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Effect of Molecular Vibrations on Gas Electron Diffraction. I. Probability Distribution Function and Molecular Intensity for Diatomic Molecules

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General expressions and their practical approximations are presented for the molecular intensity of gas electron diffraction and the radial distribution function for an atom pair in the molecule which exerts moderately anharmonic intramolecular motion in thermal equilibrium. The calculations are based on a polynomial expansion of the probability distribution function of the internuclear distance around a Gaussian function representing harmonic vibration. The coefficients of the expansion for a diatomic system are calculated by the second-order perturbation method in terms of the coefficients of the potential energy expanded to the fourth order of the displacement in the internuclear distance. The structural parameters under various definitions (the mean internuclear distances, the mean square amplitudes, and the phase parameters) of a number of diatomic molecules are tabulated by the use of the spectroscopic values ω_e, α_e, and x_e taken from the literature. The temperature dependence of the structural parameters is discussed.

Recent advances in the technique of gas electron diffraction has called for a careful examination of the theoretical formulation on which the analysis of experimental data is based. If approximations in the basic equations are inadequate, or if the structural parameters in question have uncertain physical significance, the analysis may involve appreciable systematic errors as compared with experimental precision. On the other hand, an appropriate analysis can supply useful information on various problems of molecular structure. For example, the failure of the Born approximation in heavy-metal fluorides[1] and the effects of chemical binding[2] and anharmonic vibrations[3] on the molecular scattering intensities of simple hydrides have been observed in recent experimental and theoretical studies.

It is the purpose of the present paper to investigate the molecular intensity of a system exerting anharmonic vibration in thermal equilibrium, and to derive as simple expressions as possible for use in the actual analysis of experimental data of gas electron diffraction with sufficient accuracy. The discussions in the present part will first deal with the theory of vibrational effects in general, while diatomic molecules will be studied in more detail in later sections. The discussions can be extended to polyatomic systems, particularly to the bonded atom pairs in polyatomic molecules; this will be the subject of Part II.

Except for a system making extremely anharmonic intramolecular motion, such as internal rotation or puckering oscillation with a low librational frequency, it seems to be convenient to represent the probability distribution function of an internuclear distance as a slightly distorted Gaussian function,[4] since one can expect good convergence of the polynominal expansion for an ordinary atom pair in a molecule. In a previous paper by Kuchitsu and Bartell,[5] a general expression for molecular intensity was obtained on this basis for a diatomic system and for the Morse oscillator in the ground vibrational state.

The equations derived in their paper are here extended to a system in thermal equilibrium at an arbitrary temperature. The temperature dependences of the probability distribution function and the mean values of various structural parameters are calculated by means of a second-order perturbation theory in a way similar to that reported by Reitan[6] on the probability distribution function and some of the mean values. The present calculations are based on a potential function expanded to the fourth order of the displacement, whereas the Morse function was assumed in Reitan's calculations. For an ordinary diatomic molecule, the representation of the potential energy

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[1] V. Schomaker and R. Glauber, *Nature,* **170,** 290 (1952); H. M. Seip and R. Stølevik, *Acta Chem. Scand.*, **19**, 1955 (1965); **20**, 385, 1535 (1966).

[2] R. A. Bonham and T. Iijima, *J. Chem. Phys.,* **42**, 2612 (1965).

[3] L. S. Bartell, K. Kuchitsu and R. J. deNeui, *ibid.,* **35,** 1211 (1961).

[4] L. S. Bartell, *ibid.,* **23,** 1219 (1955).

[5] K. Kuchitsu and L. S. Bartell, *ibid.,* **35,** 1945 (1961).

[6] A. Reitan, Det Kgl. Norske Videnskabers Selskabs Skrifter, Nr. 2 (1958).

by a Morse function seems to have sufficient accuracy for the present purpose. However, the present expression of the probability distribution function will be useful when polyatomic systems are studied, since the distribution functions are not necessarily Morse-like in that case.

A similar problem was discussed by Bonham and Peacher[7] and recently by Bonham and Su[8]. Analytical expressions for the moments of the probability function and molecular intensity were obtained as functions of temperature with explicit consideration of rotation-vibration interaction. The Hellman-Feynman theorem and the hypervirial theorem were used in the latter paper.

Probability Distribution Function

The probability distribution function of an internuclear distance r in a molecule in thermal equilibrium at a temperature T may be expanded around a Gaussian function representing a harmonic motion

$$P(r) = (A/\sqrt{2\pi}\, l_h)\exp(-\Delta r^2/2l_h^2)(1+\sum_{n=1}^{\infty} c_n \Delta r^n), \tag{1}$$

where A is a normalization constant close to unity given by

$$A = \{1+\sum_{m=1}^{\infty}[(2m)!/2^m m!]c_{2m}l_h^{2m}\}^{-1}, \tag{2}$$

and a variable Δr represents the displacement from the equilibrium internuclear distance in regard to the specified temperature.

$$\Delta r = r - r_e - \delta r. \tag{3}$$

Except for the hydrogen molecule at a low temperature, the centrifugal distortion δr of any diatomic or polyatomic system can be calculated classically by using the quadratic force constants of the system[9,10] and is shown to be proportional to $\boldsymbol{k}T$. As mentioned by Bonham and Peacher,[7] Eq. (3) dispenses with complicated calculations involving rotation-vibration interaction in a rotating molecule. The δr for a diatomic molecule is given by[4]

$$\delta r = \boldsymbol{k}T/2\pi^2\mu\boldsymbol{c}^2\omega_e^2, \tag{4}$$

where μ and ω_e are the reduced mass and the normal vibrational frequency, respectively.

The harmonic mean square amplitude l_h^2 can be calculated easily if the quadratic force constants of the molecule are known.[11,12] For a polyatomic molecule, it is sometimes important to discriminate the total mean-square amplitude $\langle\Delta r^2\rangle$ with the mean-square projected amplitude[13] $\langle\Delta z^2\rangle$, although either amplitude can be taken as l_h^2 if the constants c_n are adjusted accordingly. It is well known that for a diatomic molecule,[14]

$$l_h^2 = l_\alpha^2(1+\chi)/(1-\chi), \tag{5}$$

where $$l_\alpha^2 = \boldsymbol{h}/8\pi^2\mu\boldsymbol{c}\omega_e, \tag{6}$$

and $$\chi = \exp(-\boldsymbol{hc}\omega_e/\boldsymbol{k}T). \tag{7}$$

The coefficients c_n depend on temperature and on the constants which characterize the degree of anharmonicity. The $P(r)$ function depends on temperature through l_h and c_n. At the absolute zero temperature, Eq. (1) agrees with the zero-point probability distribution function defined in Ref. 5, where explicit expressions of c_n were given for the Morse oscillator and a cubic oscillator in the ground vibrational state.

General Equations

The equations derived in Ref. 5 can be applied to the present problem provided the zero-point mean amplitude l_α is replaced by the harmonic amplitude l_h. The reduced molecular intensity of gas electron diffraction is defined by[15]

$$M(s) = I_T(s)/I_B(s) - 1 = \sum_{i<j}\sum{}' M_{ij}(s). \tag{8}$$

The contribution to $M(s)$ from the i-j atom pair in a molecule is given by[16]

$$M_{ij}(s) = c_{ij}(s)\int_0^\infty P_{ij}(r)(\sin sr/sr)\,\mathrm{d}r, \tag{9}$$

where $c_{ij}(s)$ is related to the complex atomic scattering factors of the component atoms,[17]

$$c_{ij}(s) = 2|f_i(s)||f_j(s)| \times \cos[\eta_i(s)-\eta_j(s)]/[\sum_i |f_i(s)|^2 + S_i(s)]. \tag{10}$$

This equation is based on the independent-atom model,[18] which ignores the effect of chemical binding, and therefore assumes that atoms retain spherical electronic distributions even when the molecule vibrates; $c_{ij}(s)$ is hence assumed to be independent of the internuclear distance. This is a valid approximation except for hydrides at

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[7] R. A. Bonham and J. L. Peacher, *J. Chem. Phys.*, **38**, 2319 (1963).

[8] R. A. Bonham and L. S. Su, *ibid.*, **45**, 2827 (1966).

[9] M. Iwasaki and K. Hedberg, *ibid.*, **36**, 2961 (1962).

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

[11] Y. Morino, K. Kuchitsu and T. Shimanouchi, *J. Chem. Phys.*, **20**, 726 (1952).

[12] S. J. Cyvin, *Acta Polytechn. Scand.*, **Ph6**, 279 (1960).

[13] J. Karle and I. L. Karle, *J. Chem. Phys.*, **18**, 957 (1950).

[14] R. W. James, *Physik. Z.*, **33**, 737 (1932).

[15] L. S. Bartell, L. O. Brockway and R. H. Schwendeman, *J. Chem. Phys.*, **23**, 1854 (1955).

[16] P. Debye, *ibid.*, **9**, 55 (1941).

[17] R. Glauber and V. Schomaker, *Phys. Rev.*, **89**, 667 (1953).

[18] R. A. Bonham and T. Iijima, *J. Phys. Chem.*, **67**, 2266 (1963).

very small scattering angles. Since the contributions from different atom pairs in a molecule are additive, each contribution can be dealt with separately provided each $P_{ij}(r)$ is obtained. For simplicity, the subscripts ij will be left out in the following discussion.

After integration of Eq. (9) by using Eq. (1), $M(s)$ may be written with three effective parameters as

$$M(s) = Ac(s) \exp(-l_m{}^2 s^2/2) \sin s(r_a - \kappa s^2), \quad (11)$$

where r_a is a constant, and $l_m{}^2$ and κ are in general even functions of s. If the potential function is harmonic, that is, if all c_n are zero, Eq. (10) can be reduced to Debye's equation,[16] where $l_m{}^2 = l_h{}^2$ and $\kappa = 0$ when minor contributions from higher-order terms of l_h/r_e are ignored.

The basic equations may be expressed in terms of a set of constants ε_n defined as infinite polynomials of c_n,

$$\varepsilon_n = \sum_{m=0}^{\infty} [(n+2m)!/2^m n! m!] d_{n+2m} l_h{}^{2m}, \qquad (n = 0, 1, 2, \cdots) \quad (12)$$

where $\quad d_0 = 1$, and $d_n = c_n - d_{n-1}/r_e$. (13)

Since l_h is only a few percent of r_e, the summation of ε_n usually converges rapidly when n is a small number, so that the addition of the first few terms is sufficient for evaluating ε_n. The ε_n constants for large n (say $n > 6$) are relatively unimportant. The constant ε_0 is very nearly unity. Numerical calculations of the ε constants for known or assumed c_n constants may be programmed for an electronic computer.

It can be shown that the effective internuclear distance r_a is equal to $r_g(1)$, the center of gravity of the $P(r)/r$ function and that of the radial distribution function, defined by Bartell.[4] This distance is related to the center of gravity of the $P(r)$ function r_g as[5]

$$\begin{aligned} r_a &= r_e + \delta r + \varepsilon_1 l_h{}^2/\varepsilon_0 \\ &= r_g - [\varepsilon_0 + (2\varepsilon_2 - \varepsilon_1{}^2/\varepsilon_0) l_h{}^2] l_h{}^2/ \\ &\qquad (\varepsilon_0 r_e + \varepsilon_1 l_h{}^2). \quad (15) \end{aligned}$$

The effective mean square amplitude $l_m{}^2$ is defined by

$$l_m{}^2 = l_h{}^2 - s^{-2}[\ln(\sigma_1{}^2 + \sigma_2{}^2) - 2 \ln \varepsilon_0], \quad (16)$$

where

$$\sigma_1 = \sum_{n=0}^{\infty} (-1)^n \varepsilon_{2n+1} (l_h{}^2 s)^{2n+1}, \quad (17)$$

$$\sigma_2 = \sum_{n=0}^{\infty} (-1)^n \varepsilon_{2n} (l_h{}^2 s)^{2n}. \quad (18)$$

It can then be shown that

$$\begin{aligned} l_m{}^2 = l_h{}^2 &+ (2\varepsilon_2/\varepsilon_0 - \varepsilon_1{}^2/\varepsilon_0{}^2) l_h{}^4 \\ &+ (2\varepsilon_1\varepsilon_3/\varepsilon_0{}^2 + \varepsilon_2{}^2/\varepsilon_0{}^2 - 2\varepsilon_4/\varepsilon_0 \\ &- 2\varepsilon_1{}^2\varepsilon_2/\varepsilon_0{}^3 + \varepsilon_1{}^4/2\varepsilon_0{}^4) l_h{}^8 s^2 + \cdots, \quad (19) \end{aligned}$$

and that l_m is nearly equal to l_h or l_g, where l_g is related to the second moment l_e as

$$l_g{}^2 = l_e{}^2 - (r_g - r_e)^2, \quad (20)$$

and

$$\begin{aligned} l_e{}^2 = l_h{}^2 &+ 2(\varepsilon_1 + \varepsilon_2 r_e + 3\varepsilon_3 l_h{}^2) l_h{}^4/ \\ &(\varepsilon_0 r_e + \varepsilon_1 l_h{}^2) + 2(r_g - r_e)\delta r - \delta r^2. \quad (21) \end{aligned}$$

The phase parameter κ is defined by

$$\begin{aligned} \kappa &= l_h{}^2 \varepsilon_1/\varepsilon_0 s^2 - s^{-3} \arctan(\sigma_1/\sigma_2) \quad (22) \\ &= (\varepsilon_3/\varepsilon_0 - \varepsilon_1\varepsilon_2/\varepsilon_0{}^2 + \varepsilon_1{}^3/3\varepsilon_0{}^3) l_h{}^6 - [\varepsilon_5/\varepsilon_0 \\ &\quad - (\varepsilon_1\varepsilon_4 + \varepsilon_2\varepsilon_3)/\varepsilon_0{}^2 + (\varepsilon_1\varepsilon_2{}^2 + \varepsilon_1{}^2\varepsilon_3)/\varepsilon_0{}^3 \\ &\quad - \varepsilon_1{}^3\varepsilon_2/\varepsilon_0{}^4 + \varepsilon_1{}^5/5\varepsilon_0{}^5] l_h{}^{10} s^2 + \cdots. \quad (23) \end{aligned}$$

It will be shown later that the l_m and κ parameters of ordinary diatomic molecules are practically independent of s over the range of experimental interest, and hence, they can be assumed as constant.

The modified radial distribution function is defined by[19]

$$\begin{aligned} f(r) &= \int_0^\infty s M_c(s) \exp(-bs^2) \sin sr \, \mathrm{d}s \quad (24) \\ &= (\pi/16b)^{1/2} \sum_{i<j}\sum{}' c^0{}_{ij} \int_0^\infty [P_{ij}(\rho)/\rho] \\ &\quad \times \exp[-(r-\rho)^2/4b] \mathrm{d}\rho, \quad (25) \end{aligned}$$

where the s-dependence of c in Eq. (10) is compensated for by assuming a self-consistent model of molecular structure, so that $M_c(s)$ corresponds to pure nuclear scattering.[15] By using the $P(r)$ function in Eq. (1), it is possible to calculate the contribution to $f(r)$ as[5]

$$\begin{aligned} f(r) &= (Ac/2r_e)(\pi H)^{1/2} \exp(-H\Delta r^2) \\ &\quad \times [\sum_{n=0}^{\infty} \varepsilon'_n (2Hl_h{}^2)^n \Delta r^n], \quad (26) \end{aligned}$$

where

$$H = (4b + 2l_h{}^2)^{-1}, \quad (27)$$

and

$$\varepsilon'_n = \sum_{m=0}^{\infty} [(n+2m)!/2^m n! m!] d_{n+2m} (4bHl_h{}^2)^m. \quad (28)$$

Perturbation Calculations for Diatomic Molecules

The probability distribution function for a diatomic molecule may be calculated by a second-order perturbation method as a good approximation except in the case of very high temperature and/or very low frequency. The anharmonic potential functions of diatomic molecules are much better known than those of polyatomic

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19) I. L. Karle and J. Karle, *J. Chem. Phys.*, **17**, 1052 (1949).

molecules. The dependence of the vibrational energy and the rotational constant on the vibrational quantum numbers is usually represented by ω_e, x_e, and α_e, where[20]

$$E_{vib}(v)/\boldsymbol{hc} = \omega_e\left(v+\frac{1}{2}\right) - \omega_e x_e\left(v+\frac{1}{2}\right)^2 + \cdots, \quad (29)$$

and

$$B_v = B_e - \alpha_e\left(v+\frac{1}{2}\right) + \cdots. \quad (30)$$

The coefficients of the effective potential function truncated through the fourth order may be obtained in terms of ω_e, α_e and x_e.

$$V(r) = \frac{1}{2}f\Delta r^2\left(1 - a_3\Delta r + \frac{7}{12}a_4{}^2\Delta r^2\right). \quad (31)$$

It can be shown that[21]

$$f = 4\pi^2\mu\boldsymbol{c}^2\omega_e{}^2\,, \quad (32)$$

$$a_3 = \frac{2}{3}\pi\omega_e(\boldsymbol{c}\mu/2\boldsymbol{h}B_e{}^3)^{1/2}(\alpha_e + 6B_e{}^2/\omega_e)\,, \quad (33)$$

$$a_4 = (15a_3{}^2/7 - 64\pi^2\boldsymbol{c}\mu\omega_e x_e/7\boldsymbol{h})^{1/2}\,. \quad (34)$$

The a_3 and a_4 parameters for various diatomic molecules are calculated in a previous paper.[22] The a_3 values for ordinary molecules range from 1.6 Å^{-1} to 2.4 Å^{-1}, and a_4/a_3 is roughly 1.03 ± 0.03. This indicates that the Morse function is a good representation of the diatomic potential energy at least for a small displacement from the equilibrium position, since in the Morse case a_3 should be equal to a_4 in this expansion.

When the potential function is written in terms of the dimensionless normal coordinate,[21]

$$V(q)/\boldsymbol{hc} = \frac{1}{2}\omega_e q^2 + k_3q^3 + k_4q^4 + \cdots\,, \quad (35)$$

where

$$q = \Delta r/\sqrt{2}\,l_\alpha\,, \quad (36)$$

the cubic and quartic constants are given by

$$k_3 = -\frac{1}{\sqrt{2}}a_3\omega_e l_\alpha\,, \quad (37)$$

and

$$k_4 = \frac{7}{12}a_4{}^2\omega_e l_\alpha{}^2\,. \quad (38)$$

The standard perturbation procedure leads to the wave function,

$$\psi_v = \sum_j C_{vj}\psi_j{}^0(q)\,, \quad (39)$$

where C_{vj} is a function of v, k_3, and k_4, and $\psi_j{}^0$ represents the harmonic-oscillator wave function. All the nonvanishing coefficients, $j = v \pm n$ for $n=0$, 1, 2, 3, 4, and 6, are given in Reitan's paper.[6] The probability distribution function is obtained as a weighted average over the vibrational states,

$$P(q) = \sum_{v=0}^{\infty} W_v\,|\psi_v|^2\,, \quad (40)$$

where the Boltzmann factor W_v is given by

$$W_v(T) = \exp\left[-E_{vib}(v)/\boldsymbol{k}T\right]/ \left\{\sum_{v=0}^{\infty}\exp\left[-E_{vib}(v)/\boldsymbol{k}T\right]\right\}. \quad (41)$$

This weighted sum can be calculated by writing the total sum as a linear combination of the following sums,[6,23]

$$F_{nm} = \sum_{v=0}^{\infty} W_v v^n[(v+m)!/2^m v!]^{1/2}\psi^0{}_{v+m}\psi_v{}^0\,, \quad (42)$$

where[24]

$$F_{00} = [\pi(1-\chi)/(1+\chi)]^{1/2} \times \exp\left[-q^2(1-\chi)/(1+\chi)\right]. \quad (43)$$

TABLE 1. STATISTICAL SUMMATIONS[a]

n	m	F_{nm}/F_{00}
0	0	1
0	1	$a_{10}q$
0	2	$-\frac{1}{2}a_{11} + a_{20}q^2$
0	3	$-\frac{3}{2}a_{21}q + a_{30}q^3$
0	4	$\frac{3}{4}a_{22} - 3a_{31}q^2 + a_{40}q^4$
0	6	$-\frac{15}{8}a_{33} + \frac{45}{4}a_{42}q^2 - \frac{15}{2}a_{51}q^4 + a_{60}q^6$
1	0	$a_{11}\chi^2 + 2a_{20}\chi q^2$
1	1	$-a_{21}\chi(1-2\chi)q + 2a_{30}\chi q^3$
1	2	$-\frac{3}{2}a_{22}\chi^2 - 3a_{30}\chi q^2 + 2a_{40}\chi q^4$
1	3	$\frac{3}{2}a_{32}\chi(1-4\chi)q - 2a_{41}\chi(3-2\chi)q^3$ $+ 2a_{50}\chi q^5$
1	4	$\frac{15}{4}a_{33}\chi^2 + \frac{15}{2}a_{42}\chi(1-2\chi)q^2$ $- 5a_{51}\chi(2-\chi)q^4 + 2a_{60}\chi q^6$
2	0	$a_{22}\chi^2(2+\chi^2) + 2a_{31}\chi(1-2\chi+3\chi^2)q^2$ $+ 4a_{40}\chi^2q^4$
2	1	$- a_{32}\chi(1-5\chi+5\chi^2-4\chi^3)q$ $+ 2a_{41}\chi(1-4\chi+5\chi^2)q^3 + 4a_{50}\chi^2q^5$
2	2	$-\frac{3}{2}a_{33}\chi^2(2+3\chi^2) - 3a_{42}\chi(1-4\chi$ $+ 7\chi^2 - 3\chi^3)q^2 + 2a_{51}\chi(1-7\chi+7\chi^2)q^4$ $+ 4a_{60}\chi^2q^6$
3	0	$a_{33}\chi^2(4+10\chi^2+\chi^4) + 2a_{42}\chi(1-6\chi$ $+ 19\chi^2 - 12\chi^3 + 7\chi^4)q^2$ $+ 12a_{51}\chi^2(1-2\chi+2\chi^2)q^4 + 8a_{60}\chi^3q^6$

a) Reference 23 has given F_0, F_1, F_2, F_3, F_4, and G, which correspond to the present F_{00} [see Eq. (43)], F_{01}, $\frac{1}{2}(F_{01}+F_{11})$, $2F_{02}$, F_{03}, and F_{10}, respectively.

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20) G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand, Princeton, N. J. (1950).

21) H. H. Nielsen, *Rev. Mod. Phys.*, **23**, 90 (1951).

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

23) Y. Morino and T. Iijima, *ibid.*, **36**, 412 (1963).

By the use of the recursion formulas23)

$$\psi_{v+1}(q) = [2/(v+1)]^{1/2} q\psi_v^0 - [v/(v+1)]^{1/2}\psi^0_{v-1}, \quad (44)$$

and

$$F_{n+1,0} = \chi(1-\chi)(\partial/\partial\chi)[F_{n,0}/(1-\chi)], \quad (45)$$

the necessary sums are calculated as listed in Table 1. The coefficients of the resulting probability distribution function $P(r)$ given in Eq. (1) are shown to be

$$c_n = b_n/(\sqrt{2}\, l_\alpha)^n b_0, \quad (n=1, 2, \cdots) \quad (46)$$

where

$$\begin{aligned} b_0 = {} & 1 - (k_3^2/48\omega_e^2)a_{31}(167 - 50\chi + 846\chi^2 \\ & - 50\chi^3 + 167\chi^4) + (9k_4/8\omega_e)a_{11}(1+\chi^2) \\ & - a_{22}x_e\gamma\chi(2 + \chi + 2\chi^2) + \cdots, \quad (47) \end{aligned}$$

$$b_1 = -(2k_3/\omega_e)a_{20}(1-\chi)^2 + \cdots, \quad (48)$$

$$\begin{aligned} b_2 = {} & (5k_3^2/4\omega_e^2)a_{40}(3 - 38\chi + 46\chi^2 - 38\chi^3 \\ & + 3\chi^4) - (3k_4/2\omega_e)a_{20}(1 - 4\chi + \chi^2) \\ & + 4a_{31}x_e\gamma\chi(1 - \chi + \chi^2) + \cdots, \quad (49) \end{aligned}$$

$$\begin{aligned} b_3 = {} & -(2k_3/3\omega_e)a_{30} \\ & \times (1-\chi)(1 + 10\chi + \chi^2) + \cdots, \quad (50) \end{aligned}$$

$$\begin{aligned} b_4 = {} & (k_3^2/12\omega_e^2)a_{50}(1-\chi)(19 + 230\chi - 858\chi^2 \\ & + 230\chi^3 + 19\chi^4) - (k_4/2\omega_e)a_{30}(1-\chi) \\ & \times (1 + 8\chi + \chi^2) + 4a_{40}x_e\gamma\chi^2 + \cdots, \quad (51) \end{aligned}$$

$$b_6 = \frac{1}{2}b_3^2 + \cdots. \quad (52)$$

All the other b_n values vanish in this order of approximation. For simplicity, the following symbols are used:

$$a_{pq} = 1/(1+\chi)^p(1-\chi)^q, \quad (53)$$

and

$$\gamma = \boldsymbol{hc}\omega_e/\boldsymbol{kT}. \quad (54)$$

The parameters k_3, k_4, b_n and χ correspond to $c_3\omega_e/2$, $c_4\omega_e/2$, a_n, and κ, respectively, in Reitan's notations.6) The above expressions of b_n coincide with the a_n of Reitan when the Morse function is assumed, and hence, when the parameters k_3 and k_4 are represented by a single parameter x_e, $k_3 = -(x_e/2)^{1/2}$ and $k_4 = 7\omega_e x_e/12$.

Approximate Expressions

By the use of the c_n constants given above, approximate expressions for the structural parameters may be obtained as power series of $a_3 l_h$, $a_4 l_h$, and l_h/r_e, which are of a similar order of magnitude (usually about 1/10). The equations (46) through (52) indicate that c_1, c_2, $c_3 l_h^2$, $c_4 l_h^2$, and $c_6 l_h^4$ are of nearly the same order of magnitude in regard to the expansion in question, as in the case of the zero-point Morse oscillator.5) The following expressions which are correct to the l_h^4 terms may be derived:

$$\begin{aligned} r_g = {} & r_e + \delta r + c_1 l_h^2 + (3c_3 - c_1c_2)l_h^4 \\ & - 3(c_1c_4 + c_2c_3)l_h^6 + \cdots \quad (55) \\ = {} & r_e + \delta r + \frac{3}{2}a_3 l_h^2(1 + 4a_{02}x_e\gamma\chi) \\ & + \left[\frac{3}{4}a_3^3(11 + 38\chi + 11\chi^2) \right. \\ & \left. - \frac{7}{24}a_3a_4^2(31 - 6\chi + 21\chi^2)\right]a_{20}l_h^4 + \cdots, \quad (56) \end{aligned}$$

$$\begin{aligned} r_a = {} & r_g - (l_h^2/r_e)[1 + (2c_2 - c_1^2)l_h^2 \\ & + (12c_4 - 6c_1c_3)l_h^4 + (90c_6 - 9c_3^2)l_h^6] \\ & + (l_h^4/r_e^2)(c_1 + 9c_3l_h^2) - 2l_h^4/r_e^3 + \cdots \quad (57) \\ = {} & r_g - (l_h^2/r_e)(1 + 4a_{02}x_e\gamma\chi) - (l_h^4/4r_e) \\ & \times [a_3^2a_{40}(13 + 84\chi + 142\chi^2 + 84\chi^3 \\ & + 13\chi^4) - 7a_4^2] + (l_h^4/2r_e^2)a_3a_{20} \\ & \times (5 + 26\chi + 5\chi^2) - 2l_h^4/r_e^3 + \cdots, \quad (58) \end{aligned}$$

$$\begin{aligned} l_e^2 = {} & l_h^2 + 2c_2l_h^4 + 12c_4l_h^6 + 90c_6l_h^8 + \cdots \\ & + 2(r_g - r_e)\delta r - \delta r^2 \quad (59) \\ = {} & l_h^2(1 + 4a_{02}x_e\gamma\chi) + \left[\frac{1}{2}a_3^2a_{20}(11 + 38\chi \right. \\ & \left. + 11\chi^2) - \frac{7}{4}a_4^2\right]l_h^4 + \cdots \\ & + 3a_3l_h^2\delta r + \delta r^2. \quad (60) \end{aligned}$$

The third-order terms of c_1 and c_3 contribute to the l_h^4 term of r_g. They are included in Eq. (55) by means of Ehrenfest's theorem,8,25) which states that the average value of the first derivative of the potential energy should vanish. This method is equivalent to and much easier than the explicit evaluation of the second terms of b_1 and b_3 given in Eqs. (48) and (50).

The expressions of r_g and l_e^2 can be reduced to the Morse results when a_3 and a_4 are set equal to a. At 0°K, the terms to the fourth order of l_h (which is equal to l_α in this case) are $-19a^2l_\alpha^4/24$ and $15a^2l_\alpha^4/4$, respectively. The former, however, does not agree with the corresponding expression given in Eq. (12) of Ref. 5 ($+13a^3l_\alpha^4/12$), since a term in the Morse potential function to the sixth power of q, which is ignored in Eq. (35), contributes to the term of this order.

In order to obtain expressions for l_m^2 and κ to the same order, it is necessary to consider the s^2-dependence of these parameters, since l_hs is of the order of unity. It can be shown that

$$\begin{aligned} l_m^2 = {} & r_e(r_g - r_a) + (l_h^4/r_e) \\ & \times (c_1 + 3c_3l_h^2 - 1/r_e) + 2[c_1c_3 - c_4 \\ & + (3c_3^2 - 15c_6)l_h^2]l_h^8s^2 + \cdots \quad (61) \end{aligned}$$

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24) F. Bloch, *Z. Physik*, **74**, 295 (1932).

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

TABLE 2. STRUCTURAL PARAMETERS OF DIATOMIC MOLECULES[a]
(in Å units; in 10^{-6} Å^3 units)

	r_e	r_0	δr	$r_m(1)$	r_g		r_a	
					rig.[b]	approx.[c]	rig.[b]	approx.[c]
H_2	0.7413	0.7508	0.0019	0.7494	0.7660	0.7678	0.7566	0.7576
CH	1.1198	1.1304	0.0016	1.1284	1.1397	1.1403	1.1341	1.1346
CD	1.1188	1.1265	0.0016	1.1256	1.1340	1.1343	1.1298	1.1301
HCl	1.2746	1.2839	0.0013	1.2821	1.2915	1.2919	1.2870	1.2873
N_2	1.0976	1.1000	0.0003	1.0995	1.1016	1.1016	1.1007	1.1007
CO	1.1282	1.1309	0.0004	1.1303	1.1326	1.1327	1.1316	1.1316
NO	1.1508	1.1537	0.0005	1.1533	1.1558	1.1558	1.1547	1.1548
O_2	1.2074	1.2108	0.0006	1.2102	1.2129	1.2130	1.2118	1.2119
SO	1.4810	1.4841	0.0007	1.4836	1.4861	1.4861	1.4851	1.4852
Cl_2	1.9878	1.9907	0.0012	1.9907	1.9942	1.9942	1.9931	1.9932
Br_2	2.2815	2.2835	0.0015	2.2833	2.2873	2.2872	2.2863	2.2863
I_2	2.6666	2.6678	0.0018	2.6683	2.6746	2.6744	2.6734	2.6734
Eq.	—	73	4	74	15	63	14	64

	l_α	l_h	l_e	l_g	l_m	κ		Ref.[d]
						rig.[b]	approx.[c]	
H_2	0.0872	0.0872	0.0920	0.0883	0.0875	~18.0[e]	20.8	30
CH	0.0796	0.0796	0.0830	0.0805	0.0798	~12.0[e]	13.3	—
CD	0.0682	0.0682	0.0704	0.0687	0.0683	~ 6.4[e]	7.2	—
HCl	0.0759	0.0759	0.0784	0.0766	0.0760	~ 9.2[e]	10.2	31
N_2	0.0320	0.0320	0.0323	0.0321	0.0318	0.40	0.42	32
CO	0.0337	0.0337	0.0341	0.0338	0.0335	0.48	0.51	33
NO	0.0344	0.0344	0.0349	0.0346	0.0343	0.55	0.60	—
O_2	0.0365	0.0365	0.0371	0.0367	0.0364	0.68	0.74	—
SO	0.0375	0.0377	0.0381	0.0378	0.0376	0.68	0.72	34
Cl_2	0.0415	0.0444	0.0450	0.0446	0.0445	1.55	1.64	35
Br_2	0.0364	0.0451	0.0457	0.0454	0.0452	1.98	2.05	36
I_2	0.0352	0.0512	0.0522	0.0516	0.0513	4.3	4.47	37
Eq.	6	5	21	20	16	22	66	

a) Calculated at 300°K by using spectroscopic parameters according to the listed equations. See Tables 1 and 2 of Refs. 6 and 7 for the perturbation calculations for some of the parameters at 300°K and 1500°K.

b) Perturbation calculations.

c) Estimates based on the a_3 values given in Ref. 22.

d) Spectroscopic data are taken from Refs. 20 and 29, with more recent references listed in 30—37.

e) The phase parameter κ of hydride molecules have the following slight dependence on s:
$\kappa \sim 1.3\times10^{-5} + 9\times10^{-9}\ s^2$ (H_2) $\kappa \sim 5.7\times10^{-6} + 1\times10^{-9}\ s^2$ (CD)
$\kappa \sim 9.6\times10^{-6} + 4\times10^{-9}\ s^2$ (CH) $\kappa \sim 8.0\times10^{-6} + 2\times10^{-9}\ s^2$ (HCl).

$$= r_e(r_g - r_a) + (l_h{}^4/r_e)\left(\frac{3}{2}a_3 - 1/r_e\right)$$
$$- \left[\frac{1}{16}a_3{}^2a_{40}(5 + 114\chi + 318\chi^2 + 114\chi^3\right.$$
$$\left. + 5\chi^4) - \frac{7}{48}a_4{}^2a_{20}(1 + 8\chi + \chi^2)\right]l_h{}^8s^2$$
$$- \frac{1}{48}a_{02}x_e\gamma\chi^2l_h{}^6s^2 + \cdots . \qquad (62)$$

The corresponding expressions for κ based on Eq. (23) are more complicated.

Equations (56) and (58) may further be simplified into the well-known first-order expressions[4,26] which are correct to $l_h{}^2$,

$$r_g = r_e + \delta r + \frac{3}{2}a_3l_h{}^2 + \cdots , \qquad (63)$$

$$r_a = r_g - l_h{}^2/r_e + \cdots . \qquad (64)$$

It is also possible to simplify κ to this order of approximation as follows,

$$\kappa = c_3l_h{}^6 + \cdots \qquad (65)$$
$$= \frac{1}{6}a_3l_h{}^4[1 + 8\chi/(1 + \chi)^2] + \cdots . \qquad (66)$$

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26) Y. Morino, Y. Nakamura and T. Iijima, *ibid.*, **32**, 643 (1960).

It is important to note that this parameter increases rapidly with increasing temperature for a system with relatively low vibrational frequency. Equation (65) is essentially equal to those derived by Morino *et al.*[26,27]

The simplest practical expression for the radial distribution function can be derived from Eq. (26) as follows:

$$f(\Delta r) \approx (c/2r_e)(\pi H')^{1/2} \exp(-H'\Delta r^2) \times (1 + f_1\Delta r + f_3\Delta r^3)\,, \tag{67}$$

where

$$f_1 \approx 2Hl_h^2(c_1 - 1/r_e + 12c_3bHl_h^2) \tag{68}$$

$$\approx 4a_3H^2(3bl_h^2 + l_\alpha^4) - 2Hl_h^2/r_e\,, \tag{69}$$

$$f_3 \approx 8c_3H^3l_h^6 \tag{70}$$

$$\approx \frac{4}{3}a_3H^3l_h^4[1 + 8\chi/(1+\chi)^2]\,, \tag{71}$$

and

$$H' = H - 2Hl_h^2(\varepsilon_2 + 24\varepsilon_4Hbl_h^2 + 180\varepsilon_6H^2b^2l_h^4 + \cdots) \approx H. \tag{72}$$

At 0°K, Eq. (67) can be reduced to Bartell's zero-point equation [Eq. (9) of Ref. 4; see also Ref. 28].

Examples

Numerical calculations have been made for typical diatomic molecules by the use of the parameters a_3 and a_4 taken from Ref. 21 based on experimental spectroscopic data.[20,29-37] The results for 300°K are listed in Table 2. For comparison of internuclear distances, the table also includes the spectroscopic r_0 parameter defined by

$$r_0 = (\boldsymbol{h}/8\pi^2\boldsymbol{c}\mu B_0)^{1/2}\,, \tag{73}$$

and the maximum position of the $P(r)/r$ function,[4] $r_m(1)$, which is approximately given by

$$r_m(1) = r_e + \delta r + d_1l_h^2 + d_1(2d_2 - d_1^2)l_h^4 + 3d_1^2d_3l_h^6 + \cdots. \tag{74}$$

The table shows that the differences among various distance parameters possibly exceed the range of uncertainty of current diffraction experiments, as first pointed out by Bartell.[4] This may also be the case for the mean amplitudes at a temperature appreciably higher than 300°K, especially for those involving the hydrogen atom.[7] For all molecules listed in the table, the l_m and κ parameters are found to be practically independent of s in the range of the scattering angles $5 \leq s \leq 40$, except that the κ values for hydrides increase slightly with increasing s values (see footnote e of Table 2). The deviations of the l_m and the rest of the κ parameters from the values listed in the table rarely exceed one percent in the above s range. An example of the lack of s-dependence of these parameters has been illustrated by Ukaji and Kuchitsu[38] for iodine at 80°C, 300°C, and 500°C.

Conclusion

The molecular scattering intensity of a diatomic molecule can be represented by Eq. (11) with three effective constants, r_a, l_m, and κ, since the s-dependence of the latter two parameters can practically be disregarded. Table 2 shows that nearly correct expressions for r_a, l_m, and κ as functions of the temperature of the system may be obtained by Eqs. (64), (5), and (66), respectively.

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27) Y. Morino and T. Iijima, This Bulletin, **35**, 1661 (1962).

28) L. S. Bartell and R. A. Bonham, *J. Chem. Phys.*, **27**, 1414 (1957), Footnote 5.

29) D. Steele and E. R. Lippincott, *ibid.*, **35**, 2065 (1961).

30) B. P. Stoicheff, *Can. J. Phys.*, **35**, 730 (1957).

31) D. H. Rank, D. P. Eastman, B. S. Rao and T. A. Wiggins, *J. Opt. Soc. Am.*, **52**, 1 (1962).

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35) A. E. Douglas, C. K. Møller and B. P. Stoicheff, *Can. J. Phys.*, **41**, 1174 (1963).

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37) D. H. Rank and B. S. Rao, *ibid.*, **13**, 34 (1964).

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