

Comparison of Molecular Structures Determined by Electron Diffraction and Spectroscopy. Ethane and Diborane

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(Received 15 July 1968)

Gas-phase average structures for the ground-vibrational state (r_s) for ethane and diborane have been determined by a critical comparison of the experimental results obtained from electron diffraction (average internuclear distances r_e) and those obtained from high-resolution infrared and Raman spectroscopy (rotational constants $B_2^{(\alpha)}$). Experimental values have been taken from the recent literature and converted into the average structure (r_s or r_a^0). The r_e and r_a^0 distances determined from electron diffraction carry uncertainties less than those in the r_s distances determined from rotational constants, because the latter structures are very sensitive to assumptions about the unknown isotope differences in the structures. On the other hand, the average moments of inertia from spectroscopy are much more precise than those calculated from diffraction internuclear distances. Examinations of the data have led to the following r_s structures with standard errors:

For C_2H_6 ,

$$r_s(C-H) = 1.0957 \pm 0.002 \text{ \AA}, \quad r_s(C-C) = 1.531_9 \pm 0.002 \text{ \AA}, \quad \text{and} \quad \angle C-C-H = 111.5^\circ \pm 0.3^\circ;$$

for C_2D_6 ,

$$r_s(C-D) = 1.094_1 \pm 0.002 \text{ \AA}, \quad r_s(C-C) = 1.530_0 \pm 0.002 \text{ \AA}, \quad \text{and} \quad \angle C-C-D = 111.4^\circ \pm 0.3^\circ;$$

and for B_2H_6 ,

$$r_s(B-H_t) = 1.19_2 \pm 0.01 \text{ \AA}, \quad r_s(B-H_b) = 1.32_9 \pm 0.005 \text{ \AA}, \quad r_s(B-B) = 1.77_0 \pm 0.005 \text{ \AA},$$

$$\angle H_t-B-H_t = 121.8^\circ \pm 3^\circ, \quad \text{and} \quad \angle H_b-B-H_b = 96.8^\circ \pm 0.5^\circ.$$

It was possible to increase the resolving power of the diffraction analysis of diborane by inclusion of calculated B-H mean amplitudes.

The effective complementary use of electron-diffraction and spectroscopic data for determining reliable gas-phase structures and the relative merits of the two alternative representations of the *average structure* (r_e and r_s) have been discussed.

INTRODUCTION

Previous theoretical studies¹⁻⁵ have given a practical method for comparing the molecular structures determined in the gas phase by high-resolution spectroscopy and electron diffraction. The method¹ makes use of the "average" moments of inertia $I_\alpha^{(s)}$ ($\alpha = a, b, c$) obtained from rotation or rotation-vibration spectroscopy and of the internuclear distances r_a^0 obtained from electron diffraction. Experimental values of $I_\alpha^{(s)}$ and r_a^0 can be obtained from the direct observables of spectroscopy and electron diffraction, namely, the ground-state rotational constants A_0, B_0, C_0 , and the r_a distances, respectively, by making numerical corrections for various vibrational effects. The corrections are usually so small that only an approximate knowledge of the intramolecular potential function is necessary. Except for systems

with very large amplitudes of vibration, the r_a^0 distances derived in this way should be essentially equivalent to the distances between the zero-point average atomic positions represented by $I_\alpha^{(s)}$ (the so-called r_s distances) to the accuracy of current experiments and conversions.

The structures of a number of simple polyatomic molecules have been studied by this method of critical comparison. Molecules investigated so far may be classified into two categories: The first group is comprised of molecules such as CH_4 ,^{1,3,6} CO_2 ,⁷ CS_2 ,⁸ BF_3 ,⁹ and NH_3 ,¹⁰ for which the structure of any one isotope species can be determined uniquely by spectroscopy. The spectroscopic r_s structures thus far determined have agreed satisfactorily with those determined by electron diffraction, giving experimental confirmation of the present method. The second category includes

* This research was supported by a grant from the National Science Foundation.

¹ Y. Morino, K. Kuchitsu, and T. Oka, *J. Chem. Phys.* **36**, 1108 (1962).

² T. Oka, *J. Phys. Soc. Japan* **15**, 2274 (1960).

³ (a) D. R. Herschbach and V. W. Laurie, *J. Chem. Phys.* **37**, 1668 (1962). (b) V. W. Laurie and D. R. Herschbach, *J. Chem. Phys.* **37**, 1687 (1962).

⁴ K. Kuchitsu and L. S. Bartell, *J. Chem. Phys.* **36**, 2460 (1962).

⁵ K. Kuchitsu and L. S. Bartell, *J. Chem. Phys.* **36**, 2470 (1962).

⁶ L. S. Bartell, K. Kuchitsu, and R. J. deNeui, *J. Chem. Phys.* **35**, 1211 (1961).

⁷ Y. Murata, T. Fukuyama, and M. Tanimoto, "Unit for the Precise Measurement of Electron-Diffraction Intensities by Gas Molecules. II," *Bull. Chem. Soc. Japan* (to be published).

⁸ Y. Morino and T. Iijima, *Bull. Chem. Soc. Japan* **35**, 1661 (1962).

⁹ K. Kuchitsu and S. Konaka, *J. Chem. Phys.* **45**, 4342 (1966). Note that in Eq. (9) of this reference the coefficient of $\sum_{\alpha} (f_{\alpha}^{(s)})^2$ should read -3 instead of +1.

¹⁰ K. Kuchitsu, J. P. Guillery, and L. S. Bartell, *J. Chem. Phys.* **49**, 2488 (1968).

molecules such as ethylene,¹¹ cyanogen,¹² glyoxal,¹³ and butadiene,¹³ for which a spectroscopic structure determination requires either a combination of isotope data or assumptions about the structure. Since the average structure is, in general, different from the equilibrium structure, there should be finite differences among the average structures of various isotope species because of vibrational effects, and they must be taken into account in the analysis.^{3b} Structures derived for molecules in the second category may be so sensitive to assumptions about isotope effects^{14,15} that uncertainties from this origin can be much larger than those due to experimental errors in the average moments of inertia. In such cases, the combination of electron-diffraction and spectroscopic data may be significantly more powerful than either technique alone.

The average structures of two molecules of basic importance in structural chemistry, i.e., ethane and diborane (and their perdeuterides) have been examined in the present study. Since both of them belong to the second category, the r_{α}^0 distances derived from electron diffraction have been used in combination with the average moments of inertia from spectroscopy to find their best available r_z structures.

ETHANE AND DEUTEROETHANE

Precise experimental values of the r_{α} distances from electron diffraction¹⁶ and the ground-state rotational

TABLE I. Mean amplitudes for ethane and ethane- d_6 (in Ångstrom units).

	l_{α} (obs) ^a	$\langle \Delta z^2 \rangle_T^{1/2}$ ^b	$\langle \Delta z^2 \rangle_0^{1/2}$ ^c
C ₂ H ₆ C-H	0.076 ₀ ±0.001 ₀	0.078 ₅	0.078 ₆
	C-C	0.049 ₆ ±0.001 ₀	0.050 ₉
	C...H	0.106 ₇ ±0.001 ₆	0.108 ₈
C ₂ D ₆ C-D	0.066 ₈ ±0.001 ₀	0.067 ₀	0.067 ₀
	C-C	0.051 ₇ ±0.001 ₀	0.050 ₈
	C...D	0.093 ₁ ±0.001 ₆	0.095 ₀

^a Reference 16. Uncertainties indicate standard deviations.

^b Calculated for room temperature.

^c Calculated for 0°K.

¹¹ K. Kuchitsu, J. Chem. Phys. **44**, 906 (1966).

¹² Y. Morino, K. Kuchitsu, Y. Hori, and M. Tanimoto, Bull. Chem. Soc. Japan **41**, 2349 (1968).

¹³ K. Kuchitsu, T. Fukuyama, and Y. Morino, J. Mol. Struct. **1**, 463 (1968).

¹⁴ K. Kivelson, E. B. Wilson, Jr., and D. R. Lide, Jr., J. Chem. Phys. **32**, 205 (1960).

¹⁵ W. J. Lafferty, D. R. Lide, and R. A. Toth, J. Chem. Phys. **43**, 2063 (1965).

¹⁶ L. S. Bartell and H. K. Higginbotham, J. Chem. Phys. **42**, 851 (1965).

TABLE II. Rotational constants for ethane and ethane- d_6 (in cm⁻¹ units).

	A_0	B_0
C ₂ H ₆	2.671±0.005 ^b	0.66310±0.00007 ^d 0.66313 ₅ ±0.00002 ₄ ^e
C ₂ D ₆	1.3416±0.0009 ^e	0.45973±0.00008 ^f
	A_z^a	B_z^a
C ₂ H ₆	2.682	0.6621 ₆
C ₂ D ₆	1.345	0.4592 ₂

^a Average rotational constants calculated in the present study from the corresponding experimental rotational constants A_0 and B_0 .

^b Reference 18.

^c Reference 17.

^d Reference 20.

^e Reference 21.

^f References 19 and 26.

constants A_0 and B_0 from Raman^{17,18} and infrared¹⁹⁻²¹ spectroscopy have been reported for C₂H₆ and C₂D₆. They were converted into the r_{α}^0 and the A_z , B_z constants¹ by means of the mean-square amplitudes and corrections for vibration-rotation interactions (Tables I and II). The conversions were based on the following equations^{9,11}

$$r_{\alpha}^0 = [\lim(T \rightarrow 0^\circ\text{K}) r_{\alpha}] - K_0 - \delta r_{\text{cent}} \\ \simeq r_{\alpha} - \frac{3}{2} a (\langle \Delta z^2 \rangle_T - \langle \Delta z^2 \rangle_0) - K_0 - \delta r_{\text{cent}}, \quad (1)$$

where

$$K_0 = (\langle \Delta x^2 \rangle_0 + \langle \Delta y^2 \rangle_0) / 2r \quad (2)$$

and

$$B_z^{(\alpha)} = \hbar / 8\pi^2 c I_{\alpha}^{(z)} \\ = B_0^{(\alpha)} - \sum_{\sigma\sigma'} \frac{B^2}{\omega_{\sigma}} \left[3A_{\sigma\sigma\sigma}^{(\alpha\alpha)} + 4 \sum_{\sigma'\sigma'' (\sigma' \neq \sigma'')} \frac{(\xi_{\sigma\sigma'\sigma''}^{(\alpha)})^2 \omega_{\sigma'}^2}{\omega_{\sigma}^2 - \omega_{\sigma'}^2} \right. \\ \left. - 3 \sum_{\sigma'} (\xi_{\sigma\sigma\sigma'}^{(\alpha)})^2 \right] + B_{\text{cent}}^{(\alpha)} \quad (\alpha = a, b, c), \quad (3)$$

and on the force constants²² which reproduce the observed values^{17,18,23} of fundamental frequencies and degenerate Coriolis constants satisfactorily. In Eqs. (1) and (2) x , y , and z are a set of local Cartesian displacement coordinates for a particular atom pair with z

¹⁷ D. W. Leppard, D. M. C. Sweeny, and H. L. Welsh, Can. J. Phys. **40**, 1567 (1962).

¹⁸ D. W. Leppard, D. E. Shaw, and H. L. Welsh, Can. J. Phys. **44**, 2353 (1966).

¹⁹ H. C. Allen, Jr., and E. K. Plyler, J. Chem. Phys. **31**, 1062 (1959).

²⁰ W. J. Lafferty and E. K. Plyler, J. Chem. Phys. **37**, 2688 (1962).

²¹ A. R. H. Cole, W. J. Lafferty, and R. J. Thibault, "Rotational Fine Structure of the Perpendicular Band, ν_7 , of Ethane," J. Mol. Spectry. (to be published).

²² I. Nakagawa (private communication).

²³ G. E. Hansen and D. M. Dennison, J. Chem. Phys. **20**, 313 (1952).

TABLE III. Average internuclear distances for ethane and ethane- d_6 (in Ångstrom units).

	r_0 (obs) ^a	K_0 ^b	r_a^0 ^c
C ₂ H ₆ C-H	1.112 ₂ ±0.001 ₂	0.015 ₇	1.097 ₁ ±0.002 ₀
C-C	1.534 ₀ ±0.001 ₁	0.0006	1.533 ₃ ±0.001 ₅
C···H	2.194 ₁ ±0.001 ₉	0.006 ₂	2.187 ₅ ±0.002 ₅
C ₂ D ₆ C-D	1.107 ₁ ±0.001 ₂	0.011 ₂	1.095 ₃ ±0.002 ₀
C-C	1.532 ₃ ±0.001 ₁	0.0009	1.531 ₃ ±0.001 ₅
C···D	2.189 ₂ ±0.002 ₀	0.004 ₄	2.183 ₃ ±0.002 ₅

^a Observed values by electron diffraction.¹⁶ Uncertainties indicate standard deviations.

^b Calculated by the use of force constants²² by Eq. (2).

^c Calculated from r_0 by Eq. (1).

taken in the direction of the equilibrium positions of atoms. Trivial effects of centrifugal distortion^{24,25} were ignored. The differences between r_0 and r_a^0 distances (Table III) and those between A_0 , B_0 , and A_z , B_z constants (Table II) exceed the corresponding experimental errors by an order of magnitude and, hence, the above corrections for the vibrational effect are found to be significant. The mean amplitudes l_0 observed by Bartell and Higginbotham¹⁶ agree well with the present results of calculations (Table I).

In order to determine the structure from spectroscopic data alone, one has to make at least two assumptions about the structures since there are three independent parameters for each isotope species but only two observable rotational constants for each. Shaw *et al.*,²⁶ determined effective r_0 structures on the assumptions that the H-C-H and D-C-D angles were identical and that the C-C distances in C₂H₆ and C₂D₆ were also identical. In the present analysis, the following assumptions were made in regard to the isotope differences:

$$r_z(\text{C-H}) - r_z(\text{C-D}) = 0.002 \pm 0.002 \text{ \AA},$$

and

$$r_z(\text{C-C, C}_2\text{H}_6) - r_z(\text{C-C, C}_2\text{D}_6) = 0 \pm 0.002 \text{ \AA}. \quad (4)$$

The above estimates were based on the relation^{1,11}

$$r_z(\text{H}) - r_z(\text{D})$$

$$\begin{aligned} &\simeq [r_0(\text{H}) - r_0(\text{D})]_0^{\circ} \text{K} - [K_0(\text{H}) - K_0(\text{D})] \\ &\simeq \frac{3}{2} a [\langle \Delta z^2 \rangle (\text{H}) - \langle \Delta z^2 \rangle (\text{D})]_0^{\circ} \text{K} - [K_0(\text{H}) - K_0(\text{D})], \end{aligned} \quad (5)$$

with the numerical values listed in Tables I and III. The parameters of bond-stretching anharmonicity, $a_{\text{C-H}}$ and $a_{\text{C-C}}$, were assumed to be $2.6 \pm 0.5 \text{ \AA}^{-1}$ and $2.0 \pm 0.5 \text{ \AA}^{-1}$, respectively, and allowance was made for

²⁴ M. Iwasaki and K. Hedberg, *J. Chem. Phys.* **36**, 2961 (1962).

²⁵ T. Oka and Y. Morino, *J. Mol. Spectry.* **6**, 472 (1961).

²⁶ D. E. Shaw, D. W. Leppard, and H. L. Welsh, *J. Chem. Phys.* **42**, 3736 (1965).

possible additional uncertainties.²⁷ No basis exists for estimating the difference between the average angles H-C-H and D-C-D with more certainty.

The corresponding r_z structure for C₂H₆ is found to be $r_z(\text{C-H}) = 1.093 \pm 0.008 \text{ \AA}$, $r_z(\text{C-C}) = 1.534 \mp 0.012 \text{ \AA}$, and $\alpha_z(\text{H-C-H}) = 107.5^\circ \pm 1.0^\circ$. The resulting isotope difference between the HCH and DCD angles, which depends essentially on the assumption of $r_z(\text{C-H}) - r_z(\text{C-D})$ alone, turns out to be $6' \pm 16'$.

As pointed out by Laurie and Herschbach²⁸ and for C₁CN by Lafferty, Lide, and Toth,¹⁵ the average structure is quite sensitive to the assumptions about isotope differences. The ambiguity in the structure introduced from this origin is several fold larger than that propagated from the uncertainties in the experimental rotational constants listed in Table II, even when the error in the 0 to z conversion is included in the latter uncertainties. Therefore, it seems difficult to determine the r_z structure with less ambiguity from rotational constants alone, no matter how accurate they may be, unless a better *a priori* estimate can be made for the differences in isotope structures.

On the other hand, unique sets of r_a^0 distances have been determined from electron diffraction alone separately for C₂H₆ and C₂D₆. As shown in Table IV, the average moments of inertia calculated from those r_a^0 distances are only about 0.2% larger than their spectroscopic counterparts, which are an order of magnitude more precise.²⁸ The nearly uniform discrepancies observed, although none of them are really significant,

TABLE IV. Average moments of inertia for ethane and ethane- d_6 (atomic mass units \times square Ångstrom units).

	$I_a^{(s)}$	$I_b^{(s)}$
C ₂ H ₆ SP (obs) ^a	6.28 ₆ ±0.01 ₂	25.459±0.003
ED (calc) ^b	6.30 ₃ ±0.02 ₅	25.507±0.03 ₄
C ₂ D ₆ SP (obs)	12.534±0.008	36.709±0.006
ED (calc)	12.58 ₄ ±0.05 ₀	36.76 ₄ ±0.06 ₇

^a From the observed average rotational constants A_z and B_z given in Table II.

^b Calculated from the r_a^0 distances by electron diffraction given in Table I.

²⁷ From this relation, a similar $r_z(\text{C-H}) - r_z(\text{C-D})$ may be expected for ethylene. Hence, the assumption made in Ref. 11 for the difference, 0.004_0 \AA , transferred from triatomic molecules and tetratomic molecules, may have been an overestimate. An alternative assumption, 0.002 \AA , will shift the spectroscopic r_0 structures of ethylene (r_{CC} , r_{CH} , and α_{CCH} listed in Table VII of Ref. 11) by $+0.0020 \text{ \AA}$, -0.0026 \AA , and $+10'$, respectively, and accordingly, the most probable r_z structure will be: $r(\text{C-H}) = 1.089 \pm 0.003 \text{ \AA}$, $r(\text{C-C}) = 1.336 \pm 0.003 \text{ \AA}$, and $\angle \text{C-C-H} = 121.9^\circ \pm 0.4^\circ$.

²⁸ The rotational constants A_0 for C₂H₆ reported earlier (a) 2.589 cm^{-1} [L. G. Smith, *J. Chem. Phys.* **17**, 139 (1949)] and (b) 2.578 cm^{-1} [J. Ramanko, T. Feldman, and H. L. Welsh, *Can. J. Phys.* **33**, 588 (1955)] lead to $I_a^{(s)}$ of 6.484 and $6.511 \text{ amu} \cdot \text{\AA}^2$, respectively. Since they appear to deviate significantly from the present estimate from electron diffraction, $6.30_3 \pm 0.02_5 \text{ amu} \cdot \text{\AA}^2$, the A_0 constant revised by Lepard *et al.*,¹⁸ $(2.671 \pm 0.005 \text{ cm}^{-1})$, $I_a^{(s)} = 6.286 \pm 0.012 \text{ amu} \cdot \text{\AA}^2$ seems to be more reasonable.

suggest that a slight systematic error (about 0.09% for C_2H_6 and about 0.07% for C_2D_6) may be present in the scale-factor measurement of electron diffraction.¹⁸ Accordingly, a tentative adjustment within the limit of experimental errors of the r_a^0 distances was made primarily on this basis, so as to reproduce the spectroscopic moments of inertia exactly. The r_0 and r_z distances shown in Table V has been obtained in this way. The $r_0(C-H)$ and $r_0(C-D)$ bond distances in C_2H_6 and C_2D_6 appear to be longer than the corresponding distances⁶ in CH_4 and CD_4 by about 0.004 Å, whereas the projected distances r_z seem to be in the opposite direction; the difference $r_0 - r_z$ is much larger for $C_2H_6(C_2D_6)$ than for $CH_4(CD_4)$, because the amplitudes of the H(D) atoms perpendicular to the C-H(C-D) bond are much larger in $C_2H_6(C_2D_6)$ than in $CH_4(CD_4)$.⁵

The effective r_0 structure reported by Shaw *et al.*²⁶ is very close to the present r_z structure. The difference of 0.0013 ± 0.002 Å in the $r_z(C-C)$ distances for C_2H_6 and C_2D_6 (the r_z secondary-isotope effect^{16,29}) is similar to the r_a secondary isotope effect, 0.0016 ± 0.0007 Å, reported by Bartell and Higginbotham.¹⁶ However, it has not been possible to decrease the uncertainty by the additional account of spectroscopic rotational constants. A more definitive solution of this problem depends crucially either on the experimental accuracy of electron diffraction or on the correct estimation of the r_z primary isotope effects on the C-H distance and the H-C-H angle.

DIBORANE

A set of F matrix elements was obtained from observed vibrational frequencies³⁰ by a normal-coordinate analysis,³¹ and used in the calculation of mean-square

TABLE V. Average structures for ethane and ethane- d_6^a (distances in Ångstrom units).

	r_0	r_z	σ^b	r_0^c
C_2H_6 C-H	1.110 ₈	1.095 ₇	0.002	1.095 ± 0.002
C-C	1.532 ₆	1.531 ₉	0.002	1.534 ± 0.002
C...H	2.192 ₁	2.185 ₈	0.003	(2.188 ± 0.004)
∠C-C-H	...	111.5°	0.3°	(111.6° ± 0.2°)
∠H-C-H	...	107.4°	0.3°	107.8° ± 0.2°
C_2D_6 C-D	1.105 ₈	1.094 ₁	0.002	1.093 ± 0.001
C-C	1.531 ₀	1.530 ₀	0.002	(1.534)
C...D	2.187 ₆	2.182 ₁	0.003	(2.187)
∠C-C-D	...	111.4°	0.3°	(111.6°)
∠D-C-D	...	107.4°	0.3°	(107.8°)

^a See Ref. 16, Table IV for the comparison of ethane structures studied earlier.

^b Estimated standard errors for r_0 and r_z parameters.

^c Effective r_0 structure determined by Shaw *et al.*²⁶

²⁹ L. S. Bartell, *J. Chem. Phys.* **36**, 3495 (1962).

³⁰ R. C. Lord and E. Nielsen, *J. Chem. Phys.* **19**, 1 (1951).
T. Ogawa and T. Miyazawa, *Spectrochim. Acta* **20**, 557 (1964).

³¹ The author is grateful to I. Nakagawa for providing his unpublished calculations on the normal-coordinate analysis of diborane and for his helpful discussions.

TABLE VI. Mean amplitudes for diborane and diborane- d_6 (in Ångstrom units).

	l_0 (obs) ^a	$\langle \Delta z^2 \rangle_T^{1/2}$	$\langle \Delta z^2 \rangle_0^{1/2}$
B_2H_6 B-H _t	0.073 ₄ ± 0.006	0.084 ₅	0.084 ₅
B-H _b	0.085 ₇ ± 0.009	0.101 ₆	0.101 ₆
B-B	0.060 ₈ ± 0.002	0.061 ₁	0.059 ₉
B...H _t	0.117 ₈ ± 0.005	0.129 ₁	0.122 ₇
B_2D_6 B-D _t	0.064 ₃ ± 0.005	0.072 ₃	0.072 ₃
B-D _b	0.075 ₆ ± 0.006	0.087 ₁	0.086 ₈
B-B	0.059 ₅ ± 0.002	0.060 ₈	0.059 ₄
B...D _t	0.104 ₉ ± 0.005	0.117 ₇	0.106 ₄

^a Electron diffraction analysis.³² The diffraction values can be brought into conformity with the present calculated values by decreasing the differences between bridge and terminal bond lengths, as shown in Fig. 6 of Ref. 32.

amplitudes and Coriolis coupling constants with a HITAC 5020E computer of the Computer Center, University of Tokyo. Parallel amplitudes are compared in Table VI with those observed by Bartell and Carroll.³² Corresponding to Tables II and III for ethane, Tables VII and VIII list average rotational constants and r_a^0 distances.

As pointed out by Bartell,³³ secondary isotope effects on C-C and B-B amplitudes for ethane (Table I) and diborane (Table VI), respectively, are very small in contrast to the significant primary isotope effects on C-H and B-H amplitudes. The amplitudes of bridge B-H bonds are about 20% larger than those of terminal B-H bonds, in accordance with the observation and discussion in Ref. 32 in terms of Badger's empirical rule. Nevertheless, the calculated B-H and B-D amplitudes are slightly but consistently larger than the corresponding rather approximate experimental values. According to Fig. 6 of this reference, the B-H (B-D) amplitudes correlate strongly with the difference between the bridge and terminal B-H distances, greatly reducing experimental accuracy, and probably the present systematic discrepancies originate from this difficulty. For this reason, the additional information provided by the calculated amplitudes can be used to augment materially the accuracy of the B-H distances derived from the diffraction intensities. The calculated amplitudes, together with Figs. 5 and 6 of Ref. 32, lead to the corrected sets of r_0 values [$r_0(\text{cor})$] shown in Table VIII.

Average rotational constants for the $^{10}B_2H_6$ and $^{11}B_2H_6$ species have been derived from Lafferty's experimental constants,³⁴ which are so precise that the 0 to z corrections are not trivial. Since structural parameters

³² L. S. Bartell and B. L. Carroll, *J. Chem. Phys.* **42**, 1135 (1965).
For structure of diborane, see Fig. 4 of this reference.

³³ L. S. Bartell, *J. Chem. Phys.* **42**, 1681 (1965).

³⁴ W. J. Lafferty (private communication, December 1967), to which the author is indebted. T. Coyle, W. J. Lafferty, and A. G. Maki, *J. Mol. Spectry.* (to be published).

TABLE VII. Rotational constants for diborane (in cm^{-1} units).

obs ^a	A_0	B_0	C_0
$^{10}\text{B}_2\text{H}_6$	$2.6555_0 \pm 0.0005_0$	$0.64219_0 \pm 0.00008_0$	$0.58737_2 \pm 0.00006_0$
$^{11}\text{B}_2\text{H}_6$	$2.6556_9 \pm 0.0002_4$	$0.60646_3 \pm 0.00006_3$	$0.55727_9 \pm 0.00005_3$
calc ^b	A_z	B_z	C_z
$^{10}\text{B}_2\text{H}_6$	$2.651_3 \pm 0.001_0$	$0.6403_1 \pm 0.0005$	$0.5868_9 \pm 0.0002$
$^{11}\text{B}_2\text{H}_6$	$2.651_9 \pm 0.001_0$	$0.6047_4 \pm 0.0005$	$0.5568_1 \pm 0.0002$
calc ^b	$A_0 - A_z$	$B_0 - B_z$	$C_0 - C_z$
$^{10}\text{B}_2\text{D}_6$	0.0018_7	0.0010_9	0.00018
$^{11}\text{B}_2\text{D}_6$	0.0017_7	0.0010_3	0.00017

^a Observed values by infrared spectroscopy with twice standard deviations.²⁴

^b Average rotational constants and correction terms, respectively, calculated in the present study.

TABLE VIII. Average internuclear distances for diborane and diborane- d_6 (in Ångstrom units).

	r_0 (obs) ^a	r_0 (corr) ^b	K_0	r_a^0
B_2H_6 B-H _i	$1.196_0 (+0.008, -0.006)$	1.208	0.0177	1.180
B-H _b	$1.339_3 (+0.002, -0.006)$	1.329	0.0111	1.329
B-B	$1.775_0 \pm 0.003_6$	1.775	0.0006	1.774
B...H _i	$2.588_1 \pm 0.009$	2.588	0.0058	2.583
B_2D_6 B-D _i	$1.198_0 (+0.006, -0.005)$	1.210	0.0113	1.187
B-D _b	$1.333_5 (+0.002, -0.004)$	1.323	0.0076	1.326
B-B	$1.771_2 \pm 0.003_6$	1.771	0.0011	1.770
B...D _i	$2.572_3 \pm 0.008$	2.572	0.0036	2.569

^a Observed values by electron diffraction.²² Uncertainties indicate standard deviations.

^b Corrected to be consistent with calculated mean amplitudes. See Figs. 5 and 6, Ref. 32.

TABLE IX. Average structures for diborane (distances in Ångstrom units).

	r_s (SP)	r_a^0 (ED)	r_a^0 (ED, corr)	r_s^a	r_0^b
B-H _i	$1.19_0 \mp 0.01_4$	$1.18_0 \mp 0.009$	1.19 ₂	$1.19_2 \pm 0.01$	$1.200_6 \pm 0.0018$
B-H _b	1.327 ± 0.005	$1.32_9 \pm 0.008$	1.31 ₉	$1.32_9 \pm 0.005$	$1.320_4 \pm 0.0005$
B-B	$1.76_4 \pm 0.01_4$	$1.77_4 \pm 0.00_4$	1.77 ₄	$1.77_0 \pm 0.005$	$1.762_3 \pm 0.0013$
$\angle \text{H}_i\text{BH}_i$	$120.7^\circ \pm 2.4^\circ$	$118.8^\circ \pm 3.4^\circ$	120.3°	$121.8^\circ \pm 3^\circ$	$121.0^\circ \pm 0.3^\circ$
$\angle \text{H}_b\text{BH}_b$	$96.7^\circ \mp 0.5^\circ$	$96.2^\circ \pm 0.8^\circ$	95.5°	$96.8^\circ \pm 0.5^\circ$	$96.2^\circ \pm 0.1^\circ$

^a Estimated from infrared (SP) and electron diffraction (ED) structures. Uncertainties represent standard deviations.

^b Effective r_0 structure (r_s for B-B) determined by Lafferty.²⁴

TABLE X. Average moments of inertia for diborane (in atomic mass units \times square Ångstrom units).

	$I_a^{(a)}$	$I_b^{(a)}$	$I_c^{(a)}$
$^{10}\text{B}_2\text{H}_6$ SP (obs) ^a	6.357 ± 0.002	$26.32_7 \pm 0.02_1$	$28.72_4 \pm 0.010$
ED (calc) ^b	$6.1_4 \pm 0.2$	$26.6_5 \pm 0.2$	$28.8_4 \pm 0.2$
ED (corr) ^c	6.2_3	26.5_1	28.9_0
$^{11}\text{B}_2\text{H}_6$ SP (obs)	6.357 ± 0.002	$27.87_6 \pm 0.02_3$	30.275 ± 0.010
ED (calc)	$6.1_4 \pm 0.2$	$28.2_2 \pm 0.2$	$30.4_1 \pm 0.2$
ED (corr)	6.2_3	28.0_7	30.4_6

^a From the observed rotational constants given in Table VII.

^c Calculated from the r_a^0 (corr) distances given in Table IX.

^b Calculated from the r_a^0 distances given in Table VIII.

are related to the moments of inertia as

$$\begin{aligned}\Delta_a &= I_b^{(s)} + I_c^{(s)} - I_a^{(s)} \\ &= m_B R^2 + 2m_H (R + 2r_t \cos \alpha_t)^2,\end{aligned}\quad (6)$$

$$\begin{aligned}\Delta_b &= I_c^{(s)} + I_a^{(s)} - I_b^{(s)} \\ &= 8m_H r_t^2 \sin^2 \alpha_t,\end{aligned}\quad (7)$$

and

$$\begin{aligned}\Delta_c &= I_a^{(s)} + I_b^{(s)} - I_c^{(s)} \\ &= 4m_H r_b^2 \sin^2 \alpha_b,\end{aligned}\quad (8)$$

where

$$\begin{aligned}r_t &= r_z(\text{B-H}_t), & r_b &= r_z(\text{B-H}_b), \\ 2\alpha_t &= \angle \text{H}_t\text{-B-H}_t, & 2\alpha_b &= \angle \text{H}_b\text{-B-H}_b,\end{aligned}$$

and

$$R = r_z(\text{B-B}) = 2r_b \cos \alpha_b, \quad (9)$$

it is possible to determine all the parameters uniquely by ^{10}B – ^{11}B substitution, provided some assumption is made about the isotope effect on structure. By a procedure analogous to the ethane analysis, the isotope effects were estimated from Eq. (5) to be

$$r_z(^{10}\text{B-}^{10}\text{B}) - r_z(^{11}\text{B-}^{11}\text{B}) = 0 \pm 0.001 \text{ \AA},$$

and

$$r_z(^{10}\text{B-H}) - r_z(^{11}\text{B-H}) = 0 \pm 0.0001 \text{ \AA}. \quad (10)$$

The uncertainty in the B–B isotope difference turned out to be the principal source of error in the spectroscopic r_z structure derived in this way [$r_z(\text{SP})$ in Table IX]; should this uncertainty be disregarded, the B–B and B–H bond distances would have errors of only about 0.002 Å, which originate from those in the average rotational constants. On the other hand, average moments of inertia calculated from the diffraction distances (Table X) have uncertainties several fold larger than those from spectroscopy because of the lack of accuracy in the diffraction parameters related to hydrogen positions.

Within the estimated uncertainties of about 0.01 Å, the average structures obtained from diffraction and spectroscopy are compatible. Small discrepancies between the diffraction and spectroscopic distances can be decreased if one assumes that the $r_z(^{10}\text{B-}^{10}\text{B})$ distance is larger than the $r_z(^{11}\text{B-}^{11}\text{B})$ by about 0.0005 Å. This suggests that the effective $a_{\text{B-B}}$ parameter in Eq. (5) is positive (as for any bonded atom pair) and of the order of $a_{\text{C-C}}$ ($\sim 2 \text{ \AA}^{-1}$).

The estimated average structure, which is consistent with the moments of inertia and with the diffraction distances, is compared in Table IX with the effective r_0 structure³⁴ obtained from ground-state rotational constants without regard to the isotope difference in structure. In order to determine the average structure of diborane with more accuracy [particularly the secondary isotope difference³² between the $r_z(\text{B-B})$ distances for B_2H_6 and B_2D_6], it would seem to be helpful, as in the case of ethane, to re-analyze electron diffraction intensities measured with the improved accuracy now available, taking into account the average rotational constants given in Table VII.

DISCUSSION

Use of Spectroscopic and Electron-Diffraction Data for Structure Determination

As is well known, high-resolution spectroscopy and electron diffraction are powerful and complementary experimental methods for determining gas-phase molecular structure. In the following cases spectroscopy is by far the more suitable method: (a) For diatomic and for some of the simple polyatomic molecules such as linear and bent XY_2 , where high-resolution spectroscopy is applicable and where precise r_0 and r_z structures can be determined uniquely from the rotational constants of a single isotope species; (b) For molecules such as OCS and NF_3 where the *equilibrium* rotational constants sufficient to determine the complete r_0 substitution structure can be obtained for various isotope species.

Conversely, for certain nonpolar molecules with large moments of inertia, electron diffraction is the only method available at present for determining precise internuclear distances in gas phase.

In many of the other situations, the use of electron diffraction distances, which may or may not be sufficient to determine the structure uniquely, should be effective to decrease the uncertainty in the spectroscopic average structure, as has been shown for ethane and diborane in the present study. On the other hand, spectroscopic moments of inertia may be helpful to discriminate closely spaced and nonequivalent internuclear distances, if any, and to calibrate the scale factor with more accuracy. Major limitations of the electron-diffraction method may be overcome in this way.^{12,13}

Merits of r_0 and r_z Representations

While the most complete description of "molecular geometry" seems to be the equilibrium internuclear distances r_0 plus the harmonic and anharmonic potential constants around the equilibrium positions, this description is available for only a limited number of simple molecules. For the rest of the molecules, the *average* structures r_0 and r_z are probably among the best possible representations of molecular geometry, since both structures have clear physical significance, and since they are more easily accessible from experiment than the r_0 structure.

When the average lengths of chemical bonds are of primary concern, the r_0 distance,¹ which represents "the average value of an instantaneous internuclear distance," should be a more suitable measure than r_z . On the other hand, r_0 distances for nonbonded atom pairs do not correspond exactly to any geometrical arrangement consistent with the r_0 distances for bonded pairs. As is well known in terms of the linear and non-linear shrinkage effect,^{35,36} effective bond angles calcu-

³⁵ Y. Morino, J. Nakamura and P. W. Moore, *J. Chem. Phys.* **36**, 1050 (1962).

³⁶ Y. Morino, S. J. Cyvin, K. Kuchitsu, and T. Iijima, *J. Chem. Phys.* **36**, 1109 (1962).

lated from bonded and nonbonded r_0 distances are, in general, different from average or equilibrium bond angles. In this connection, the r_z structure² is more convenient than r_0 as a representation of the geometrical arrangement of atoms, since r_z corresponds to "the distance between the average positions of atoms with respect to a molecule-fixed coordinate system."¹⁻³ However, the r_z distance for a bond should be interpreted as the average projection of the bond onto the line joining the equilibrium positions of the atoms in question ($r_0 + \langle \Delta z \rangle$) in the local Cartesian coordinate system of Eq. (1) instead of a real average bond distance ($r_0 + \langle \Delta r \rangle$). In any event, the difference between the r_0 and r_z representations is not a serious problem since they are readily interconvertible within current experimental uncertainty (except for large-amplitude cases).

The r_z distances of bonded atom pairs can be estimated approximately^{4,6,10,11} from the corresponding r_0 distances by the use of a parameter of bond-stretching anharmonicity a , which may be transferred from the corresponding diatomic molecules.³⁷ On the other hand, there is very limited information at present about the difference between average and equilibrium bond angles. Existing experimental evidence to date, however, suggests that the difference may be only a small fraction of a degree.

ACKNOWLEDGMENTS

The author wishes to thank Professor Yonezo Morino for his encouragement and Professor L. S. Bartell for his hospitality and valuable advice.

³⁷ K. Kuchitsu and Y. Morino, *Bull. Chem. Soc. Japan* **38**, 805 (1965).

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 49, NUMBER 10 15 NOVEMBER 1968

Analysis of Distortion Effects of the H₂O Molecule

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(Received 26 June 1968)

The method of moments is used to determine the centrifugal-distortion constants of the water molecule. However, to obviate the inclusion of sixth-power terms of the angular-momentum operators in the Hamiltonian, an expression obtained from a second-order transformed Hamiltonian is included to determine the independent centrifugal-distortion constants. By application of the method to infrared spectral data, nine distortion constants were obtained, as were the rotational constants.

INTRODUCTION

The general motion of a molecular system may be considered as the vibrational motion of the individual nuclei plus the rotational motion of the system as a whole. The latter type of motion gives rise to "centrifugal" forces, which cause distortion effects on the individual nuclei. Thus, the Hamiltonian expression describing the motion of the molecule, must include zero-order terms and perturbation terms, arising from the centrifugal effects. These perturbation terms are functions of the total angular-momentum components and certain parameters called centrifugal-distortion constants.

From the method of moments, as developed by Parker and Brown,¹⁻⁴ expressions relating spectral

data to the parameters of the molecular system may be obtained. Since the water molecule is a very "stretchy" molecule, if P^6 terms in the Hamiltonian are neglected, these expressions are not sufficient to describe its motion. Hence, we have resorted to a perturbation treatment given by Nielsen⁵ for additional information. With this information we have obtained equations which allow us to calculate the centrifugal-distortion constants from experimental spectral data.

THEORY

Since the method of moments is the basis for our development, a brief discussion of the method, as given by Parker and Brown,¹⁻⁴ will be given as introduction to our problem.

In matrix notation the energy eigenvalues of the Schrödinger equation

$$H\psi_n = E\psi_n \quad (1)$$

¹ L. C. Brown and P. M. Parker, *J. Chem. Phys.* **27**, 1108 (1957).

² P. M. Parker and L. C. Brown, *J. Chem. Phys.* **30**, 909 (1959).

³ P. M. Parker and L. C. Brown, *J. Chem. Phys.* **31**, 1227 (1959).

⁴ P. M. Parker and L. C. Brown, *Am. J. Phys.* **27**, 509 (1959).

⁵ H. H. Nielsen, *Rev. Mod. Phys.* **23**, 90 (1951).