—	—
ND_2 est.	0.05	(−0.013)	0.07	−19	6	−27	4	−80	−30	−1
obs.	—	−0.011	—	—	8.1	—	—	—	—	—

	α_1	α_2	α_3	x_{11}	x_{33}	x_{12}	x_{23}	$x_{22}+x_{ll}$	$x_{12}+4x_{22}$
BO_2 est.	0.0015	−0.0007	0.0031	−5	−15	−20	−11	−0.2	−5
obs.[c]	0.0002	−0.0003	0.0023	0	—	—	—	—	~-12

a) Present estimates. Assumed values are enclosed in parentheses.
b) Refs. 24 and 25.
c) Ref. 26.

subject of detailed vibrational analyses. Dressler and Ramsay[24,25] have reported on the $\omega_1^0+x_1^0$, ω_2^0, x_{12}^0, x_{22}^0, α_1, α_2, and B_0 values of NH_2 and ND_2 in the $^2A_1\Pi_u$ excited electronic state, while Johns[26] has given ω_1, ω_2, $(1/2)(2\nu_3)$, α_1, α_2, α_3, x_{22}, and x_{12} of BO_2 in the $A^2\Pi_u$ state. Although exact ω_3 values are unknown, it seems worthwhile to apply the present technique to these molecules in order to make an approximate prediction of the orders of magnitude of the α and x values.

On the basis of a preliminary estimation of x and the product rule of the NH_2 and ND_2 frequencies, f_1 and f_2 are estimated to be 7.16 and 0.085 md./Å respectively. With the further assumption that $f_{r'}=0$, ω_3 is found to be $3.7_1\times10^3\ cm^{-1}$ (NH_2) and $2.7_9\times10^3\ cm^{-1}$ (ND_2). The parameters a_3 and a_4 are estimated, by the method discussed in the preceding section, to be 2.19 Å^{-1} and 2.28 Å^{-1} respectively. The f_{rrr} and f_{rrrr} constants are, then, 7.64 and 10.32 md./Å respectively. Higher-order potential constants, $f_{r\alpha\alpha}$, $f_{rr\alpha\alpha}$, $f_{rr'\alpha\alpha}$ and $f_{\alpha\alpha\alpha\alpha}$, are adjusted to make the outputs of α_2, x_{12}, and x_{22} nearly agree with the observed values; they are thus taken to be −0.37, 0.96, 0.41, and 0.03 md./Å respectively.

The estimates of the anharmonic constants resulting from the present crude approximations are given in Table VII.

For BO_2, a preliminary estimation based on the vibrational data of Johns suggests that $\omega_3\sim2422\ cm^{-1}$, $f_r\sim11.73$, $f_{r'}\sim-2.42$, and $f_\alpha\sim$ 0.30 md./Å. With the parameters a_3 and a_4 transferred from those of the BO radical listed in Table VII, and with $f_{r\alpha\alpha}$ arbitrarily assumed to be $f_{r\alpha\alpha}(CO_2)\cdot f_\alpha(BO_2)/f_\alpha(CO_2)\sim0.28$, the anharmonic constants α and x are predicted (Table VII). The magnitude of k_{122} ($\sim60\ cm^{-1}$) indicates the presence of the strong Fermi resonance observed by Johns, which must influence the observed values of α_1 and α_2 by intermixing the ν_1 and $2\nu_2$ vibrational states. The agreement of α_3 is fair.

Summary

On the basis of a normal-coordinate analysis of a series expansion of the anharmonic potential field, a set of general expressions has been derived for a linear XY_2 molecule for relating the cubic and quartic potential constants (k) to the coefficients (f) of the potential function expanded in terms of the internal coordinates. The constants k and f for CO_2 and CS_2 have been calculated by using the observed values of α and x taken from the literature, and the physical significance of the dependence of k on f has been studied.

The anharmonic constants related to the C–O(C–S) bond-stretching vibrations are represented as functions of the parameters of anharmonicity, a_3 and a_4, which are shown to be transferable from the CO(CS) diatomic molecule. Most of the k, α, and x values for CO_2 and CS_2 can be predicted quantitatively by assuming a simple potential function, comprised of ordinary quadratic terms and the anharmonic terms for the bond-stretching vibrations mentioned above, with all other higher-order potential terms ignored.

A number of methods for estimating the parameters a_3 and a_4, and a general rule regarding their relative magnitudes, have been discussed. The k, α, and x values of the linear radicals, NH_2, ND_2, and BO_2, may be predicted

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[24] K. Dressler and D. A. Ramsay, *Phil. Trans. Roy. Soc.*, **A251**, 553 (1959).

[25] D. A. Ramsay, *Advances in Spectroscopy*, **1**, 1 (1959).

[26] J. W. C. Johns, *Can. J. Phys.*, **39**, 1738 (1961).

in the present scheme by making simple assumptions about their potential constants.

The authors are indebted to Dr. Takao Iijima for his help in the calculations.

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Appendix

The interrelations among the coefficients of the potential function in terms of the internal symmetry and normal coordinates are given by the following sets of equations:

$$\left.\begin{aligned}
&f_r=\frac{1}{2}(f_1+f_3),\quad f_r{}'=\frac{1}{2}(f_1-f_3),\quad f_\alpha=f_2\\
&f_{rrr}=\frac{1}{2\sqrt{2}}(f_{111}+f_{133})\\
&f_{rrr'}=\frac{1}{2\sqrt{2}}(3f_{111}-f_{133}),\quad f_{r\alpha\alpha}=\frac{1}{\sqrt{2}}f_{122}\\
&f_{rrrr}=\frac{1}{4}(f_{1111}+f_{1133}+f_{3333})\\
&f_{rrrr'}=f_{1111}-f_{3333},\\
&f_{rrr'r'}=\frac{1}{2}(3f_{1111}-f_{1133}+3f_{3333})\\
&f_{rr\alpha\alpha}=\frac{1}{2}(f_{1122}+f_{2233}),\quad f_{rr'\alpha\alpha}=f_{1122}-f_{2233}\\
&f_{\alpha\alpha\alpha\alpha}=f_{2222}
\end{aligned}\right\}\quad\text{(A-1)}$$

The cubic and quartic constants in Eq. 6 depend on the force constants of Eq. 5:

$$\left.\begin{aligned}
&k_{111}=\frac{2\sqrt{2}}{r_e}h_{111}g_1{}^3f_{111}\\
&k_{122}=\frac{1}{r_e}h_{122}g_1g_2{}^2(f_1-4f_2+4\sqrt{2}f_{122})\\
&k_{133}=\frac{2\sqrt{2}}{r_e}h_{133}g_1g_2{}^2f_{133}\\
&k_{1111}=\frac{4}{r_e{}^2}h_{1111}g_1{}^4f_{1111}
\end{aligned}\right.$$

$$\left.\begin{aligned}
&k_{1122}=\frac{1}{r_e{}^2}h_{1122}g_1{}^2g_2{}^2(-f_1+6f_2+3\sqrt{2}f_{111}\\
&\qquad-8\sqrt{2}f_{122}+8f_{1122})\\
&k_{1133}=\frac{4}{r_e{}^2}h_{1133}g_1{}^2g_2{}^2f_{1133}\\
&k_{2222}=\frac{1}{r_e{}^2}h_{2222}g_2{}^4\Big(\frac{1}{4}f_1-\frac{4}{3}f_2+2\sqrt{2}f_{122}\\
&\qquad+16f_{2222}\Big)\\
&k_{2233}=\frac{1}{r_e{}^2}h_{2233}g_2{}^4(4f_2-f_3+\sqrt{2}f_{133}+8f_{2233})\\
&k_{3333}=\frac{4}{r_e{}^2}h_{3333}g_2{}^4f_{3333}\\
&\text{where}\quad h_{ijj}=h^{1/2}/8\pi^3c^{5/2}\omega_i{}^{1/2}\omega_j\\
&\text{and}\quad h_{iijj}=h/16\pi^4c^3\omega_i\omega_j
\end{aligned}\right\}\quad\text{(A-2)}$$

It has been shown by Dennison[8,15] that these cubic and quartic constants are related to α and x by the following expressions:

$$\left.\begin{aligned}
&\alpha_1=-6B_e{}^2/\omega_1-3(2B_e/\omega_1)^{3/2}k_{111}\\
&\alpha_2=B_e{}^2[1/\omega_2-2/(\omega_3+\omega_2)+2/(\omega_3-\omega_2)]\\
&\qquad-(2B_e/\omega_1)^{3/2}k_{122}\\
&\alpha_3=2B_e{}^2[1/\omega_3-2/(\omega_3+\omega_2)-2/(\omega_3-\omega_2)]\\
&\qquad-(2B_e/\omega_1)^{3/2}k_{133}\\
&x_{11}=\frac{3}{2}k_{1111}-(15/4\omega_1)k_{111}{}^2\\
&x_{33}=\frac{3}{2}k_{3333}-\frac{1}{8}[4/\omega_1+1/(2\omega_3+\omega_1)\\
&\qquad-1/(2\omega_3-\omega_1)]k_{133}{}^2\\
&x_{13}=k_{1133}-(3/\omega_1)k_{111}k_{133}-\frac{1}{2}[1/(2\omega_3+\omega_1)\\
&\qquad+1/(2\omega_3-\omega_1)]k_{133}{}^2\\
&x_{23}=k_{2233}-(1/\omega_1)k_{122}k_{133}\\
&\qquad+[\omega_3/\omega_2+\omega_2/\omega_3]B_e\\
&x_{22}+x_{ll}=k_{2222}-(1/2\omega_1)k_{122}{}^2\\
&x_{12}+4x_{22}=k_{1122}+6k_{2222}-(3/\omega_1)k_{111}k_{122}\\
&\qquad-[2/\omega_1+1/(2\omega_2+\omega_1)]k_{122}{}^2
\end{aligned}\right\}\quad\text{(A-3)}$$

The last two equations are adopted in order to eliminate the resonance contribution, $1/(2\omega_2-\omega_1)$, from the expressions.