Internuclear Distance Parameters

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IT is the equilibrium internuclear distance r_e that has the fundamental significance in the determination of the molecular structure, but it is scarcely obtained by the usual measurements except for diatomic or very simple polyatomic molecules. Accordingly, a number of parameters of the nuclear distance have been in use. For example, the center of gravity of the probability distribution function r_g is derived by the electron diffraction experiment,[1] while by the measurement of microwave or infrared spectra an "effective" r_0 structure is obtained from the rotational constants in the ground vibrational state,[2] and in some cases an r_s structure by the isotope substitution.[3]

The parameter r_g is related to r_e by the following expression:

$$r_g \equiv \langle r \rangle = r_e + \delta r + \langle \Delta z \rangle + (\langle \Delta x^2 \rangle + \langle \Delta y^2 \rangle)/2r_e + \cdots, \quad (1)$$

where the z axis of the Cartesian coordinates is taken along the equilibrium positions of the nuclei, and Δz, Δx, and Δy denote the instantaneous relative displacements, the average being taken over the probability distribution function. A small correction for the centrifugal distortion δr is included. The linear term $\langle \Delta z \rangle$ depends on the cubic potential constants and should vanish if the molecular vibrations were harmonic. The quadratic terms $\langle \Delta x^2 \rangle$ and $\langle \Delta y^2 \rangle$, on the other hand, are primarily dependent on the quadratic potential constants and remain finite even if the vibrations were harmonic. The term $\langle \Delta z \rangle$ corresponds to the real variation in the mean positions of the nuclei due to the anharmonicity of the vibration, while the terms involving $\langle \Delta x^2 \rangle$ and $\langle \Delta y^2 \rangle$ come from the perpendicular harmonic vibrations by which the mean positions of the nuclei do not change. Thus it seems appropriate to consider a parameter r_α by subtracting the harmonic and the centrifugal contributions from r_g,

$$r_\alpha = r_g - (\langle \Delta x^2 \rangle + \langle \Delta y^2 \rangle)/2r_e - \delta r = r_e + \langle \Delta z \rangle + \cdots. \quad (2)$$

Since it is not difficult to calculate the harmonic and the centrifugal contributions by the theory of molecular vibrations,[4] the conversion of the experimental r_g to r_α is generally straightforward. If the anharmonic term $\langle \Delta z \rangle$ is also known, one can derive r_e from r_α, and even when $\langle \Delta z \rangle$ is unknown as in usual cases, one may often get a fair estimate of r_e based on r_α.

It should be mentioned in this connection that another distance parameter r_z has been suggested by Oka and Morino,[5,6] and a similar proposal has been made by Laurie and Herschbach.[7] The effect of molecular vibrations on the rotational constant B_0 is represented by constants α of the rotation-vibration interaction which consist of harmonic and anharmonic

contributions,

$$B_0 = B_e - \sum_s g_s \alpha_s / 2 = B_e - \sum_s g_s (\alpha_s{}^{harm} + \alpha_s{}^{anharm}) / 2. \quad (3)$$

Except for very simple molecules the constants α are not obtained experimentally for all vibrational modes of the molecule. Even in such cases, the harmonic parts can be calculated in good approximation based on the analysis of vibrational spectra. As stated before,[5] $\alpha_s{}^{anharm}$ is due to the real shifts of the positions of nuclei while $\alpha_s{}^{harm}$ is not. The situation is similar to that for r_0. One may thus define a moment of inertia in the ground state I_{zero} subtracting the harmonic contribution from the "effective" moment of inertia I_0

$$I_{zero} \equiv I_0 (1 - \sum_s g_s \alpha_s{}^{harm} / 2B_0)$$

$$= I_e (1 + \sum_s g_s \alpha_s{}^{anharm} / 2B_e). \quad (4)$$

The parameter r_z which is derived from I_{zero} corresponds to a mean distance in the ground vibrational state, and therefore, it has a clearer physical significance than r_0.

It is proven in general that $\lim(T \to 0^\circ K) r_\alpha \equiv r_\alpha{}^0 = r_z$ to the approximation we are concerned. If all normal frequencies of the molecule are much higher than kT/hc at the room temperature, no excited vibrational states contribute significantly, so that r_α is essentially equal to r_z. In such cases, the diffraction parameter r_g can be directly correlated with the spectroscopic parameter and vice versa with no reference to the anharmonicity. For molecules which have lower normal frequencies, r_α may depend on the temperature, but even in that case one may estimate r_z from r_α by means of an extrapolation, for instance.

An experimental demonstration of the above situation has been given for CH_4 and CD_4 by Bartell et al.[8] For these molecules, r_α is $1.098_7 \pm 0.001_2$ A (C—H) and $1.096_5 \pm 0.001_3$ A (C—D) from electron diffraction, while r_z is 1.099_5 A (C—H) and 1.096_0 A (C—D) from spectroscopy.[9]

For the C—S bond of CS_2, r_α is $1.555_4 \pm 0.002_1$ A ($288^\circ K$) from a recent diffraction experiment in this laboratory,[10] $r_\alpha{}^0$ (estimated from r_α) is 1.555_9 A, and r_z is 1.554_8 A from spectroscopy. It should also be noted that the equilibrium H—Se distance of hydrogen selenide has been obtained with a reasonable accuracy by extrapolating the r_z parameters of H—Se of H_2Se and D—Se of D_2Se.[6]

It is not our intention to cause a confusion by introducing new distance parameters, but it seems to be of practical importance to get a reasonable way of correlating diffraction and spectroscopic parameters with each other and of reaching the equilibrium distance r_e based on these experimental quantities.

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[8] L. S. Bartell, K. Kuchitsu, and R. J. deNeui, J. Chem. Phys. 35, 1211 (1961).
[9] Similar values of r_z have also been reported by Laurie and Herschbach. See reference 7.
[10] T. Iijima and Y. Morino (to be published).