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Study of Anharmonic Vibrations of Polyatomic Molecules by Gas Electron Diffraction

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The effect of anharmonic intramolecular vibrations on various quantities to be obtained by gas electron diffraction is studied theoretically. Calculations are made for a polyatomic molecule in general, and a method is given for calculating the average internuclear distance and the mean amplitude by means of the theory of normal vibrations and a first-order perturbation treatment.

The method is then applied to methane and deuteromethane as an example, and the results are compared with corresponding experimental data. The observed difference between r_g of C-H and C-D (an r_g isotope effect), and the inherent discrepancy of the diffraction distance, r_g, and the spectroscopic distance, r_0, are all explained consistently in terms of molecular vibrations.

It is shown that the uniform frequency modulation of the molecular intensity curve is caused by the anharmonicity, and the Morse asymmetry parameter estimated from experimental phase shifts is found to be in line with the theoretical estimation.

There has been a rapid progress in recent years in the studies of gas electron diffraction motivated by the development of its experimental techniques. As a result, interatomic distances and mean amplitudes can be determined with a standard error of about ±0.001 A which is of comparable precision to those of the studies of microwave, infrared, and rotational Raman spectroscopy. The method of electron diffraction, therefore, offers a powerful means of studying molecular structure and vibrations.

One of the most interesting problems is the anharmonicity of the intramolecular potential field. The effect of anharmonicity manifests itself in three experimental parameters to be determined by gas diffraction, i.e., the internuclear distance, r_g, the mean amplitude, l, and the asymmetry parameter, a. A theoretical study has been made in a previous paper[1] to clarify the physical significance of these parameters in a diatomic molecule, and the theory is given experimental support[2]. The present work is intended to be its extension to a polyatomic molecule, and in particular, our recent experiment on methane and deuteromethane[3] is examined in detail from the viewpoint of anharmonic molecular vibrations.

Effect of anharmonicity on the internuclear distance

General theory

If all molecules are assumed to be in the ground vibrational state, and let ψ be its vibrational wave function, the average internuclear distance, or the center of gravity of the probability distribution, r_g, is related to the equilibrium distance, r_e, by the following formula,

$$r_g=r_e+(\psi|\Delta r|\psi)=r_e+\langle\Delta r\rangle\,, \qquad (1)$$

where $\langle\Delta r\rangle$ is an instantaneous displacement of the distance from r_e averaged over the vibration. The displacement Δr can be expanded in terms of its projection on to the Cartesian coordinates, Δx, Δy, and Δz,

$$\Delta r=\Delta z+[(\Delta x)^2+(\Delta y)^2]/2r_e+\cdots\,, \qquad (2)$$

where the z axis is taken along the equilibrium direction of the nuclei.

With the aid of the theory of normal vibrations[4], it is possible to express Δu ($u=x$, y, and z) as a linear combination of normal

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coordinates, Q_k,

$$\Delta u=\sum_{l,m,k} D^u(M^{-1}B')_l U'_{lm}(\mathfrak{L}^{-1})'_{mk}Q_k\ , \qquad (3)$$

where all matrix notations are defined in the reference[5)], and their elements are shown to depend on the geometry, masses, and normal frequencies of the molecule.

The wave function, ϕ, on the other hand, is very nearly that of a multi-dimensional harmonic oscillator, ϕ_0, but it suffers a slight distortion due to the anharmonic terms of the potential, $V=V_0+V'$, where

$$V_0=\frac{1}{2}\sum \lambda_i Q_i^2\ , \qquad (4)$$

and

$$V'=\sum k_{ijk}Q_iQ_jQ_k+\sum k_{ijkl}Q_iQ_jQ_kQ_l+\cdots\ . \qquad (5)$$

It is shown that the terms higher than the cubic are not important in our calculation. By a method of first-order perturbation, the wave function is given by

$$\phi=\phi_0-\sum\,[(\phi_i|\,V'|\phi_0)/(E_i-E_0)]\phi_i\ . \qquad (6)$$

By substituting ϕ into Eq. (1), $\langle \Delta r\rangle$ can be calculated. At a nonzero temperature, it is necessary to take the average of $\langle \Delta r\rangle$ over all excited vibrational states with proper Boltzmann factors. However, for molecules like methane, where all normal frequencies are much higher than kT at the room temperature, it is only necessary to take the ground state into account.

Calculation of r_g for methane

For tetrahedral molecules, it is shown that the potential function V' can be written as[6)]

$$V'=k_{111}Q_1{}^3+k_{122}Q_1(Q_{2a}^2+Q_{2b}^2)+k_{133}Q_1(Q_{3x}^2+Q_{3y}^2+Q_{3z}^2)+k_{144}Q_1(Q_{4x}^2+Q_{4y}^2+Q_{4z}^2)+\cdots\ , \qquad (7)$$

and the wave function ϕ as*

$$\phi=\phi_0+\lambda_1\phi_1\ , \qquad (8)$$

where

$$\lambda_1=-(3/2\sqrt{2}\,\nu_1)\Big(c_{111}+\frac{2}{3}c_{122}+c_{133}+c_{144}\Big)\ , \qquad (9)$$

and

$$c_{ijk}=(N^{3/2}h^{1/2}/8\pi^3c^{5/2}\nu_i^{1/2}\nu_j^{1/2}\nu_k^{1/2})k_{ijk}\ . \qquad (10)$$

The function ϕ_1 corresponds to the state in which only the A_1 vibration, ν_1, is singly excited. Accordingly, the meaning of ϕ is that the wave function is slightly distorted in a totally symmetric way due to the anharmonic perturbation. The extent of the distortion, λ_1, depends on the cubic constants, the estimation of which is the crucial problem of the calculation of $\langle \Delta r\rangle$. Since no experimental information regarding c_{ijk} is available, it is estimated from spectroscopic data following the method proposed by the authors[7)] and mean values of the normal coordinates are calculated by the use of the above wave function. It is shown that

$$\langle Q_1\rangle=\lambda_1(h/2\pi^2c\nu_1)^{1/2},$$

and

$$\langle Q_2\rangle=\langle Q_3\rangle=\langle Q_4\rangle=0\ . \qquad (11)$$

The effect of anharmonicity is clearly shown in $\langle Q_1\rangle$, since it vanishes in the case of the harmonic vibration. It is also easy to derive $\langle Q_i{}^2\rangle$, which, in contrast to $\langle Q_1\rangle$, is only slightly different from their harmonic values,

$$\langle Q_i{}^2\rangle=h/8\pi^2c\nu_i\ . \qquad (12)$$

In other words, $\langle Q_1\rangle$ is "anharmonic", whereas $\langle Q_i{}^2\rangle$ is "harmonic".

Necessary vibrational data have been given by Jones and McDowell[8)], so that the combination of Eqs. (2), (3), (11), and (12) leads to the evaluation of $\langle \Delta r\rangle$. At the room temperature, a minor correction for the centrifugal stretching, $\delta r\sim 0.0005$ Å (independent of the atomic mass) should also be included. The final estimation of $r_g-r_e=\langle \Delta r\rangle+\delta r$ is listed in Table I.

According to our experiment, r_g of C-H in CH_4 is larger than that of C-D in CD_4 by about 0.004 Å, but they agree satisfactorily with each other when reduced to r_e. Such an "isotope effect" of r_g, observed for the first time in this experiment, can be explained in terms of the mass-sensitive anharmonic vibrations. The situation is demonstrated in the following simple formula[1)] which is often used by analogy of diatomic molecules and is found to hold approximately in this case,

$$r_g=r_e+\frac{3}{2}a\langle \Delta z^2\rangle\ . \qquad (13)$$

where a is a constant of the asymmetry, and $\langle \Delta z^2\rangle$ is shown to be very nearly proportional to $m_H{}^{-1/2}$.

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* In a more rigorous treatment, ψ is normalized by including the effect of other nine nonzero cubic coefficients[7)]. The effect, however, is so slight that it does not alter the following discussion significantly.

Table I. Comparison of the Internuclear Distances of Methane, (Å).

Distance	r_g (exp)	r_0 (exp)	r_g-r_0 (exp)	r_g-r_0 (calc)	r_g-r_e (calc)	r_0-r_e (calc)	r_e[a] (ED)	r_e[b] (SP)
C-H(CH_4)	$1.106_8 \pm 0.001_2$	1.0940	0.012_8	0.013_1	0.022_1	0.009_0	1.084_7	1.085_0
C-D(CD_4)	$1.102_7 \pm 0.001_3$	1.0923	0.010_4	0.009_7	0.016_4	0.006_7	1.086_3	1.085_6

a) From electron diffraction.
b) From spectroscopy.

Calculation of r_0 for methane

The spectroscopic parameter, r_0, of methane is obtained from the rotational constant of the ground state, B_0, by

$$r_0=(3h/64\pi^2 m_H c B_0)^{1/2}\ . \tag{14}$$

By using the method of Wilson and Howard[9], B_0 is related to B_e $(64\pi^2 m_H c r_e^2/3h)$ as

$$\begin{aligned}B_0=B_e\Big\{&1-(1/m_H{}^{1/2}r_e)\langle Q_1\rangle+\Big(2\langle Q_1{}^2\rangle+\langle Q_2{}^2\rangle\\&+\frac{3}{2}\zeta_{23}^2\langle Q_3{}^2\rangle+\frac{3}{2}\zeta_{24}^2\langle Q_4{}^2\rangle\Big)\Big/I_e\\&-B_e[\zeta_{23}^2(\nu_2-\nu_3)^2/\nu_2\nu_3(\nu_2+\nu_3)+\zeta_{24}^2(\nu_2\\&-\nu_4)^2/\nu_4(\nu_2+\nu_4)+2\zeta_{23}\zeta_{24}(\nu_3-\nu_4)^2/\nu_3\nu_4(\nu_3+\nu_4)]\Big\}\end{aligned} \tag{15}$$

where I_e is the equilibrium moment of inertia, $8m_H r_e^2/3$, ν_i is the normal frequencies, and ζ can be calculated from the masses and the L matrix elements. The formula (15) is also derived by Hecht[10]. By substituting (11) and (12) into (15), it is possible to calculate r_0-r_e as listed in Table I. It is noteworthy that r_0 should not be identified with $\langle r^{-2}\rangle^{-1/2}$ except in the case of diatomic molecules, nor is B_0 equal to $(h/8\pi^2c)\langle 1/I\rangle$ as is often assumed to be.

The experimental data of r_0 in Table I are seemingly the most reliable ones. It is to be noted that r_g-r_0 is shown to be independent of the anharmonic terms, $\langle Q_1\rangle$. Namely, r_z which is derived from r_0 by eliminating the harmonic contribution is proved to be equal to $r_g-[\langle\Delta x^2\rangle+\langle\Delta y^2\rangle]/2r_e$ to a good approximation (for molecules like methane), and since the second term of the latter is also harmonic, r_0 can be converted to r_g by a harmonic transformation[11].

It is clearly shown in Table I that the diffraction and the spectroscopic results of CH_4 and CD_4 correspond to one another consistently, and they lead to the C-H equilibrium distance of about 1.085 Å.

Mean amplitude

According to Eq. (2), the root mean square amplitude, or so-called the "mean amplitude", l_e, can be expanded as

$$l_e^2=\langle\Delta r^2\rangle=\langle\Delta z^2\rangle+[\langle\Delta z\Delta x^2\rangle+\langle\Delta z\Delta y^2\rangle]/r_e+\cdots\ . \tag{16}$$

The theoretical calculation of l_e from spectroscopic data by Eq. (16) is similar to that of r_g. The second term of Eq. (16) is "anharmonic", but it is usually very small. In most conventional work[12], therefore, l_e is calculated by the following "harmonic" approximations, where i) fundamental frequencies, ν_0, are used in place of normal frequencies, ν_e, in Eq. (12) and in the calculation of the L matrix, and ii) $\langle\Delta r^2\rangle$ is approximated by $\langle\Delta z^2\rangle$. A calculation is made for methane to examine the above approximation. As shown in Table II, conventional values are almost equal to the rigorous l_e, as errors in the approximation are nearly cancelled.

Nevertheless, it is not necessarily justifiable to ignore the effect of anharmonicity on the mean amplitude, and it is particularly important to make a clear distinction among various parameters when an experimental value of a very high precision is required as in the case of using it to the determination of force constants[13]. Our recent study[14] has shown that the mean amplitudes as conventionally derived from the diffraction experiment by fitting distribution peaks with Gaussian, or by fitting molecular intensity curves to theoretical ones are both very nearly l_g, where

$$l_g^2=\langle(r-r_g)^2\rangle=l_e^2-\langle\Delta r\rangle^2\ , \tag{17}$$

and they can, in principle, be reduced to l_g and l_e. Various mean amplitudes of methane are listed in Table II, where the experimental results[3] are found to be in good agree-

Table II. Comparison of the Mean Amplitudes of Methane, (Å).

	l_e (exp)	l_e (calc)	l_g (exp)	l_g (calc)	$\langle\Delta z^2\rangle^{1/2}$*
C-H(CH$_4$)	$0.078_1\pm0.002$	0.078_1	0.075_1	0.075_1	0.078_0
C-D(CD$_4$)	$0.068_4\pm0.002$	0.068_4	0.066_5	0.066_3	0.066_0

* Harmonic approximation.

ment with the theoretical calculations.

Asymmetry parameter

It seems reasonable to represent the probability distribution function $P(x)$ of an anharmonic oscillator corresponding to a bond in a diatomic or polyatomic molecule by

$$P(x)=A(\alpha/\pi)^{1/2}(1+\sum c_n x^n)\exp(-\alpha x^2)\,, \quad (18)$$

where $x=r-r_e$, and A is a constant of normalization. The parameter α can be determined from the experimental mean amplitude, and it has a particularly simple expression in the case of a diatomic molecule,

$$\alpha=4\pi^2\mu c\nu_e/h\,. \quad (19)$$

The coefficients c_n depend on the form of the potential fuuction, and they represent a distortion from a Gaussian distribution.

General expressions of the radial distribution function, $f(r)$, the molecular intensity curve, $M(s)$, the distance, and the mean amplitude corresponding to the probability function (18) have been derived[14] in terms of c_n and α. They take simple analytical expressions when the potential function is assumed to be of a Morse type[15], which is regarded as a reasonable representation for our purpose,

$$V(x)=D_e[\exp(-2ax)-2\exp(-ax)]\,. \quad (20)$$

It is shown in this case that the coefficients c_n can be given simply in terms of α and "the asymmetry parameter" a. For example, $c_1=a$, and $c_3=a\alpha/3$, in its ground state. It is accordingly possible to represent $f(r)$ and $M(s)$ in terms of a and α. It is shown that there should appear a uniform frequency modulation in $M(s)$, which is given by[1),14)]

$$M(s)\sim c\exp(-l_g^2s^2/2)\{\sin s[r_g-1/2\alpha r_e+\phi(s)]\}/sr_e\,. \quad (21)$$

An approximate expression of the phase factor, $\phi(s)$, is as follows[13].

$$\phi(s)\sim-[a/24+(a/16-1/24r_e)(a^2+1/r_e^2)/\alpha](s^2/\alpha)+a^3s^4/320\alpha^4\cdots. \quad (22)$$

The effect of anharmonic vibrations is clearly demonstrated in our experiment of methane[3], where the skewness of the C-H and C-D radial distribution peaks corresponds to the asymmetry parameter a of about 3Å^{-1}, and the observed molecular intensity curve is uniformly "pulled out" from a pure sine curve. An analysis of the shifts of its nodes leads to a determination of a to be 3.1 ± 0.5Å^{-1}, which is in line with our theoretical estimation[7] based on the anharmonicity characteristic of the C-H bond and on the effect of the repulsion between the nonbonded hydrogen atoms[16].

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DISCUSSION

J. KAKINOKI: The molecular intensity is given by the difference of the total intensity from the background intensity. Both these intensities are large, and the ratio of the molecular intensity to the total intensity is 1:10 or less. Can we get an accurate experimental intensity which can give necessary information with high accuracy? It must be remembered in this connection that there are a number of experimental features which might cause serious errors in the intensity measurement, such as a finite distribution of the gas specimen and a finite width of the microphotometer trace.

K. KUCHITSU: Yes, as far as we believe. It is true that the molecular intensity we measure is only a small fraction of the total intensity, so that one has to be extremely careful to eliminate errors from various sources such as those you have indicated. But it is our opinion that one can get sufficiently reliable molecular intensity, if necessary experimental precaution is taken in taking diffraction photographs, microphotometering, and in measuring photometer traces.

There are some systematic errors which are of crucial importance on the determination of internuclear distances and others to which mean amplitudes are very sensitive. Most of such errors, as we believe, can be estimated and corrected for, at least approximately, and random errors can be treated by a proper statistical treatment.

The standard errors quoted in our final results have been determined after such consideration, and are seemingly reasonable in view of the high index of resolution and of the good agreement with spectroscopic conclusions.

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The Effect of Molecular Vibration upon Interatomic Distances of Carbon Disulfide

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In order to confirm the consistency between the interatomic distances obtained by electron diffraction and those obtained by spectroscopy, the average distances r_g's of carbon disulfide were calculated from spectroscopic data, and compared with r_g's measured by electron diffraction. They were in good agreement with one another. The results are, $r_g(\text{C-S})=1.558_3\pm0.002_3$Å and $r_g(\text{S-S})=3.114_4\pm0.004_0$Å by electron diffraction, and 1.558_0 $\pm0.000_5$ and $3.109_0\pm0.001_0$Å by spectroscopy.

It is shown that a simple model that the bond stretching potential is expressed by a Morse function yields cubic constants which are in good agreement with those obtained by the spectroscopic studies.

1. Introduction

In some recent works[1) 2)] on the studies of the molecular structure by gas electron diffraction, attentions have been paid to the differences among various distance parameters in comparing the results with those by other techniques. In almost all cases, however, it is impossible to show the consistency of the results of electron diffraction with those of spectroscopy because of the limited knowledge on the anharmonicity of molecular vibration.