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Effect of Molecular Vibrations on Gas Electron Diffraction. II. Probability Distribution Function and Phase Parameter for Polyatomic Molecules

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A method has been presented for calculating the first, second, and third moments of the displacement of an internuclear distance in a polyatomic molecule, $\langle \Delta r\rangle$, $\langle \Delta r^2\rangle$, and $\langle \Delta r^3\rangle$. The moments, which depend on the frequencies of normal vibrations, the cubic potential constants, and the temperature of the system, have been related to the extent of distortion of the probability distribution function of the internuclear distance from a Gaussian function caused by the anharmonicity in the potential function. An approximate expression has been obtained for the phase parameter κ in the molecular intensity of gas electron diffraction in terms of the moments. Numerical results are given for CO_2, CS_2, SO_2, H_2O, D_2O, CH_4, and CD_4 by the use of experimental or estimated cubic potential constants. The phase parameters for bonded distances agree with simple estimates based on "diatomic approximation" to the accuracy of current experimental studies, while the phase parameters for nonbonded distances are similar in magnitude to those for bonded distances in spite of their larger mean-square amplitudes of vibration.

In the preceding paper1) (Part I), general expressions have been obtained for the molecular scattering intensity and the radial distribution function. The structural parameters related to gas electron diffraction have been written in terms of the constants c_n of the probability distribution function $P_{ij}(r)$ of the i-j internuclear distance in a molecule,

$$P_{ij}(r_{ij}) = A_{ij}(2\pi\langle \Delta r_{ij}^2\rangle)^{-1/2}\exp(-\Delta r_{ij}^2/2\langle \Delta r_{ij}^2\rangle) \times (1 + \sum_{n=1}^{\infty} c_{nij}\Delta r_{ij}^n), \tag{1}$$

where

$$\Delta r_{ij} = r_{ij} - r_{eij} - \delta r_{ij}, \tag{2}$$

and A_{ij} is a normalization constant. The equilibrium distance and the displacement caused by the centrifugal force are denoted by r_e and δr, respecitvely. Since δr can be calculated easily when the quadratic force field is known2,3) and since δr is usually much smaller than the average Δr, the centrifugal effect will not be discussed further in this paper.

Among the more important structural parameters are the effective internuclear distance r_a, the effective mean-square amplitude l_m, and the phase parameter κ, which appear in the expression of molecular intensity

$$M(s) = \sum\sum_{i<j}{}' A_{ij}c_{ij}(s)\exp(-l_{mij}^2 s^2/2) \times \sin s(r_{aij} - \kappa_{ij}s^2). \tag{3}$$

The subscripts ij will be omitted in the following discussion, since the contributions from different atom pairs are simply additive. The coefficients c_n of the probability function for diatomic molecules have been discussed in detail in Part I by the second-order perturbation method, which relates the c_n coefficients to the constants characterizing the vibrational potential function including anharmonicity.

In the present paper, the above discussion will be extended to polyatomic molecules. Approximate expressions for the most important c_n constants representing anharmonicity, c_1 and c_3, will be obtained by the use of the moment method, with the view of making reasonable estimates for the phase parameters for polyatomic molecules.

There have recently been extensive studies of the internuclear distances3-7) and their mean-square amplitudes8-10) under various definitions: how they differ from one another in pyhsical

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1) K. Kuchitsu, This Bulletin **40**, 498 (1967), preceding paper.

2) M. Iwasaki and K. Hedberg, *J. Chem. Phys.*, **36**, 2961 (1962).

3) M. Toyama, T. Oka and Y. Morino, *J. Mol. Spectry.*, **13**, 93 (1964).

4) Y. Morino, Y. Nakamura and T. Iijima, *J. Chem. Phys.*, **32**, 643 (1960).

5) Y. Morino, K. Kuchitsu and T. Oka, *ibid.*, **36**, 1108 (1962).

6) L. S. Bartell, *ibid.*, **38**, 1827 (1963).

7) K. Kuchitsu, *ibid.*, **44**, 906 (1966).

8) A. Reitan, *Acta Chem. Scand.*, **12**, 785 (1958); Thesis (Trondheim, Norway) (1958).

9) S. J. Cyvin, *Acta Polytechn. Scand.*, **Ph6**, 279 (1960).

10) L. S. Bartell, *J. Chem. Phys.*, **42**, 1681 (1965).

significance and how to derive them experimentally or theoretically by the use of vibrational potential constants. On the other hand, less information has yet been obtained for the phase parameters of polyatomic molecules. Particular attention was paid in the experimental studies of CCl_4,[4,11] $GeCl_4$,[4] CS_2,[12] and $SiCl_4$[13] to the presence of the phase parameters predicted by scattering theory.[14,15] The phase modulation in the molecular intensity was so much more pronounced in hydrides and deuterides that it was possible to determine quantitatively the anharmonicity parameters for methane[16] and water[17] by the aid of the simple theory originally formulated for diatomic molecules.[14,18] Since the experimental or theoretical uncertainty in the phase parameters may become one of the largest sources of systematic errors in the experimental internuclear distances,[15] it seems to be profitable to investigate the nature of the phase parameters in search for the answers to the following questions[14]: To what extent can the κ parameters for bonded distances be represented by the "diatomic approximation," which assumes that the stretching anharmonicity of a bond A–B is similar to that of the AB diatomic molecule? Are the κ parameters for nonbonded distances much larger than those for bonded distances because of the larger mean-square amplitudes?

Perturbation Method

Since the phase parameter is primarily related to the c_3 constant of the $P(r)$ function,[1,4]

$$\kappa = c_3\langle \varDelta r^2\rangle^3 + \cdots, \tag{4}$$

the estimation of κ depends on that of c_3. A method for calculating the c_n constants of the probability function was first formulated by Reitan.[8] He applied the second-order perturbation method to a polyatomic system with nondegenerate normal vibrations and without accidental degeneracies, and obtained general expressions for the probability function in terms of the normal coordinates, for the mean distance, and for the mean-square amplitude correct to this order. He further applied the theory to the linear and bent XY_2 molecules for deriving the probability functions for the X–Y and Y–Y distances, $P(r_{X-Y})$ and $P(r_{Y-Y})$, to the first order of approximation; the c_1 and c_3 constants for CO_2 and H_2O were calculated numerically by the use of the experimental cubic potential constants. A similar method was applied by Morino *et al.* to CS_2[19] and SO_2[20].

In the above approach, the anharmonic potential terms in the vibrational potential function,

$$V/\boldsymbol{hc} = \frac{1}{2}\sum_i \omega_i q_i^2 + \sum\sum\sum_{i\leqq j\leqq k} k_{ijk} q_i q_j q_k + \cdots, \tag{5}$$

where q_i denotes the dimensionless normal coordinates,[21]

$$q_i = (4\pi^2 \boldsymbol{c}\omega_i/\boldsymbol{h})^{1/2} Q_i, \tag{6}$$

are taken as perturbations, and the vibrational wave functions for various quantum states $v(v_1, v_2,\cdots)$, $\psi_v(Q_1, Q_2,\cdots)$, are obtained. The probability distribution function of the whole system is then given in terms of the normal coordinates,

$$P(Q_1, Q_2,\cdots) = \sum_v W_v |\psi_v(Q_1, Q_2,\cdots)|^2, \tag{7}$$

where

$$W_v = \exp[-E(v)/\boldsymbol{k}T]/\sum_v \exp[-E(v)/\boldsymbol{k}T]. \tag{8}$$

In order to derive the probability function for an internuclear distance r_{AB}, given in Eq. (1), one has to make a transformation of coordinates into those involving $\varDelta r_{AB}$, and then to carry out a multiple integration over all the rest of the coordinates leaving $\varDelta r_{AB}$.

Although the above-mentioned procedure can in principle be applied to any system, it requires lengthy calculations even in the first order, particularly when the molecule in question has a large number of atoms. Nor is it practical to perform direct integrations of the molecular intensity or the radial distribution function with respect to the normal coordinates,[22-24]

$$M(s) = c(s)\int_0^\infty \cdots \int_0^\infty P(Q_1,\cdots) \times \frac{\sin s[r_e + \delta r + \varDelta r(Q_1,\cdots)]}{s[r_e + \delta r + \varDelta r(Q_1,\cdots)]}\,\mathrm{d}Q_1\cdots, \tag{9}$$

or

$$f(r) = \left(\frac{\pi}{16b}\right)^{1/2} c^0 \int_0^\infty \cdots \int_0^\infty \frac{P(Q_1,\cdots)}{r_e + \delta r + \varDelta r(Q_1,\cdots)} \times \exp\left\{-\frac{[r_e + \delta r + \varDelta r(Q_1,\cdots) - r]^2}{4b}\right\}\mathrm{d}Q_1\cdots, \tag{10}$$

when anharmonicity is taken into account.

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11) L. S. Bartell, L. O. Brockway and R. H. Schwendeman, *ibid.*, **23**, 1854 (1955).
12) Y. Morino and T. Iijima, This Bulletin, **35**, 1661 (1962).
13) Y. Morino and Y. Murata, *ibid.*, **38**, 104 (1965).
14) L. S. Bartell, *J. Chem. Phys.*, **23**, 1219 (1955).
15) Y. Morino, K. Kuchitsu and Y. Murata, *Acta Cryst.*, **18**, 549 (1965).
16) L. S. Bartell, K. Kuchitsu and R. J. deNeui, *J. Chem. Phys.*, **35**, 1211 (1961).
17) S. Shibata and L. S. Bartell, *ibid.*, **42**, 1147 (1965).
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19) Y. Morino and T. Iijima, This Bulletin, **36**, 412 (1963).
20) Y. Morino and T. Fukuyama, to be published.
21) H. H. Nielsen, *Rev. Mod. Phys.*, **23**, 90 (1951).
22) R. W. James, *Physik. Z.*, **33**, 737 (1932).
23) J. Karle and I. L. Karle, *J. Chem. Phys.*, **18**, 957 (1950).
24) Y. Morino and E. Hirota, *ibid.*, **23**, 737 (1955).

Moment Method

Provided the observed or estimated potential constants are available, it is easier and more straightforward than the above procedure to calculate the moments of the displacements.[16,25] To the first order of approximation, the probability function may be written as[8,14]

$$P(r) = (2\pi\langle\Delta r^2\rangle)^{-1/2}\exp(-\Delta r^2/2\langle\Delta r^2\rangle) \times (1 + c_1\Delta r + c_3\Delta r^3). \tag{11}$$

In order to calculate c_1 and c_3, it is sufficient to evaluate the first three moments, $\langle\Delta r\rangle$, $\langle\Delta r^2\rangle$, and $\langle\Delta r^3\rangle$. It is easily shown that

$$c_1 = (5\langle\Delta r\rangle\langle\Delta r^2\rangle - \langle\Delta r^3\rangle)/2\langle\Delta r^2\rangle^2, \tag{12}$$

$$c_3 = (\langle\Delta r^3\rangle - 3\langle\Delta r\rangle\langle\Delta r^2\rangle)/6\langle\Delta r^2\rangle^3. \tag{13}$$

The latter equation may be combined with Eq. (4), which leads to

$$\kappa \approx \frac{1}{6}(\langle\Delta r^3\rangle - 3\langle\Delta r\rangle\langle\Delta r^2\rangle). \tag{14}$$

To this order of approximation, the other parameters given in Eq. (3) are shown to be[1]

$$r_a \approx r_e + \delta r + \langle\Delta r\rangle - \langle\Delta r^2\rangle/r_e, \tag{15}$$

and

$$l_m{}^2 \approx \langle\Delta r^2\rangle. \tag{16}$$

The calculation of the moments depends on the expansion of the displacement Δr in terms of the normal coordinates on one hand, and on the calculation of the quantum-mechanical average of the normal coordinates on the other.

Since this expansion is nonlinear,[26] it is convenient to express Δr first in terms of the local Cartesian displacement coordinates, which can then be transformed linearly into the normal coordinates. For a given pair of atoms A–B, the local z axis may be taken along the equilibrium positions of the atoms, and the x and y axes perpendicular to z. A matrix of the coefficients of the orthogonal transformation from any set of Cartesian displacement coordinates, Δx, Δy, Δz, into the normal coordinates, Q, is often denoted by $\boldsymbol{L_X}$[27]; the method for deriving $\boldsymbol{L_X}$ by the use of the $\boldsymbol{B}$ and $\boldsymbol{L}^{-1}$ matrices of the molecule is well known.[3,24]

A geometrical consideration shows that[25]

$$\langle\Delta r\rangle = \langle\Delta z\rangle + \langle\Delta\rho^2\rangle/2r_e - \langle\Delta z\Delta\rho^2\rangle/2r_e{}^2 + \langle\Delta z^2\Delta\rho^2\rangle/2r_e{}^3 - \langle\Delta\rho^4\rangle/8r_e{}^3 + \cdots, \tag{17}$$

$$\langle\Delta r^2\rangle = \langle\Delta z^2\rangle + \langle\Delta z\Delta\rho^2\rangle/r_e - \langle\Delta z^2\Delta\rho^2\rangle/r_e{}^2 + \langle\Delta\rho^4\rangle/4r_e{}^2 + \cdots, \tag{18}$$

$$\langle\Delta r^3\rangle = \langle\Delta z^3\rangle + 3\langle\Delta z^2\Delta\rho^2\rangle/2r_e + 3\langle\Delta z\Delta\rho^4\rangle/4r_e{}^2 - 3\langle\Delta z^3\Delta\rho^2\rangle/2r_e{}^2 + 3\langle\Delta z^4\Delta\rho^2\rangle/2r_e{}^3 - 15\langle\Delta z^2\Delta\rho^4\rangle/8r_e{}^3 + \langle\Delta\rho^6\rangle/8r_e{}^3 + \cdots, \tag{19}$$

where

$$\Delta\rho^2 = \Delta x^2 + \Delta y^2. \tag{20}$$

The summations converge quickly in ordinary circumstances; $\langle\Delta r\rangle$ and $\langle\Delta r^3\rangle$ are essentially represented by the first two terms, and as is well known,[8,28] $\langle\Delta r^2\rangle$ by the first term alone. The mean values $\langle\Delta z\rangle$, $\langle\Delta z^3\rangle$, and $\langle\Delta z\Delta\rho^2\rangle$ involve anharmonic potential constants to the first order, while the rest of the mean values in the above equations (17) and (18) can be evaluated without regard to the anharmonicity to this order of approximation. Since the axes are orthogonal to one another, the higher-order terms $\langle\Delta z^2\Delta\rho^2\rangle$ and $\langle\Delta\rho^4\rangle$ can be reduced in this harmonic approximation to quadratic products, $\langle\Delta z^2\rangle\langle\Delta\rho^2\rangle$ and $3\langle\Delta\rho^2\rangle^2-4\langle\Delta x^2\rangle\langle\Delta y^2\rangle$, respectively. The latter result stems from the fact that, if the potential function is harmonic, $\langle Q_i{}^4\rangle$ is equal to $3\langle Q_i{}^2\rangle^2$ for any normal coordinate Q_i. The last two anharmonic terms in Eq. (19) may be approximated by products in a similar way.

Mean Values of Normal Coordinates

It is possible to calculate by the first-order perturbation theory the linear, quadratic, and cubic mean values of the normal coordinates for a system in thermal equilibrium at an arbitrary temperature T. The linear mean value has been given by Toyama *et al.*[3] as:

$$\langle Q_i\rangle = -(\boldsymbol{h}/16\pi^2\boldsymbol{c}\omega_i{}^3)^{1/2}(3k_{iii}T_i + \sum_{j\neq i} k_{ijj}T_j), \tag{21}$$

where

$$T_i = \coth(\boldsymbol{hc}\omega_i/2\boldsymbol{k}T). \tag{22}$$

For a molecule with degenerate vibrations, a different number should be assigned to each one of the degenerate set of normal coordinates ($s\sigma$ and $s\sigma'$, *etc.*, in Nielsen's notation[21]) so that the total number of i or j is $3N$-5 and $3N$-6 for linear and nonlinear molecules, respectively. By the requirement of symmetry, only those linear mean values which correspond to the totally symmetric vibrations are nonvanishing. The same expression has been derived by Bartell[6] directly from the zeroth-order quadratic mean values by the use of the requirement, $\langle\partial V/\partial Q_i\rangle=0$.

The quadratic mean values are given by[22]

$$\langle Q_iQ_j\rangle = (\boldsymbol{h}/8\pi^2\boldsymbol{c}\omega_i)T_i\delta_{ij}, \tag{23}$$

in which the first-order effect of the quartic

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[25] Y. Morino, J. Nakamura and P. W. Moore, *ibid.*, **36**, 1050 (1962).

[26] J. Pliva, *Collection Czech. Chem. Commun.*, **23**, 777 (1958).

[27] B. L. Crawford, Jr., and W. H. Fletcher, *J. Chem. Phys.*, **19**, 141 (1951).

constants and the sceond-order effect of the cubic constants are ignored.

Calculations of the cubic mean values are similar to but more complicated than those of the linear mean values. With the aid of the relations in regard to the Boltzmann weight factor given in Eq. (8),

$$\sum_v W_v = 1, \qquad \sum_v (v_i + 1/2) W_v = T_i,$$

and

$$\sum_v (2v_i^2 + 2v_i + 1) W_v = T_i^2, \tag{24}$$

the following equations are obtained (for $i \neq j \neq k$):

$$\begin{aligned}\langle Q_i^3 \rangle &= -(\boldsymbol{h}/4\pi^2 \boldsymbol{c}\omega_i)^{3/2}(4\omega_i)^{-1} \\ &\quad \times [k_{iii}(15T_i^2 - 4) + 3T_i \sum_j k_{ijj} T_j],\end{aligned} \tag{25}$$

$$\begin{aligned}\langle Q_i Q_j^2 \rangle &= -(\boldsymbol{h}/4\pi^2 \boldsymbol{c}\omega_i)^{3/2}(4\omega_j)^{-1} \\ &\quad \times \{T_i(3k_{iii}T_i + \sum_k k_{ikk}T_k) + k_{ijj}[2T_j^2 - 1 \\ &\quad + \frac{1}{2}\omega_i(\omega_i + 2\omega_j)^{-1}(T_j^2 + 1 + 2T_i T_j) \\ &\quad + \frac{1}{2}\omega_i(\omega_i - 2\omega_j)^{-1}(T_j^2 + 1 - 2T_i T_j)]\},\end{aligned} \tag{26}$$

$$\begin{aligned}\langle Q_i Q_j Q_k \rangle &= -(\boldsymbol{h}/4\pi^2 \boldsymbol{c})^{3/2}(16\omega_i\omega_j\omega_k)^{-1/2} \\ &\quad \times k_{ijk}(\omega_i^4 + \omega_j^4 - 2\omega_i\omega_j - 2\omega_j\omega_k - 2\omega_k\omega_i)^{-1} \\ &\quad \times \{[\sum_{\substack{ijk \\ \text{(cyclic)}}} \omega_i(\omega_i^2 - \omega_j^2 - \omega_k^2)T_j T_k] + 2\omega_i\omega_j\omega_k\}.\end{aligned} \tag{27}$$

When the k_{ijj} constant is zero, $\langle Q_i Q_j^2 \rangle$ is simply equal to $\langle Q_i \rangle \langle Q_j^2 \rangle$. In contrast to the case of the linear mean values, some of the cubic mean values related to degenerate normal coordinates may not vanish by symmetry, since their direct-product representations may contain totally symmetric species. Thus all the nonvanishing cubic potential constants should be counted in the above equations. For example, the cubic potential term $k_{333}(Q_{3a}^3 - 3Q_{3a}Q_{3b}^2)$ is finite for the planar or nonplanar XY_3 molecule,[21] where the coordinates Q_{3a} and Q_{3b} are so chosen that they transform into Q_{3a} and $-Q_{3b}$, respectively, by a vertical reflection σ_v. The corresponding mean values are shown to be:

$$\begin{aligned}\langle Q_{3a}^3 \rangle &= -\langle Q_{3a} Q_{3b}^2 \rangle \\ &= -(\boldsymbol{h}/4\pi^2 \boldsymbol{c}\omega_3)^{3/2}(k_{333}/\omega_3)(3T_3^2/2 - 1).\end{aligned} \tag{28}$$

The present theory is applicable to any molecular system, although at present the lack of experimental information about the cubic potential constants confines its application to some of the simplest molecules. Studies are being made in recent years to determine cubic constants (or relations among cubic constants) from the rotation-vibration interaction constants α, l-type doubling constants,[29] and the resonance interaction constants[30] observed by high-resolution spectroscopy. Methods for making plausible estimates of the cubic constants have also been discussed.[31,32]

Equations (25) to (27) take simpler forms when all the frequencies are so high that all the T_i factors are essentially unity. The last term in Eq. (26) with a resonance denominator vanishes in that case. In the case of strong accidental degeneracy, where ω_i is nearly equal to $2\omega_j$, this term needs a separate consideration associated with a direct solution of secular equations. For the CO_2 and CS_2 molecules, for example, the resonance term in $\langle Q_1(Q_{2a}^2 + Q_{2b}^2) \rangle$ is essentially determined by the first two contributions from the $(10, 02^0)$ and $(11^1, 03^1)$ diads,[33]:

$$\begin{aligned}\langle Q_1(Q_{2a}^2 + Q_{2b}^2) \rangle_{res.} &= -(\boldsymbol{h}/4\pi^2 \boldsymbol{c})^{3/2} \\ &\quad \times (16k_{122}/\omega_1^{1/2}\omega_2)\sinh(\boldsymbol{hc}\omega_1/\boldsymbol{k}T) \\ &\quad \times \sinh^2(\boldsymbol{hc}\omega_2/\boldsymbol{k}T)\exp[-\boldsymbol{hc}(\omega_1 + 2\omega_2)/2\boldsymbol{k}T] \\ &\quad \times [\sinh(\boldsymbol{hc}\Delta_1/2\boldsymbol{k}T)/\Delta_1 \\ &\quad + 4\exp(-\boldsymbol{hc}\omega_2/\boldsymbol{k}T)\sinh(\boldsymbol{hc}\Delta_2/\boldsymbol{k}T)/\Delta_2],\end{aligned} \tag{29}$$

where

$$\Delta_1^2 = (\omega_1 - 2\omega_2)^2 + 2k_{122}^2,$$

and

$$\Delta_2^2 = (\omega_1 - 2\omega_2)^2 + 4k_{122}^2. \tag{30}$$

Numerical Results and Discussion

Numerical calculations are made for the following molecules for which all the cubic constants have been reported: CO_2,[32,34] CS_2,[12] SO_2,[35] H_2O,[31,36] D_2O[31] by spectroscopic measurements, and CH_4,[37] CD_4[37] by an estimation based on a simple potential function. The moments and the c_1 and c_3 constants are listed in Tables 1 and 2, respectively,[38] for bonded and nonbonded distances. The effect of the Fermi resonance between ν_1 and $2\nu_2$ for CO_2 and CS_2 is taken into account by Eq. (29) in

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28) Y. Morino, K. Kuchitsu and T. Shimanouchi, *ibid.*, **20**, 726 (1952).

29) Y. Morino and T. Nakagawa, *ibid.*, **44**, 841 (1966).

30) Y. Morino and T. Saito, *J. Mol. Spectry.*, **19**, 435 (1966).

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

32) K. Kuchitsu and Y. Morino, This Bulletin, **38**, 805, 814 (1965).

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

34) D. M. Dennison, *Rev. Mod. Phys.*, **12**, 175 (1940).

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

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

37) K. Kuchitsu and L. S. Bartell, *J. Chem Phys.*, **36**, 2470 (1962).

38) Some of the linear and quadratic mean values, which agree essentially with the present results, have been reported in the literature.[8,12,31,37]

TABLE 1. MEAN VALUES OF INTERNUCLEAR DISPLACEMENTS

	Units	$\langle \Delta z\rangle$ 10^{-2} Å	$\langle \Delta z^2\rangle$ 10^{-2} Å^2	$\langle \Delta\rho^2\rangle$ 10^{-2} Å^2	$\langle \Delta z^3\rangle$ 10^{-4} Å^3	$\langle \Delta z\Delta\rho^2\rangle$ 10^{-4} Å^3	$\langle \Delta r\rangle$ 10^{-2} Å	$\langle \Delta r^2\rangle$ 10^{-2}Å^2	$\langle \Delta r^3\rangle$ 10^{-4} Å^3	Ref.[a]
CO_2	C-O	0.235	0.120	0.622	0.116	0.090	0.503	0.121	0.213	32
	O-O	0.471	0.156	0	0.250	0	0.471	0.156	0.250	
CS_2	C-S	0.098	0.150	1.089	0.082	−0.104	0.448	0.151	0.241	12
	S-S	0.196	0.170	0	0.129	0	0.196	0.170	0.129	
SO_2	S-O	0.408	0.123	0.196	0.187	0.074	0.477	0.124	0.212	35
	O-O	0.757	0.302	0.023	0.729	0.021	0.762	0.302	0.733	
H_2O	O-H	1.43	0.458	0.549	2.47	0.637	1.71	0.465	2.84	31
	H-H	2.26	1.278	2.95	8.57	0.857	2.35	1.282	8.93	
D_2O	O-D	1.06	0.334	0.405	1.35	0.336	1.27	0.337	1.55	31
	D-D	1.59	0.911	1.88	4.19	0.392	1.65	0.913	4.36	
CH_4	C-H	1.47	0.576	1.66	3.16	1.116	2.23	0.590	4.51	37
	H-H	2.40	1.493	1.85	11.21	4.63	2.91	1.516	13.49	
CD_4	C-D	1.06	0.423	1.25	1.69	0.426	1.64	0.431	2.43	37
	D-D	1.74	1.067	1.32	5.78	2.40	2.11	1.079	6.96	

a) Calculated by the use of the cubic potential constants given in the references.

TABLE 2. PARAMETERS OF PROBABILITY DISTRIBUTION FUNCTION[a]

(Units: c_1 in Å^{-1}, c_3 in Å^{-3})

Molecule	Method	Bonded atom pair c_1	Bonded atom pair c_3	Nonbonded atom pair c_1	Nonbonded atom pair c_3	Ref.
CO_2	Perturbation[b]	2.75	294	2.21	84.7	8
	Moment[c]	3.13	281	2.41	129	
	Approximate[d]	2.39	333	(2.10	344)	
CS_2	Perturbation	2.16	186	0.65	98.9	19
	Moment	2.13	186	0.65	98.9	
	Approximate	1.95	217	(0.99	306)	
SO_2	Perturbation	2.71	312	2.29	26.7	20
	Moment	2.72	301	2.29	26.5	
	Approximate	2.05	285	(1.84	207)	
H_2O	Perturbation	2.64	85.6	2.16	0.60	8
	Moment	2.64	75.4	1.87	−0.90	
	Approximate	2.31	83.8	(2.16	28.1)	
D_2O	Moment	2.60	115	1.90	−3.41	
	Approximate	2.41	120	(2.14	40.1)	
CH_4	Moment	2.95	46.5	1.87	1.17	
	Approximate	1.98	57.3	(2.15	24.2)	
CD_4	Moment	2.95	65.6	1.89	1.82	
	Approximate	1.98	78.0	(2.10	34.8)	

a) Coefficients of the first-order probability distribution function (Eq. (1)) calculated at room temperature.

b) First-order perturbation calculations given in the references.

c) Derived from the moment method, Eqs. (12) and (13), by the use of the mean values given in Table 1.

d) Approximate estimates according to Eqs. (31) and (32) in analogy with diatomic molecules with the a_3 parameters taken from Ref. 32.

the calculation of the $\langle \Delta z\Delta\rho^2\rangle$ for the C–O and C–S distances. For the first four molecules, the c_1 and c_3 constants obtained by the perturbation procedure[8,19,20] are in essential accord with those obtained by the moment method in the present calculations, in which the same potential constants are used. However, since more reliable vibrational frequencies and rotation-vibration interaction constants are available for CO_2[39] and HO_2[40], the cubic constants based on these experimental values[31,32] are also used for the calculations, and only the latter results are listed in the tables. The phase parameters calculated by Eq. (14) are given in Table 3 with previous estimates[12] and experimental values.[16,17]

In order to test the diatomic approximation, the c_1 and c_3 constants for a bonded distance are calculated by[1]:

$$c_1 = a_3(1 - \chi)^2/(1 + \chi)^2, \tag{31}$$

$$c_3 = a_3(1 + 10\chi + \chi^2)/6(1 + \chi)^2\langle \Delta r^2\rangle, \tag{32}$$

where

$$\chi = \exp(-\boldsymbol{hc}\omega_{\text{effective}}/\boldsymbol{k}T). \tag{33}$$

The parameter a_3 is taken from that for the corresponding diatomic molecule listed in Ref. 32. The mean-square amplitude of the bond and an effective Boltzmann factor corresponding to a characteristic frequency of the bond-stretching vibration are adopted instead of those for the corresponding diatomic molecule. The diatomic c_1 constants are smaller than the bond c_1 constants by only a few tenths, while for c_3 the predictions seem to be slightly larger than the bond values. A comparison of the parameters calculated by Eq. (4) given in Table 3 asserts the utility of the diatomic approximation for bonded distances to the current need in gas electron diffraction, since the

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[39] C. P. Courtoy, *Can. J. Phys.*, **35**, 608 (1957); *Ann. soc. sci. Bruxelles*, **I73**, 5 (1959).

[40] W. S. Benedict, N. Gailar and E. K. Plyler, *J. Chem. Phys.*, **24**, 1139 (1956).

TABLE 3. ESTIMATION OF THE PHASE PARAMETERS κ
(in 10^{-6} Å^3 units)

Molecule	CO_2		CS_2		SO_2	
pair	C-O	O-O	C-S	S-S	S-O	O-O
Moment[a]	0.51	0.49	0.64	0.49	0.58	0.73
Diatomic[b]	0.59	(1.3)	0.74	(1.5)	0.55	(0.57)
Est.[c]	—	—	1.0	0.6	—	—

Molecule	H_2O		D_2O		CH_4		CD_4	
pair	O-H	H-H	O-D	D-D	C-H	H-H	C-D	D-D
Moment	7.6	−1.9	4.4	−2.6	9.9	4.1	5.3	2.3
Diatomic	8.4	(59)	4.6	(30)	11.8	(84)	6.3	(44)
Exp.[d]	$9._5$	—	$5._1$	—	$16._1$	—	$9._5$	—

a) Estimates by Eq. (14) based on the mean values listed in Table 1. Room temperature.
b) Estimates based on the assumption that the atom pair in question were a diatomic molecule. Calculated by the use of Eq. (4) with the $\langle \Delta r^2 \rangle$ in Table 1 and the "Approximate" c_3 in Table 2.
c) Estimates reported in Ref. 12.
d) Experimental values reported in Refs. 16 and 17.

discrepancies are within the uncertainties of ordinary experiments.

Similar estimates for nonbonded atom pairs are given in parentheses, since the physical significance of the diatomic approximation is questionable in this case. The a_3 parameter of the atom pair is tentatively set equal to that of the corresponding diatomic molecule, and the Boltzmann factor corresponding to the bond-bending frequency is used. Probably the simplest method for making a crude guess of the c_1 constant of a nonbonded atom pair is to use Eq. (31) with the a_3 parameter assumed to be 2 Å^{-1} and with a suitable χ factor. Because of the χ factor, c_1 should be somewhat smaller than 2 Å^{-1}. The c_3 and the κ parameters for nonbonded distances appear several-fold smaller than the diatomic estimates, and the values are of comparable order of magnitude with those of the bonded distances.

As expected from Eq. (2), the contribution to the molecular intensity from a nonbonded pair damps much faster than that of a bonded pair, because the mean-square amplitude of the former is larger. With the κ values of a similar magnitude, the phase modulation caused by κ should be much less significant for a nonbonded atom pair than for a bonded pair. Nevertheless, the phase parameter for a nonbonded pair may be measured by a careful experiment if a suitable molecule is selected. For example, carbon tetrachloride, which has nonbonded Cl–Cl distances with a relatively strong scattering power, is probably a molecule of this category. The experimental κ parameter for a nonbonded distance determined in this way will be a valuable guide in the study of the origin of anharmonicity, and especially the anharmonicity in bending vibrations, on which very little is known at present.[41]

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41) K. Kuchitsu and Y. Morino, *Spectrochim. Acta*, **22**, 33 (1966).