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Molecular Structure of Ethane. Comparison of the Structure Parameters of CH_3CD_3 in the Torsionally Excited State and in the Ground State

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The structure parameters of ethane have been re-examined by the use of the spectroscopic moments of inertia and the electron diffraction results, on the basis of the large amplitude theory for the torsional motion. The results have been applied to the CH_3CD_3-species in order to see whether or not the change of the moment of inertia in the torsionally excited state observed by Hirota and Matsumura is consistent with the theoretical prediction on the deformation of the molecular frame upon torsion proposed by Veillard. The conclusion has been affirmative. The elongation of the C–C distance by 0.0028 Å and the decrease of the HCH angle by 0.05° in the torsionally excited state as expected from the theoretical calculation have been found to be consistent with the experimental result of microwave spectroscopy.

According to several experimental results obtained by microwave spectroscopy[1–3] and a series of theoretical studies,[4–7] it seems that the torsional motion of molecules involves sizable deformations of the frame and/or the top. Meyer and Wilson[2] extensively investigated the rotational constants of torsionally excited states

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[1] P. Meakin, D. O. Harris, and E. Hirota, *J. Chem. Phys.*, **51**, 3775 (1969).

[2] R. Meyer and E. B. Wilson, Jr., *ibid.*, **53**, 3969 (1970).

[3] E. Hirota and C. Matsumura, *ibid.*, **55**, 981 (1971).

[4] A. Veillard, *Chem. Phys. Lett.*, **3**, 128 (1969).

[5] H. J. Monkhorst, *ibid.*, **3**, 289 (1969).

[6] A. Veillard, *ibid.*, **3**, 565 (1969).

[7] A. Veillard, *ibid.*, **4**, 51 (1969).

of ethyl formate and two other compounds. They concluded that observed changes of rotational constants upon torsional excitation could not be explained without allowing distortions of the molecular geometry upon torsion. An *ab-initio* molecular Hartree-Fock calculation of ethane was carried out by Veillard,[4] where the C–C distance and the HCH angle were optimized. The barrier hindering internal rotation was calculated to be 3.07 kcal/mol, which was very close to the experimental value 2.93 kcal/mol. The C–C distance of the eclipsed conformation was found to be longer than that of the staggered conformation by 0.019 Å, and the HCH angle was smaller by 0.34°. It was not necessary to vary the C–H distance.

In order to get experimental confirmation of this theoretical prediction, ethane is naturally the most suitable molecule. However, since ordinary ethane is inactive in microwave, the rotational constant of the torsionally excited state had not been available. Recently, Hirota and Matsumura[3] made successful observation of the microwave spectrum of CH_3CD_3 species and obtained the rotational constants of both the ground state and the torsionally excited state. The present study is an analysis of the structure parameters of ethane, especially for the purpose of seeing whether or not the theoretical calculation by Veillard is consistent with the experimental observation by Hirota and Matsumura. The conclusion of the present study is that they are consistent with each other. This is also to support the theoretical implication of Veillard's calculation that the electron correlation is not important in the barrier to internal rotation, contrary to the binding energy in which the effect of electron correlation (molecular correlation) is considerable.[8] The deformation of molecular geometry upon torsion is to give an additional correction in the structure determination by a joint use of spectroscopic and diffraction data, since the observed values of diffraction experiment are averaged quantities over torsionally excited state. The force constants determined by Nakagawa and Shimanouchi[9] were used throughout this work.

Analysis

Changes of the Structure Parameters between the Ground State and the First Excited State of Torsional Motion. On the basis of Veillard's calculation, the changes of the C–C distance and the HCH angle for different torsional states were estimated by assuming that the variation of the structure parameters follows the trigonometric function as that of the torsional potential, *viz.*,

$$\Delta r = \frac{c}{2}(1-\cos 3\phi) \tag{1}$$

where c is 0.019 Å for the C–C distance and −0.34 Å for the HCH anlge, and ϕ is the torsional angle. The average value of Δr for the torsional state τ was evaluated by

$$\langle \Delta r\rangle_\tau = \frac{9}{4}c\langle \phi^2\rangle_\tau \tag{2}$$

where the $<\phi^2>$ was calculated by a harmonic approximation.

The values of $<\Delta r>$ calculated by Eq. (2) are summarized in Table 1 for the ground state ($\tau=0$) and the first excited state ($\tau=1$). The thermal average values $\tau=T$ at the room temperature are also shown. A similar table for the HCH angle are shown also in the Table 1. From the values in Table 1, it is expected that the structure parameters of CH_3CD_3 for the first excited state of torsion is different from those of the ground state in such a way that the C–C distance is longer by 0.0028 Å and the HCH angle is smaller by 0.05°.

Table 1. Changes of the C–C distance and the HCH angle for different torsional states

	CH_3CH_3	CD_3CD_3	CH_3CD_3
$\langle\Delta r\rangle_0$	17(−31)[b]	12(−22)	14(−25)
$\langle\Delta r\rangle_1$	51(−92)	36(−65)	42(−76)
$\langle\Delta r\rangle_T$[a]	27(−49)	26(−47)	25(−45)

a) Thermal average values at $T=288$ K
b) Values in the parentheses are the corresponding averages of the HCH angle in 10^{-3} degree units.

Even without the detailed analysis described in the following section, it can be seen that the b-axis moments of inertia I_b obtained by Hirota and Matsumura show a trend which is consistent with the estimation mentioned above. The increase in the C–C distance of 0.02% roughly corresponds to an increase in I_b of 0.04%. Observed value of I_b for the excited state is 0.03% as large as the I_b for the ground state (see Table 2).

Since the thermal average values $<\Delta r>_T$ are almost equivalent for all the isotopic species, the isotope effect originating from the torsional distortion can not be expected to appear in r_g values obtained by electron diffraction. On the other hand, the small differences in $<\Delta r>_0$ will be the isotope effect of this origin upon $r_\alpha{}^0$ or r_z, *i.e.*, the zero-point average distances. More important is the difference between $<\Delta r>_T$ and $<\Delta r>_0$ which should be included in the correction of r_g to $r_\alpha{}^0$ in the joint analysis of electron-diffraction and spectroscopic data on the basis of the zero-point average structure.[10]

Structure Parameters. The structure parameters of CH_3CH_3 and CD_3CD_3 were previously determined by Kuchitsu[10] by means of a joint use of electron diffraction data and spectroscopic moments of inertia. In his treatment, the torsional motion was regarded as a small-amplitude vibrational motion, which was valid since the torsional amplitudes of these molecules are not very large. In the present study, the structure parameters of h_6 and d_6-species were re-determined on the basis of the large amplitude theory for a molecule containing a single internal rotor,[11] simply in order to apply the obtained parameters to the torsionally excited state of CH_3CD_3 in which the small-amplitude approximation would probably fail. In fact the determined parameters of h_6 and d_6-species have shown

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[8] E. Clementi and H. Popkie, *J. Chem. Phys.*, **57**, 4870 (1972).
[9] I. Nakagawa and T. Shimanouchi, *J. Mol. Spectrosc.*, **39**, 255 (1971).
[10] K. Kuchitsu, *J. Chem. Phys.*, **49**, 4456 (1968).
[11] T. Iijima and S. Tsuchiya, *J. Mol. Spectrosc.* **44**, 88 (1972).

Table 2. Moments of inertia of ethane (in amu. Å^2 units)

		I_0[f]	ΔI	I_z(SP)	I_z(ED)	I_z^{calcd}
CH_3CH_3	a	6.313[a] (12)[e]	0.040	6.353 (20)	6.365 (25)	6.348
	b	25.430[b] (3)	0.126	25.556 (13)	25.513 (34)	25.554
CD_3CD_3	a	12.569[a] (8)	0.059	12.628 (18)	12.658 (50)	12.632
	b	36.680[c] (6)	0.165	36.845 (16)	36.785 (67)	36.847
CD_3CH_3	a	—	0.051	—	—	9.490
	b	30.686[c]	0.142	30.828 (10)	—	30.827
CD_3CH_3[g]	a	—	0.051	—	—	9.484
	b	30.790[d]	0.142	30.932 (10)	—	30.921

a) Ref. 13, b) Ref. 14, c) Ref. 15, d) Ref. 3.

e) Values in the parentheses are the uncertainties as cited from Ref. 10, except for the uncertainties of I_z(SP) which were estimated in the present study.

f) Conversion factor 505531 Mc. amu. Å^2 was used. g) Torsionally excited state.

Table 3. Structure parameters of ethane[a] (in Å and degree units)

	I	II[b]		II	II[d]
	CH_3CH_3			CD_3CH_3	
C–C	1.5323	1.5323	C–C	1.5310	1.5338
C–H	1.1017	1.1017	C–H	1.1017	1.1017
HCH	107.51	107.30	C–D	1.0990	1.0990
	CD_3CD_3		HCH	107.30	107.25
C–C	1.5299	1.5299	DCD	107.35	107.30
C–D	1.0990	1.0990		Uncertainties[c]	
DCD	107.51	107.35	C–C ± 0.002, C–H(D) ± 0.002		
			HCH(DCD) ± 0.3°		

a) I; the $r_\alpha{}^0$ parameters obtained from electron diffraction data. II; the best r_z-parameters.

b) The r_g-parameters consistent with the r_z-values of the set II are equivalent to the electron diffraction results of Ref. 17, except for the HCH and DCD angles or the non-bonded C···H and C···D distances, which are 2.196_4 Å for C···H and 2.190_9 Å for C···D.

c) To be applied to all the isotopic species. Note that these are uncertainties in the absolute values of the parameters and that the uncertainties in the relative scale are much smaller.

d) Torsionally excited state.

no significant discrepancy from those by Kuchitsu, if the difference in the operational definitions of the parameters is taken into account in the comparison.[12]

In Table 2 are listed the observed values of moments of inertia, the vibrational corrections calculated by the method reported elsewhere,[11,16] and the zero-point average moments of inertia I_z(SP). The moments of inertia calculated by the use of the $r_\alpha{}^0$-parameters obtained from the electron diffraction result by Bartell and Higginbotham[17] are compared as I_z(ED). Although a trend that I_z(ED) was systematically larger than I_z(SP) by 0.02% was observed in the analysis by Kuchitsu, it is not seen in the present result. This is partly because of the correction for the torsional deformation included in the conversion of r_g into $r_\alpha{}^0$.

A comparison of I_z(ED) and I_z(SP) suggests that a slight adjustment of HCH angle would lead to a set of parameters consistent with the I_z(SP). The values of I_z calculated by the adjusted parameters are listed in the column I_z^{calcd} of Table 2, while the values of the parameters are shown in Table 3.

The structure parameters for the ground state of CH_3CD_3 were then determined as follows. The C–C distance was set equal to the average of those of h_6 and d_6-species. The HCH and DCD angles were transferred from h_6 and d_6-species, respectively. The agreement of the calculated I_z^{calcd} with the observed I_z(SP) is satisfactory. For the torsionally excited state, the C–C distance and HCH (DCD) angle were varied according to the estimation described in the preceding section. The agreement of the calculated value of the moments of inertia with the observed is remarkable. It may be said that the theoretical prediction on the deformation of molecular frame upon torsion has been

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[12] The zero-point average structure in Ref. 10 is a representation of the atomic positions averaged over all zero-point motions including torsion, while the torsional motion is not included in the averaging in the present treatment. The effect of this difference appears mainly in the structure parameters related to hydrogen atoms.

[13] D. E. Shaw and H. L. Welsh, *Can. J. Phys.*, **44**, 3823 (1967) and two preceding papers.

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

[15] H. C. Allen and E. K. Plyler, *ibid.*, **31**, 1062 (1959).

[16] In order to reduce the off-diagonal term of the moments of inertia tensor in the kinetic energy Hamiltonian, the molecular-fixed coordinate-axes for h_6 and d_6-species were chosen in such a way that the torsion of an angle ϕ was represented by a rotation of $\phi/2$ of both ends in the opposite directions. For CH_3CD_3, the rotations of the two tops CH_3 and CD_3 were chosen to be inversely proportional to the moment of inertia of each top around the axis.

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

given quantitative confirmation by experimental observation.

In the present analysis, the secondary isotope effect in the C–C distance was retained as originally reported in the electron diffraction study.[17] If this isotope effect is ignored and an average of the C–C distances in the h_6 and d_6-species is taken as the diffraction value, a slightly different set of structure parameters can be obtained, although the difference is of no significance. However, there would be no revision in the conclusion about the comparison of the ground state and the torsionally excited state of the CD_3CH_3 species.

As for the estimation of the uncertainties of the determined parameters, the present study has nothing to revise the values reported in Ref. 10, which are reproduced in Table 3. However, these are the uncertainties in the absolute values of the parameters, and the uncertainties in the relative scale, *i.e.*, the difference between the torsionally excited state and the ground state, are much smaller.

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