BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 3526—3530 (1972)

Zero-point Average Structure of a Molecule Containing Two Symmetric Internal Rotors. Acetone

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(Received May 18, 1972)

The theory of vibrational correction to the observed moments of inertia of a molecule which contains an internal rotor has been extended to the case of two symmetric internal rotors, and applied to the analysis of the structure of acetone. The zero-point average structure has been determined by using the moments of inertia obtained by microwave spectroscopy and the bond distances from gas electron diffraction. The zero-point average parameters have been determined as follows: C–C 1.517±0.003 Å; C=O 1.210±0.004 Å; C–H 1.091±0.003 Å; ∠HCH 108° 30′±30′; ∠CCC 116° 0′±15′. The isotope effects in the structure parameters have also been observed in terms of the increase caused by deuteration to be δ(DCD)$+10'\pm12'$; δ(CCC) $-17'\pm2'$. The tilt angle of the methyl top was determined to be 2° 0′±30′.

Large amplitude intramolecular motions give rise to additional complexity in the method of vibrational correction to the rotational constants. This was discussed in some detail in a previous paper, where the theory for a molecule with internal torsion was presented.[1] However, the scope was restricted to the molecule containing only one internal top. In view of ever increasing interest in the accurate structure parameters of many simple molecules which have two internal rotors, the method has been extended to the two-top case, and the zero-point average structure of acetone has been determined. The present study is to replace the previous one on the average structure of acetone,[2] where the torsional motion was treated as a vibrational one.

The treatment is based on a specified condition that the molecule has at least one symmetry plane by which the two tops are exchanged with each other. The restriction is compensated by the simplicity of numerical procedure and the applicability to many two-top molecules.

Theory for the One-top Case[1]

First, a brief survey of the theory for the one-top case seems to be necessary. The essential part of the procedure for vibrational correction is to calculate the effective values of the rotational constants $\sigma_{\alpha\beta}$ which are supposed to differ from the rigid values due to vibrational motions. The theoretical expression for the vibrational correction is therefore characterized by matrices l and n which specify the relations between the normal coordinate Q_s, torsional velocity $\dot{\gamma}$, Cartesian displacement $\boldsymbol{\rho}_i$ and velocity vector $\mathbf{v}_i$ of each atom in the molecule. The relations are

$$\sqrt{m_i}\,\boldsymbol{\rho}_i = \textstyle\sum_s l_{is} Q_s \tag{1}$$

$$\sqrt{m_i}\,\mathbf{v}_i = \textstyle\sum_s l_{is} \dot{Q}_s + \sum_s \dot{\gamma} n_{is} Q_s \tag{2}$$

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[1] T. Iijima and S. Tsuchiya, *J. Mol. Spectrosc.*, **44**, 88 (1972).
[2] T. Iijima, This Bulletin, **43**, 1049 (1970).

where m_i is the mass of the i-th atom. The components of $\boldsymbol{\rho}_i$ and $\mathbf{v}_i$ are given as projected onto the frame-fixed coordinate axes, the matrix element n_{is} vanishing for the atoms belonging to the frame.

The four dimensional moments of inertia tensor, for three angular velocities of overall rotation and an additional one of the torsional motion, are calculated in terms of l and n for an instantaneous situation where only the s-th normal coordinate Q_s has a non-zero value. It may be denoted by $I(Q_s)$. A slightly modified inertia tensor I' is set up as

$$I'(Q_s)_{\alpha\beta} = I(Q_s)_{\alpha\beta} - \textstyle\sum_{s'} \zeta_{ss'}^{(\alpha)}\zeta_{ss'}^{(\beta)}Q_s^2 \tag{3}$$

in order to make conversion of the velocity representation of the kinetic energy into the momentum representation.[3] The zeroth and first order term of the rotational constants can be obtained by taking the inverse of I'. The averaging over the ground vibrational state and appropriate repetition of the process over all normal coordinates are performed according to the equations

$$\sigma_{\alpha\beta} = \sigma_{\alpha\beta}^{(0)} + \sigma_{\alpha\beta}^{(1)} + \sigma_{\alpha\beta}^{(2)} \tag{4}$$

$$\sigma_{\alpha\beta}^{(0)} + \sigma_{\alpha\beta}^{(1)} = \textstyle\sum_s \dfrac{1}{2}\{\mu_{\alpha\beta}(D_s)+\mu_{\alpha\beta}(-D_s)\} \tag{5}$$

$$\begin{aligned}\sigma_{\alpha\beta}^{(2)} &= -\textstyle\sum_{ss'}\dfrac{D_s^2}{2}\cdot\dfrac{(\omega_s-\omega_{s'})^2}{\omega_{s'}(\omega_s+\omega_{s'})}\\ &\quad\times \textstyle\sum_{\alpha'\beta'}\zeta_{ss'}^{(\alpha')}\zeta_{ss'}^{(\beta')}\mu_{\alpha\alpha'}^{\circ}\mu_{\beta\beta'}^{\circ}\end{aligned} \tag{6}$$

$$(a, \beta, \alpha', \beta' = x, y, z, \gamma)$$

where D_s is the root mean square value of Q_s and μ is the inverse of I'.

The elements of I and ζ for the principal axis components are given by ordinary expressions, and the γ-components are given by the following.[1]

$$I_{\gamma\gamma} = J_{\gamma\gamma} + \textstyle\sum_i(n_{is}\cdot n_{is})Q_s^2 + 2\boldsymbol{\lambda}\cdot\sum_i(\Lambda_{is}\times n_{is})Q_s^2 \tag{7}$$

$$I_{\gamma\alpha} = \lambda_\alpha J_{\gamma\gamma} + \textstyle\sum_i(l_{is}\times n_{is})_\alpha Q_s^2 - (\boldsymbol{\lambda}\times L_{R'S})_\alpha Q_s \tag{8}$$

$$(\alpha = x, y, z)$$

$$\zeta_{ss'}^{(\gamma)} = \boldsymbol{\lambda}\cdot\textstyle\sum_i(\Lambda_{is}\times l_{is'}) + \sum_i n_{is}\cdot l_{is'} \tag{9}$$

where all notations follow Ref. 1, and the subscript i runs over the atoms belonging to the top. $J_{\gamma\gamma}$ is the geometrical moment of inertia of the top around its axis where the vibrational displacement of each atom due to Q_s is taken into account; $L_{R's}$ is the L matrix which relates the symmetry coordinate of the infinitesimal rotation of the top to the Q_s and Λ_{is} is the l-matrix relative to the center of gravity of the top.

Extension of the Method to the Two-top Case

The angular velocity vector ω for a two-top molecule consists of five components, three for the overall rotation and two for the torsinal motions. Accordingly the tensors of moments of inertia and rotational constants are (5×5) dimensional ones. The $\zeta_{ss'}$ also has five components.

Eq. (1) is still valid for the relation between the frame-fixed Cartesian displacement $\boldsymbol{\rho}_i$ and Q_s, and so is the time derivative Eq. (2). It is obvious that the $\mathbf{v}_i$ for an atom of top 1 is independent of the torsional velocity of top 2, and *vice versa*. It is thus concluded that the elements of I-tensor and ζ are given by exactly the same expressions as Eqs. (7), (8) and (9), if the numbering of atoms i covers top 1 for the $\gamma_1\alpha$-components and top 2 for the $\gamma_2\alpha$-components. The $\gamma_1\gamma_2$-term of I does not appear.

The (4×4) part of the (5×5) I-tensor can therefore be obtained by making full use of the routine procedure for the one-top case, where one of the two tops, *e. g.* top 2, is included in the frame group, both γ_2 and $\dot{\gamma}_2$ being put equal to zero. The remaining $\gamma_2\alpha$-components can be obtained by simple symmetry consideration.

Top 1 is transferred to top 2 by symmetry operation σ_h. If atom i_1 of top 1 is transferred to atom i_2 of top 2 by σ_h, every component of $l_{i2,s}$ projected onto the principal axes x, y, and z is equivalent either to that of $l_{i1,s}$ or $-l_{i1,s}$ depending on the symmetry of the s-th normal coordinate. Consistency between the direction of torsinal motion for positive γ and the direction of the unit vector λ should be maintained within each top in such a manner that clockwise rotation around λ facing towards its direction is the motion corresponding to positive γ. However, arbitrary choice is allowed for the symmetry property of one of them in relation to the transference between the two tops. In the present treatment, λ is taken to be symmetric to σ_h. Then γ becomes anti-symmetric with respect to σ_h. By choosing the yz-plane to be the plane of symmetry and the x-axis perpendicular to it, the symmetry property of l_{is} and that of n_{is} *etc.* are easily obtained as summarized in Table 1. The entry $-$, for example, in column (x) for l_{is} means that $l_{i2,s}^{(x)}$ is equal to $-l_{i1,s}^{(x)}$, and so on.

TABLE 1. SYMMETRY PROPERTIES OF l_{is}, Λ_{is}, n_{is} AND $L_{R's}$

	l_{is} and Λ_{is}			n_{is} and $L_{R's}$		
	(x)	(y)	(z)	(x)	(y)	(z)
$s\subset A'$	$-$	$+$	$+$	$+$	$-$	$-$
$s\subset A''$	$+$	$-$	$-$	$-$	$+$	$+$

By means of Eqs. (7), (8) and Table 1, the $\gamma_2\alpha$-components of I-tensor can be related to those of $\gamma_1\alpha$-components, simply as

$$I(Q_s)_{\gamma2,x} = -I(Q_s)_{\gamma1,x} \tag{10}$$

$$I(Q_s)_{\gamma2,\alpha} = I(Q_s)_{\gamma1,\alpha} \quad \text{for } \alpha=y \text{ and } z, \tag{11}$$

and

$$I(Q_s)_{\gamma2,\gamma2} = I(Q_s)_{\gamma1,\gamma1} \tag{12}$$

if Q_s belongs to the symmetry species A' which is symmetric with respect to σ_h. If Q_s belongs to A'', the Q_s on the right-hand side of the above equations should be replaced by $-Q_s$. Changing the sign of Q_s is relevant to the term linear in Q_s and also to $J_{\gamma\gamma}$ and λ_α which implicitly contain terms linearly dependent on Q_s.

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[3] E. B. Wilson, Jr. and J. B. Howard, *J. Chem. Phys.*, **4**, 260 (1936).

Similarly, $\zeta_{ss'}^{(\gamma_2)}$ is given by

$$\zeta_{ss'}^{(\gamma_2)} = \zeta_{ss'}^{(\gamma_1)},\ \text{if } s\subset A',\ s'\subset A'' \text{ and } \textit{vice versa} \tag{13}$$

and

$$\zeta_{ss'}^{(\gamma_2)} = -\zeta_{ss'}^{(\gamma_1)},\ \text{if } s\subset A',\ s'\subset A' \text{ or } s\subset A'',\ s'\subset A'' \tag{14}$$

The second term of Eq. (3) and $\sigma_{\alpha\beta}^{(2)}$ of Eq. (6) are thus easily calculated in terms of $\zeta_{ss'}^{(\gamma_1)}$ and the above symmetry rule.

The symmetry property of $\zeta_{ss'}^{(\gamma)}$, combined with the non-vanishing conditions (Table 2) leads to the symmetry properties of the second term of Eq. (3) and that of $\sigma_{\alpha\beta}^{(2)}$ of Eq. (6). The result is simply that the sign should be changed only for the x-components and otherwise equivalent to the corresponding $\gamma_1\alpha$-terms. The $\gamma_1\gamma_2$-term of I' is not necessarily zero in contrast to that of I.

TABLE 2. NON-VANISHING CONDITIONS FOR $\zeta_{ss'}^{(\alpha)}$

	(x)		(y)		(z)		(γ)	
	s	s'	s	s'	s	s'	s	s'
	A'	A'	A'	A''	A'	A''	A' or A''	A' or A''
or								
	A''	A''	*vice versa*					

The whole symmetry consideration may be stated in a more compact way as follows. The γ_2-components of I' and $\sigma_{\alpha\beta}^{(2)}$ tensors are obtained by applying a symmetry operation σ_h to the γ_1-components. The symmetry operation σ_h implies change of the sign of Q_s, if Q_s, is anti-symmetric to σ_h and change of the sign of γx-components. Naturally the new cross terms, $\gamma_1\gamma_2$-elements, can not be covered by this symmetry operation.

Zero-point Average Structure of Acetone

Zero-point Moments of Inertia and Angle between the two Top-axes. The formulation was applied to the determination of the zero-point average structure of acetone which has two internal rotors. The microwave spectra of this molecule and those of isotopic species were investigated by Nelson and Pierce.[4] The spectra of the d_6-species were observed by Swalen and Costain.[5]

The vibrational correction was calculated by assuming an appropriate set of structure parameters and by use of the force constants determined by Cossee and Schachtschneider.[6] The observed moments of inertia, the corrections for the vibrational effect and the zero-point values are listed in Table 3 for the normal and the d_6-species. The microwave data of $(^{13}CH_3)_2CO$ and $(CH_3)_2C^{18}O$ were also used. The vibrational corrections for these species were almost equivalent to those of the normal species.

The direction cosines of the top-axes λ_a and λ_b were determined from the parameters α and β reported by Nelson and Pierce.[4] The effective values of λ_a and λ_b were obtained by the relation

TABLE 3. EFFECTIVE AND ZERO-POINT MOMENTS OF INERTIA OF ACETONE. (in amu Å^2 units)

		$I^{\text{eff a)}}$	ΔI	$I^{(z)}$
$(CH_3)_2CO$	a	49.730	0.096	49.826
	b	59.370	0.106	59.476
	c	102.956	0.029	102.985
	γ	(3.226)$^{\text{b)}}$	−0.067	3.159
$(CD_3)_2CO$	a	59.690	0.106	59.796
	b	78.748	0.119	78.867
	c	126.028	0.027	126.055
	γ	(6.398)$^{\text{b)}}$	−0.094	6.304

a) Determined by Nelson and Pierce.[4]
b) Estimated from $I_\gamma^{(z)}$.

$$\frac{\beta}{\alpha} = \frac{\lambda_b I_a}{\lambda_a I_b} \tag{15}$$

which is derived from the definitions of α and β, and the constraint $\lambda_a^2+\lambda_b^2=1.0530$ for the normal species and 1.0352 for the d_6-species. The ratio β/α was used as an experimental value, since it is independent of I_γ, the effective moment of inertia of methyl top around its axis, and might be free from possible systematic errors introduced in the course of the barrier height analysis.

The effective values were then converted into the zero-point values by corrections which were evaluated by the model calculation for the vibrational effect. The zero-point value of the angle between the two top-axes $2\theta_z$ was then evaluated to be 120.0±0.4° for both normal and d_6-species. The two values of $2\theta_z$ obtained from λ_a and λ_b were in excellent agreement with each other within 0.1°.

Adjustment of Structure Parameters. The r_z-parameters were determined from the $I^{(z)}$ values and C–C and C=O r_z-distances obtained by means of electron diffraction[2,7,8] in a way quite parallel to that for acetaldehyde.[1] The isotope effect on the C–H and C–D distances was evaluated by $\langle\Delta z\rangle_0$ or the mean displacement projected along the equilibrium bond direction, by use of the calculated values of the parallel and perpendicular mean amplitudes[9] and the Morse anharmonicity parameter a. Two values were assumed for a, 2.0 Å^{-1} and 2.6 Å^{-1}, which are supposed to be the possible extremes of the a value for a C–H bond.[10] The difference between r_z values for the C–H bond was 0.001 Å and 0.002 Å for the two extremes.

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

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

[6] P. Cossee and J. H. Schachtschneider, *ibid.*, **44**, 97 (1966).

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

[8] The centrifugal stretchings of C–C and C–O distances were assumed to be 0.0002 Å in the previous study. Resently Dr. Hilderbrandt calculated them rigorously and obtained 0.0006 Å and 0.0002 Å for C–C and C–O, respectively. (Private communication *via* Professor R. A. Bonham.) There is no important change in the r_z(ED) values even with these exact numbers.

[9] Dr. S. J. Cyvin kindly informed the author of his calculated values of the mean amplitudes of the normal species. His results are in excellent agreement with the author's. It should be noted, however, that the mean amplitudes should not include the contribution from the torsional motions in the present scheme of analysis.

[10] K. Kuchitsu, *J. Chem. Phys.*, **49**, 4456 (1968).

The mean value 0.0015Å was then assumed to be the difference r_z(C–H) $-r_z$(C–D) in the following analysis.

A large shortening of r_z from the equilibrium bond length, obtained as a result of the calculation in the preceding paper,[2] originated from a large perpendicular amplitude due to the torsional motion of the methyl tops. In the present treatment, however, the torsional motion is separated out of the vibrational motions and the r_z(C–H) becomes the average value on the vibrational ground state not including the torsional motion. The methyl tops undergo the torsional motion while performing vibrational harmonic motions about the structure expressed in terms of the zero-point structure parameters.

The adjusted structure parameters were r_z(C=O), r_z(C–C), r_z(C–H). α_z(CCC) and α_z(HCH). In addition to these, α_z(CCC) and α_z(DCD) of the d_6-species were included as independent parameters. The $2\theta_z$ values were fixed to the value obtained in the preceding section. The trial values of r_z(C=O) and r_z(C–C) were varied within the error limits of electron diffraction values. For each set of these two parameters, the remaining parameters were so adjusted that the calculated moments of inertia might best fit the observed zero-point values.

In a scheme where the diffraction values are utilized as much as in the present treatment, the contribution from the isotopically substituted species, especially the ^{13}C and ^{18}O species, to the structure parameters is rather small and the final result would have been substantially the same if the parameters had been adjusted by use of the normal species only. This was pointed out by Kuchitsu *et al.*[11] Inclusion of the deuterated species would produce no more than additional ambiguity if the possible isotope effects in the structure parameters were assumed to be estimated values, unless the estimates are somehow known accurately enough. In the present treatment the isotope effects in the α_z(CCC) and α_z(DCD) were regarded as adjustable, or in other words, unknown parameters. As a result, the spectroscopic moments of the deuterated species had a role not only of affording additional information on the overall structure parameters but also of giving experimental evidence of the isotope effects on the less known parameters such as bond angles. The assumption that there is no appreciable isotope effect in the C–C and C=O distances seems to be reasonable.

Although the addition of two more independent parameters for the deuterated species seems to reduce the usefulness of the d_6-data as supplementary information, it actually turns out that the d_6-data are still very useful in alleviating strong mutual correlation existing between the structure parameters of the molecule.

The best fit values of the parameters are listed in Table 4 together with the ranges indicating the uncertainties, which were estimated by criteria discussed in Ref. 1. The corresponding r_g-values are also shown in Table 4. The allowable amounts of deviations of the parameters are not independent of, but related to, each other by the mutual correlation. Since it is difficult to show the correlation scheme in the Table, the listed values simply indicate the widest possible deviations which could be allowed by an appropriate combination of the values of the parameters. The zero-point moments of inertia calculated by use of these best fit values of the parameters are in agreement with the observed values within 0.01 amu. Å^2 for all of the twelve $I^{(z)}$ of the four species. The consistency between spectroscopic and diffraction data is almost perfect.

TABLE 4. STRUCTURE PARAMETERS OF ACETONE[a)]
(in Å units)

	r_z and α_z		
C–C	1.517 (3)	∠HCH	108°30′ (30′)
C=O	1.210 (4)	δ(DCD)[b)]	+10′ (12′)
C–H	1.091 (3)	∠CCC	116° 0′ (15′)
δ(C–D)[b)]	−0.0015 (assumed)	δ(CCC)[b)]	−17′ (2′)
$2\theta_z$	120°0′ (24′)	tilt	2° 0′ (30′)
	r_g[c)]	r_e and α_e	
C–C	1.520	C–H	1.083
C=O	1.213	∠CCC	114°57′
C–H	1.103	∠HCH	109° 8′

a) Limits of error are shown in parentheses, the number being attached to the last digit. b) δ(C–D) $=r_z$(C–D) $-r_z$(C–H); δ(DCD)= ∠DCD − ∠HCH; δ(CCC)= ∠CCC(d_6) − ∠CCC. c) Cf. the diffraction results, r_g; C–C 1.517 (5) and C=O 1.211 (4) Å.[7)]

Isotope Effects in Deuterated Species. We see from Table 4 that appreciable isotope effects due to deuterium substitution were observed in the zero-point average values of CCC and HCH angles. The CCC angle of the d_6-species is less than that of the normal species by 17′. A similar amount 18′ was obtained and discussed in a previous paper,[2] where it was interpreted to be caused by anharmonicity in the symmetric rocking motion of the two methyl tops. The same argument holds in the present case, although there seems to be no sound reason to exclude intramethyl HCH bending from the possible source of anharmonicity, because there has also been an isotope effect observed in the DCD angle.

However, the fact that the DCD angle is not smaller but larger than HCH by 10′ strongly suggests that a repulsive force between the two methyl tops might be the major source of anharmonicity. Such a force would push the two tops so that the three hydrogens are bent closer to each other, and the zero-point vibration would suffer such anharmonicity as to make it harder for the methyl tripod to open than to close. This is the type of anharmonicity which lead to a larger DCD angle than HCH, and be predominant in the cubic term of the symmetric rocking mode.

The same manipulation as was applied to the CCC angle[2] was also applied to the HCH angle, and the $\langle \Delta\alpha \rangle_0$ value of HCH was evaluated to be −38′ assuming that the anharmonicity is mainly due to the methyl rocking.

The direction of tilt is also consistent with the presence of repulsive interaction between the two tops.

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11) K. Kuchitsu, T. Fukuyama and Y. Morino, *J. Mol. Structure*, **4**, 41 (1969).

However, according to the microwave studies by Pierce and co-workers on several molecules, the existence of tilted methyl tops is closely related to the presence of an unsaturated carbon atom adjacent to the methyl top.[12] The tilt in acetone is probably caused by superposed effect of both repulsive interaction and the electronic state of the central carbon. More exact pinning down of the origin of the tilting is still left to future investigations.

Approximate equilibrium values of the structure parameters can be estimated from the zero-point average values and $\langle \Delta z \rangle_0$ and $\langle \Delta \alpha \rangle_0$. The estimated values for C–H, ∠CCC and ∠HCH are shown also in Table 4. r_e(C–H) 1.08_3 Å is fairly reasonable as compared with some reported values of C–H, *viz.*, 1.08_7 Å of CH_3CHO[1] and 1.085 Å of CH_4.[13] As for the equilibrium values of the bond angles, no data are available for comparison. It is interesting, however, to note that the equilibrium angle of HCH in the methyl top seems to be very close to that of acetaldehyde 108°42′, while the zero-point average values are apart from each other because of the opposite direction of the effect of anharmonicity.

Determination of the barrier height by use of the effective value of the moment of inertia of the methyl top and the non-unity constraint of $\lambda^2_a+\lambda^2_b$ would be interesting, if it were possible to follow the sophisticated procedure of the barrier height analysis by Nelson and Pierce.

The author wishes to thank Professor Masao Kimura for his encouragement, and Dr. Shigehiro Konaka for his helpful comments. Numerical computations were performed on a FACOM 230—60 of the Hokkaido University Computing Center and also on a FACOM 270—20 at the laboratory of Professor Kimio Ohno, to whom the author's thanks are also due.

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[12] See reference 4 and the references cited therein.

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