EQUILIBRIUM BOND LENGTHS IN METHANE AND
DEUTERIOMETHANE AS DETERMINED BY ELECTRON DIFFRACTION
AND SPECTROSCOPIC METHODS*

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The absolute significance of experimental bond lengths reported for polyatomic molecules is often appreciably obscured by zero-point effects. In only a handful of spectroscopic studies has sufficiently detailed information been obtained to permit reduction of "effective" lengths, r_0 , to equilibrium lengths, r_e . In no electron diffraction investigations heretofore have the results been accurately reduced to r_e , even though the diffraction averaging problem, being essentially a purely vibrational one, is simpler than the spectroscopic problem. A really critical experimental comparison of the electron diffraction and spectroscopic methods, properly taking into account the different types of averaging over the zero-point motions, has never been made.

It seemed crucial to make a definitive comparison of the two methods, now that the precision of the diffraction method, properly applied, has approached that of the spectroscopic method. It is particularly important to examine molecules in which zero-point effects are large, as for example, molecules containing hydrogen atoms which

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exhibit unusually large and asymmetric vibrational motions because of their small mass. Methane, then, affords an especially suitable test.

Preliminary analyses have been made of diffraction patterns of CH_4 and CD_4 taken with the new electron diffraction apparatus of Iowa State University. Diffraction photographs were taken using 400eV electrons and an r^3 sector on Kodak 4" x 5" Process plates. Molecular diffraction features of CD_4 were observed to $q = 140$, whereas those of the more energetically vibrating CH_4 damped out at about $q = 130$. The data were analyzed by the radial distribution method as described elsewhere,¹ and reduced to molecular parameters by the method of steepest ascents, taking into consideration the asymmetry of vibration. Small corrections were made for the failure of the Born approximation² and for the measured delocalization of the noncondensable gas sample. The resulting mean distances, r_g , and root-mean-square amplitudes of vibration, l , are presented in Table I. Standard errors for the bonded distances appear to be not much greater than 0.001 Å. For comparison are listed amplitudes calculated from spectroscopic data, including effects of anharmonicity.

It should be noted that the experimental differences between hydrogen and deuterium parameters are significant. This represents the first demonstration by electron diffraction of an isotope effect on molecular parameters. The effect of anharmonicity in the intramolecular vibrations was shown to be present as a uniformly increasing phase shift of the molecular intensity features, and as a deviation from

Table I. Structural Parameters (angstrom units)

	CH ₃		CD ₃	
	C-H	H-H	C-D	D-D
r _e	1.107 ₀	1.811	1.102 ₃	1.895
I	0.076 ₀	0.121	0.066 ₀	0.104
I (calc)	0.075 ₆	0.121 ₆	0.066 ₉	0.102 ₆

a symmetrical Gaussian shape in the radial distribution curve. The asymmetry constant³ of the stretching potential derived from the intensity curve agreed well with the predicted constant, $a \sim 2.3 \text{ \AA}^{-1}$, and represents the first such value measured by electron diffraction.

The reduction of the mean bond lengths to equilibrium bond lengths requires the quadratic and cubic potential constants of the molecule. These were deduced as described elsewhere⁴ by representing the potential energy by a modified, anharmonic Urey-Bradley field in which stretching and nonbonded potentials were assumed to have the Lippincott and Buckingham forms, respectively. Several lines of evidence allow reasonable estimates to be made of potential parameters for which insufficient spectroscopic data are available. The required difference, $r_g - r_e$, was then calculated by a perturbed normal coordinate treatment. The results are given in Table II.

No reliable derivation of r_e from the spectroscopically measured r_0 is available for comparison. Therefore we have used the potential constants derived above to deduce the equilibrium distance, using the methods of Wilson and Howard,⁵ and of Hecht.⁶ The results, shown in Table II, indicate that the uncorrected spectroscopic and diffraction parameters differ appreciably from each other and from r_e . The excellent agreement between the equilibrium distances derived by the two methods lends weight to the present interpretation of the absolute significance of the parameters of each.

Table II. Correction of Electron Diffraction
and Spectroscopic Bond Lengths to r_0

	C-H in CH ₄	C-D in CD ₄
Electron Diffraction		
r_g (exp) ^a	1.107 ₀	1.102 ₃
$r_g - r_0$ (calc) ^b	0.022 ₁	0.016 ₅
r_0	1.084 ₉	1.085 ₈
Spectroscopy		
r_0 (exp)	1.094 ₁ ^c	1.092 ₈ ^d
$r_0 - r_g$ (calc) ^b	0.009 ₁	0.006 ₈
r_g	1.005 ₀	1.085 ₇

^a This investigation.

^b Reference 4.

^c E. P. Stoicheff (private communication); K. T. Hecht (private communication).

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