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The Zero-point Average Structure of Acetone

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The zero-point average structure of acetone has been determined from the moments of inertia obtained by means of microwave spectroscopy by Nelson and Pierce, as incorporated with the average distances from gas-electron diffraction by Kato *et al.* In addition to the normal species $(CH_3)_2CO$, three isotopically-substituted species, $(^{13}CH_3)_2CO$, $(CH_3)_2C^{18}O$, and $(CD_3)_2CO$, have been used in the analysis. The following values of the r_z-parameters have been determined: C=O, 1.2122±0.0025 Å; C–C, 1.5190±0.0008 Å; C–H, 1.0614±0.0010 Å; ∠HCH, 108°30′±6′; and ∠CCC, 116°9′±10′ (∠CCC for $(CD_3)_2CO$, 115°51′±10′). The slightly smaller value of ∠CCC found for the deuterated species has been reasonably attributed to the anharmonicity associated with the symmetric rocking motion of the two methyl tops. The equilibrium values for C–H(D) and ∠CCC have also been estimated to be 1.078 Å and 115°0′ respectively.

The molecular structure of acetone was studied by Nelson and Pierce[1] by means of microwave spectroscopy. They obtained the moments of inertia of $(CH_3)_2CO$ and three isotopically-substituted molecules $(^{13}CH_3)_2CO$, $(CH_3)_2{}^{18}O$ and $(CD_3)_2CO$, and determined the so-called r_s-structure of this molecule. For the deuterated species $(CD_3)_2CO$, they used the spectra which had previously been observed by Swalen and Costain.[2] The moments of inertia calculated by the use of their r_s-parameters differed from the observed moments by as much as 0.4 amu.Å^2. This is not surprising, however, because correction is necessary for the vibrational effect on the observed effective moments of inertia in order to find a set of parameters which will account for all the moments of inertia of isotopically-substituted species.

In the present study, the observed effective moments of inertia for the ground vibrational state have been reduced to the zero-point moments of inertia by applying vibrational correction, and the zero-point average structure has been determined. In the process of the structure determination, the previous electron-diffraction results by the present author and his collaborators[3] have also been used. As a result, an isotope effect has been found in the zero-point average values of the CCC angles.

Determination of r_z-Parameters

The procedure of applying the vibrational correction to the observed effective moments of inertia, $I_\alpha^{(0)}$, in order to obtain the zero-point moments of inertia, $I_\alpha^{(z)}$, is the same as that reported in the previous paper on the zero-point average structure of acetaldehyde.[4] Accordingly, only the results are shown in the present paper (Table 1). The quadratic force field by Cossee and Schachtschneider[5] (the set VF3) was used in the calculation of the vibrational correction. The vibrational averages of the linear displacements along the equilibrium bond direction were also calculated for the C–H and C–D bonds in order to estimate the possible isotope effect on the r_z(C–H), or r_z(C–D) value of each isotopically-substituted species. As

TABLE 1. MOMENTS OF INERTIA OF ACETONE (in amu.Å^2 units)

		$I_\alpha^{(0)}$ a)	$I_\alpha^{(z)}$
$(CH_3)_2CO$	a	49.7296	49.5970
	b	59.3698	59.3108
	c	102.9559	102.9230
$(^{13}CH_3)_2CO$	a	50.6695	50.5198
	b	62.6916	62.6339
	c	107.2219	107.1782
$(CH_3)_2C^{18}O$	a	53.0613	52.9124
	b	59.3701	59.3046
	c	106.2938	106.2482
$(CD_3)_2CO$	a	59.6897	59.4442
	b	78.7481	78.6188
	c	126.0280	125.9675

a) Determined by Nelson and Pierce.[1]

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[1] R. Nelson and L. Pierce, *J. Mol. Spectry.*, **18**, 344 (1965).

[2] J. D. Swalen and C. C. Costain, *J. Chem. Phys.*, **31**, 1562 (1959).

[3] C. Kato, S. Konaka, T. Iijima and M. Kimura, This Bulletin, **42**, 2148 (1969).

[4] T. Iijima and M. Kimura, *ibid.*, **42**, 2159 (1969).

[5] P. Cossee and J. H. Schachtschneider, *J. Chem. Phys.*, **44**, 97 (1966).

may be seen from Table 2, the r_z value of the C–D bond can be expected to be longer than r_z(C–H) by 0.007 Å.

Table 2. Calculated values of $\langle \Delta z \rangle_0$ of C–H(D)[a] (in Å units)

	$\langle \Delta z \rangle_0$
$(CH_3)_2CO$	−0.017
$(^{13}CH_3)_2CO$	−0.016
$(CH_3)_2C^{18}O$	−0.017
$(CD_3)_2CO$	−0.010

a) Morse anharmonicity constant a_3 was assumed to be 1.98 $Å^{-1}$.

The angle between the axes of the two methyl tops is denoted by 2θ; it was determined by Nelson and Pierce1) as 119° 54′±30′*1 by an analysis of the multiplet separation of the spectrum caused by the coupling between the internal rotation and the overall rotation of the molecule. Since the value of 2θ was determined independently of the other structure parameters, the Nelson and Pierce value, namely, 119°54′, has been assumed in the present study.

The r_g distances of C–C and C=O, as determined by gas-electron diffraction, were converted to the r_z values shown in Table 3 in order to afford additional information for the structure determination. The details of the process of conversion have been reported in a previous paper.4)

Table 3. Conversion from r_g to r_z (in Å units)

	r_g	l_T^2	l_0^2	K_0
C–C	1.517	0.00262	0.00254	0.0023
C=O	1.211	0.00154	0.00153	0.0032

	δr_{cent}[a]	a_3[b]	r_z
C–C	0.0002	2.1	1.514
C=O	0.0002	2.4	1.208

a) assumed.
b) Morse anharmonic constant.

We assumed that the molecule including the methyl hydrogens had a C_{2v} symmetry and that the outer two hydrogens were on the plane formed by the molecular frame. However, the results of the present study are independent of the assumed conformation of the methyl hydrogens. In other words, no definite information has been obtained on the conformation of the methyl hydrogens by either the present analysis or the previous studies.1–3)

For the value of $I_a^{(z)}+I_b^{(z)}-I_c^{(z)}$, the out-of-plane coordinate (c-coordinate) of the hydrogen atom was determined for each isotopically-substituted species. As is shown in Table 4, the coincidence between the c-coordinates of the H-atoms is quite satisfactory, while the larger value for the D-atom is well accounted for by assuming that r_z(C–D) is longer than r_z(C–H) by 0.006 Å. This amount of difference between r_z(C–D) and r_z(C–H) is in good agreement with the expected value, 0.007 Å, estimated by the use of $\langle \Delta z \rangle_0$, shown in Table 2. A similar situation has already been reported in the cases of ethane6) and acetaldehyde.4)

Table 4. Out-of-plane coordinates of H and D atoms[a] (in Å units)

$(CH_3)_2CO$	0.8616
$(^{13}CH_3)_2CO$	0.8609
$(CH_3)_2C^{18}O$	0.8604
$(CD_3)_2CO$	0.8664

a) Calculated from $I_a^{(z)}+I_b^{(z)}-I_c^{(z)}$.

By keeping 2θ fixed at 119°54′, we tried to adjust the five structure parameters, r_z(C–O), r_z(C–C), r_z(C–H), α_z(CCC), and α_z(HCH), so as to make the calculated moments of inertia fit all the observed moments well, with the additional condition that r_z(C–D) was longer than r_z(C–H) by 0.006 Å. The α_z(DCD) was assumed to be equivalent to α_z(HCH). However, it was revealed that no satisfactory set of parameters could be obtained as long as the moments of inertia of the deuterated species were included. This implies that, in addition to r_z(C–D), at least one r_z-parameter of the deuterated species should take different values from those of other species provided the procedure of data handling is appropriate. Accordingly, the structure parameters were determined without the moments of inertia of the deuterated molecule.

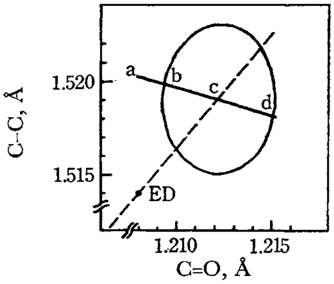

Fig. 1. The parameters r_z(C=O) *vs.* r_z(C–C) of acetone. The solid line gives sets of parameters which account almost equally well for the observed moments of inertia. The diffraction values are denoted by ED, which may vary along the broken line if an uncertainty of the scale factor is allowed for. The circle shows the errors of the ED-values without those originating in the scale factor.

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*1 The values of 2θ for $(^{13}CH_3)_2CO$ and $(CD_3)_2CO$ were also determined by them to be 119° 42′ and 119° 54′ respectively.

6) K. Kuchitsu, *J. Chem. Phys.*, **49**, 4456 (1968).

Table 5. Deviations of the calculated moments of inertia from the observeda) (in amu.Å^2)

		Set a	Set b	Set c	Set d
$(CH_3)_2CO$	I_a	+0.016	+0.016	+0.015	+0.015
	I_b	−0.001	+0.003	+0.009	+0.014
$(^{13}CH_3)_2CO$	I_a	−0.013	−0.013	−0.013	−0.014
	I_b	−0.009	−0.007	−0.003	0.000
$(CH_3)_2C^{18}O$	I_a	−0.022	−0.025	−0.013	−0.016
	I_b	+0.011	+0.015	+0.003	+0.008
$(CD_3)_2CO$	I_a	—	—	+0.154 (−0.012)b)	—
	I_b	—	—	−0.220 (−0.002)b)	—

a) Values of (obs'd)—(calc'd) are tabulated.
b) With CCC angle reduced by 18′.

As is shown in Fig. 1 and Table 5, a rather wide range of variation in parameters accounts equally well for the observed values of $I_a^{(z)}$ if the mutual correlation between the parameters is properly taken into account. The situation graphically shown in Fig. 1, where a point on the solid line indicates a definite set of parameters which gives a good fit between the calculated $I_a^{(z)}$ and observed $I_a^{(z)}$ values. Although the values of the parameters other than r_z(C–O) and r_z(C=C) are not explicitly shown in Fig. 1, a definite value for each parameter corresponds to each point on the solid line.

The strong correlation between parameters was alleviated by the use of electron-diffraction results as additional information, as has been successfully done in the cases of acetaldehyde4) and also several other molecules.7) The point ED in Fig. 1 shows the diffraction values. By allowing for an uncertainty in the scale factor of the ED data, the set ED may vary along the broken line. Therefore, the cross point of the broken line and the solid line, namely, the set c, was obtained as the most reliable set of structure parameters.[*2] The region of the solid line cut out by the error circle of the ED data determines the error of the parameters of the set c. The error circle does not, however, include the error associated with the uncertainty of the scale factor. The values of the parameters of the set c are listed in Table 6.

Table 6. The r_z-parameters of acetone (in Å units)

C–C	1.5190±0.0008
C=O	1.2122±0.0025
C–H	1.0614±0.0010a)
∠HCH	108°30′±6′
∠CCC	116°9′±10′b)
2θ	119°54′±30′ (assumed)

a) 1.0674 for C–D of $(CD_3)_2CO$
b) 115°51′ for CCC of $(CD_3)_2CO$

For the deuterated species which has been left out, the set c still leaves a rather large deviation of the calculated $I_a^{(z)}$ value from the observed value, as is shown in Table 5. This deviation, however, can be eliminated only if α_z(CCC) is reduced by 18′ for the deuterated species.[*3] Accordingly, the present author takes the view that the zero-point average value of the CCC angle of $(CD_3)_2CO$ is less than that of $(CH_3)_2CO$ by 18′. This can most easily be understood as an effect of the bending anharmonicity, which makes it harder for the CCC angle to narrow than to widen. The anharmonicity will be discussed further below.

The above conclusion on the isotope effect found in the CCC angle is not vulnerable to the ambiguity of the value of 2θ. Even if the value of 2θ for $(CD_3)_2CO$ were 1° less than that of $(CH_3)_2CO$, the CCC angle of the deuterated species would be required to be only 1.4′ smaller from I_a value and 1.5′ larger from I_b value; that is, substantially no change would be required in the sense of a least-squares fitting. It should be noted, however, that the question of whether the 2θ value obtained by the spectroscopic analysis can be interpreted as $2\theta_z$, *i. e.*, the angle between the two top-axes in the zero-point average structure, is still unsettled. The equivalence of 2θ and $2\theta_z$ within the reported area of uncertainty has been assumed in the present study.

From the difference between 2θ and α_z(CCC), it is seen that the methyl tops are tilted outwards by nearly 2°.

Discussion

The Effect of Bending Anharmonicity on α_Z(CCC). If it is assumed that a cubic term of the kth symmetry coordinate is present in the intramolecular potential function in such a form as:

$$V' = F_k^{(3)} S_k^3, \qquad (1)$$

the zero-point average of the lth symmetry coordinate can be given by a rather simple relation (see

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7) References 6 through 10 cited in the reference 4: S. Konaka and M. Kimura, "Determination of the molecular structures of AsF_3 and $AsCl_3$ by gas electron diffraction." This Bulletin, to be published.

[*2] It may be seen in Fig. 1 that an error of 0.3% was included in the scale factor of the ED value. This is slightly larger than the limit of error reported in current ED studies. Since there is evidence which strongly suggests that the stabilizing circuit of the accelerating voltage of the electron beam was in a threatening condition at the time acetone was studied, a reinvestigation of this molecule by electron diffraction is now under way.

[*3] A similar situation was observed by Swalen and Costain2) in their determination of r_0-parameters. The difference between the CCC angles of the normal and the deuterated species was 32′ in their case.

Appendix for the derivation) as:

$$\langle S_l \rangle_0 = -3F_k^{(3)}(F^{-1})_{lk}\langle S_k^2 \rangle_0, \qquad (2)$$

where F^{-1} is the inverse of the symmetrized F matrix. The symmetry coordinates, S_l and S_k, must belong to the totally symmetric species.

In the case of acetone, the average of the vibrational displacement of the CCC angle is expressed as*4:

$$\langle \Delta\alpha(\mathrm{CCC}) \rangle_0 = \frac{2}{\sqrt{6}}\langle S_8 \rangle_0$$
$$= -\sqrt{6}F_k^{(3)}(F^{-1})_{8k}\langle S_k^2 \rangle_0. \qquad (3)$$

It can be seen from Eq. (3) that the difference in α_z between the normal and the deuterated species must be caused by the difference in $\langle S_k^2 \rangle_0$, if any. By rewriting Eq. (3) simply as:

$$\langle \Delta\alpha \rangle_0 = a\langle S_k^2 \rangle_0, \qquad (4)$$

a relation which enables one to estimate $\langle \Delta\alpha \rangle_0$ values from the difference in α_z, that is, the difference in $\langle \Delta\alpha \rangle_0$, between the normal and the deuterated species, can be obtained as:

$$\langle \Delta\alpha \rangle_0^{\mathrm{H}} = [\langle \Delta\alpha \rangle_0^{\mathrm{H}} - \langle \Delta\alpha \rangle_0^{\mathrm{D}}]\cdot\frac{\langle S_k^2 \rangle_0^{\mathrm{H}}}{\langle S_k^2 \rangle_0^{\mathrm{H}} - \langle S_k^2 \rangle_0^{\mathrm{D}}}. \qquad (5)$$

The mean square values, $\langle S_k^2 \rangle^{\mathrm{H}}$ and $\langle S_k^2 \rangle^{\mathrm{D}}$, are quantities which are easily calculated, and the $\langle \Delta\alpha \rangle_0^{\mathrm{H}} - \langle \Delta\alpha \rangle_0^{\mathrm{D}}$ has been estimated to be 18′. The superscripts H and D denote the normal and the deuterated species respectively. The values of $\langle \Delta\alpha \rangle_0^{\mathrm{H}}$ have been calculated by Eq. (5) for each of the k-numbers, from 5 through 9, corresponding to the bending symmetry coordinates of the totally symmetric species of this molecule. The results are tabulated in Table 7.

TABLE 7. ESTIMATED VALUES OF $\langle \Delta\alpha \rangle_0^{\mathrm{H}}$

k	Mode of vibration	$\langle \Delta\alpha \rangle_0^{\mathrm{H}}$
5	HCH bending (nearly redundant)	1°7′
6		1°16′
7		1°16′
8	CCC bending	9°
9	CH_3 rocking	1°9′

If it is accepted as a reasonable judgment that a value of 9° is too large for $\langle \Delta\alpha \rangle_0^{\mathrm{H}}$, the coordinate of CCC bending (k=8) is excluded as a possible source of the anharmonicity. Among the rest, the coordinates with the k numbers of 5, 6, and 7 all represent an intra methyl-top bending motion. In the present results, as well as in the case of acetaldehyde, the zero-point average values of the HCH angle and the DCD angle of the methyl top have been found to be equivalent. Therefore, it is implausible that an appreciable amount of anharmonicity is associated with the intra-methyl bending motion. Accordingly, the coordinate of the rocking motion of the tops (k=9) must be the source of the anharmonicity which brings about the difference between $\langle \Delta\alpha \rangle_0^{\mathrm{H}}$ and $\langle \Delta\alpha \rangle_0^{\mathrm{D}}$. A strong anharmonicity of the rocking motion is the most plausible in view of the fact that the methyl tops are tilted outwards, most probably by mutual repulsive interaction.

From the $\langle \Delta\alpha \rangle_0^{\mathrm{H}}$ value thus estimated, the equilibrium value, α_e(CCC), has been evaluated to be 115°0′ by the relation:

$$\alpha_z = \alpha_e + \langle \Delta\alpha \rangle_0. \qquad (6)$$

The numerical value of the cubic constant, $F_9^{(3)}$, could be calculated if $(F^{-1})_{89}$ were known. In the present case, however, $(F^{-1})_{89}$ is simply zero because the quadratic force field used is a rather simplified one. Accordingly, $F_9^{(3)}$ is left undetermined, although it would be very interesting to evaluate it by the use of a more sophisticated set of quadratic force constants.[8]

Equilibrium C-H(D) Bond Length. From the r_z-values thus determined and from the $\langle \Delta z \rangle_0$ values in Table 2, the equilibrium bond length, r_e, can be estimated by the relation:

$$r_z = r_e + \langle \Delta z \rangle_0. \qquad (7)$$

From both r_z(C–H) and r_z(C–D), the r_e-value of 1.077—1.078 Å was obtained. This is close to the value, 1.078 Å, obtained for the methyl C–H of acetaldehyde.[4] It should be noted that the rather smaller value of the r_z(C–H) of acetone is simply due to the environment effect, that is, the larger torsional amplitude of the methyl top around the axis.

The author wishes to thank Professor M. Kimura for his helpful advice and Mr. C. Kato for his help in the early stages of this study. The numerical calculations were performed on a HITAC 5020E of the Computing Center of the University of Tokyo and on a FACOM 270-20 in the laboratory of Professor Kimio Ohno, Hokkaido University, to whom the author's thanks are also due.

Appendix

Derivation of Eq (2). By applying the theorem that the expectation value of the force with respect to any coordinate should be zero for a system in a stationary state,[9] the following simultaneous linear equations for

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*4 The correspondence between the vibrational mode and the sequence number of the symmetry coordinate is arbitrary. In the present treatment, the number 8 has happened to be assigned to the symmetry coordinate of the CCC bending.

8) G. Dellepiane and J. Overend, *Spectrochim. Acta*, **22**, 593 (1966).

9) L. S. Bartell, *J. Chem. Phys.*, **38**, 1827 (1963).

$<S_l>$'s are obtained:

$$\left\langle \frac{\partial V}{\partial S_j} \right\rangle = \sum_l F_{jl} \langle S_l \rangle + 3F_k{}^{(3)} \langle S_k{}^2 \rangle \delta_{kj} = 0 \qquad (j = 1, 2, \cdots) \tag{A1}$$

where the potential function, V, is given as:

$$V = \frac{1}{2} \sum_{j,l} F_{jl} S_l S_j + F_k{}^{(3)} S_k{}^3 \tag{A2}$$

in terms of the symmetry coordinates. By solving Eq. (A1) for $<S_l>$, this relation:

$$\langle S_l \rangle = -3F_k{}^{(3)} (F^{-1})_{lk} \langle S_k{}^2 \rangle \tag{A3}$$

can easily be derived. In the event that the cubic potential is given by such a sum of terms as $\sum_k F_k{}^{(3)} S_k{}^3$, $<S_l>$ is obtained simply by taking a sum of the right-hand side of Eq. (A3) over k.