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Zero-point Average Structure of Acetaldehyde

Takao IIJIMA and Masao KIMURA

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo

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The zero-point average structure of acetaldehyde has been determined by the use of the moments of inertia and the average distances, obtained by microwave spectroscopy and electron diffraction respectively. The following r_z parameters have been determined: 1.515±0.005 Å for C–C, 1.207±0.004 Å for C=O, 1.073±0.002 Å for C–H(methyl), 123°48′±9′ for ∠CCO, and 108°52′±17′ for ∠HCH of the methyl top.

The molecular structure of acetaldehyde was studied by Kilb, Lin, and Wilson$^{1)}$ by means of microwave spectroscopy. They determined the structure parameters (the so-called r_0 structure) from the moments of inertia for normal acetaldehyde and its six isotopically-substituted molecules, assuming that the bond distances and angles, except for those of the methyl group, were the same for all isotopic species.

Recently the present authors and their collaborators made an electron diffraction study of the structure of this molecule.$^{2)}$ The results were not in close agreement with those from the microwave study, as may be seen by comparing the C–C and C=O distances in Table 1. However, this does not necessarily mean that the results are inconsistent with each other, for the distance parameters reported do not have exactly the same physical significance.

TABLE 1. PREVIOUS RESULTS FOR r(C–C) AND r(C=O) OF ACETALDEHYDE (IN Å)

	r(C–C)	r(C=O)
r_0(MW)$^{a)}$	1.501±0.005	1.216±0.002
r_g(ED)$^{b)}$	1.514±0.005	1.209±0.003

a) Microwave spectroscopy. Ref. 1.
b) Electron diffraction. Ref. 2.

Recent theoretical studies$^{3-5)}$ have provided methods of converting the original spectroscopic and diffraction results into common physical quantities in order to facilitate their comparison. One practical way is to reduce the structure parameters determined experimentally to those of the zero-point average structure. Furthermore, several investigations$^{6-10)}$ have shown that the cooperative use of spectroscopic and diffraction results is successful in the determination of the accurate structures of gas molecules. In the present study, the zero-point average structure of acetaldehyde has been determined by a cooperative use of microwave and electron diffraction data.

Zero-point Moments of Inertia

The moments of inertia obtained by microwave spectroscopy are effective moments of inertia for the ground vibrational state. They are converted to zero-point moments of inertia by correcting for apparent variations due to intramolecular harmonic vibrations. The relations between the effective moments $(I_{\alpha\alpha})_{eff}$ and the moments of inertia of a non-vibrating rigid molecule, $I^0{}_{\alpha\alpha}$, are given by the following equations:$^{3,4),*1}$

$$\frac{1}{(I_{\alpha\alpha})_{eff}}=\frac{1}{I^0{}_{\alpha\alpha}}+\frac{1}{(I^0{}_{\alpha\alpha})^2}\sum_s\frac{\boldsymbol{h}}{8\pi^2\boldsymbol{c}\omega_s}\times\left[\sum_{s'}{}'\frac{4\omega_{s'}{}^2}{\omega_s{}^2-\omega_{s'}{}^2}(\zeta_{ss'}{}^{(\alpha)})^2+3A_{ss}{}^{(\alpha\alpha)}\right]+\frac{\boldsymbol{h}^3}{8\pi^2}(3\tau_{\beta\gamma\beta\gamma}-2\tau_{\alpha\beta\alpha\beta}-2\tau_{\alpha\gamma\alpha\gamma})\tag{1a}$$

and:

$$\frac{1}{(I_{\alpha\beta})_{eff}}=\frac{1}{I^0{}_{\alpha\alpha}I^0{}_{\beta\beta}}\sum_s\frac{\boldsymbol{h}}{8\pi^2\boldsymbol{c}\omega_s}$$

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1) R. W. Kilb, C. C. Lin and E. B. Wilson, Jr., *J. Chem. Phys.*, **26**, 1695 (1957).

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

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

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

5) K. Kuchitsu and L. S. Bartell, *J. Chem. Phys.*, **36**, 2460, 2470 (1962).

6) K. Kuchitsu, *ibid.*, **44**, 906 (1966).

7) Y. Morino, K. Kuchitsu, Y. Hori and M. Tanimoto, This Bulletin, **41**, 2349 (1968).

8) K. Kuchitsu, T. Fukuyama and Y. Morino, *J. Mol. Structure*, **1**, 463 (1967—68).

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

10) K. Kuchitsu and S. Konaka, *ibid.*, **45**, 4342 (1966).

[*1] No degenerate mode of vibration exists in this molecule.

TABLE 2. MOMENTS OF INERTIA OF ACETALDEHYDE (IN amu. Å^2)

	CH_3CHO			CD_3CDO		
	a	b	c	a	b	c
I_{eff}(obs)[a]	8.933	49.741	55.553	14.456	58.936	67.123
$I_\alpha^{(z)}$(obs)[b]	8.887	49.773	55.589	14.387	58.957	67.178

	CD_3CHO			$^{13}CH_3{}^{13}CHO$		
	a	b	c	a	b	c
I_{eff}(obs)[a]	12.114	58.853	64.672	—	51.313	57.325
$I_\alpha^{(z)}$(obs)[b]	12.053	58.868	64.729	—	51.352	57.370

	$^{13}CH_3CHO$			$CH_3CH^{18}O$		
	a	b	c	a	b	c
I_{eff}(obs)[a]	—	51.292	57.130	—	52.245	58.157
$I_\alpha^{(z)}$(obs)[b]	—	51.328	57.168	—	52.282	58.196

a) Effective moments of inertia for the ground vibrational state observed by microwave spectroscopy (Ref. 1).

b) Zero-point moments of inertia reduced from I_{eff} by Eq. (3).

$$\times\left[\sum_{s'}{}' \frac{4\omega_{s'}^2}{\omega_s^2-\omega_{s'}^2}\zeta_{ss'}^{(\alpha)}\zeta_{ss'}^{(\beta)} + 3A_{ss'}^{(\alpha\beta)}\right]. \tag{1b}$$

The last term of Eq. (1a) comes from the quadratic term of centrifugal distortion, where $\tau_{\alpha\beta\gamma\delta}$ is given by:[11]

$$\tau_{\alpha\beta\gamma\delta} = -\sum_s \frac{1}{I^0_{\alpha\alpha}I^0_{\beta\beta}I^0_{\gamma\gamma}I^0_{\delta\delta}} \cdot \frac{a_s^{(\alpha\beta)}a_s^{(\gamma\delta)}}{8\pi^2 \boldsymbol{hc}^2\omega_s^2}. \tag{2}$$

All the notations are the same as in Ref. 4. The non-vanishing off-diagonal elements, $1/(I_{\alpha\beta})_{eff}$, indicate that the principal axes in a vibrating molecule deviate slightly from those in equilibrium. However, numerical calculations have shown that these terms are negligibly small for acetaldehyde and its isotopic species.

When the $(I_{\alpha\alpha})_{eff}$ represents the observed principal moments of inertia for the ground vibrational state, the $I^0_{\alpha\alpha}$ is the zero-point moment of inertia according to Oka[3] and Laurie and Herschbach.[12,13] In other words, $I^0_{\alpha\alpha}$ is the moment of inertia of such a rigid molecule that each atom is fixed at an average position which may be slightly different from an equilibrium position because of the first-order effect of anharmonicity. By using the observed moments of inertia, I_α(obs), of Table 2, the zero-point moments of inertia, $I_\alpha^{(z)}$(obs), were obtained by:

$$I_\alpha^{(z)}(\text{obs}) = I_\alpha(\text{obs}) - [(I_{\alpha\alpha})_{eff} - I^0_{\alpha\alpha}]_{calc}, \tag{3}$$

where $(I_{\alpha\alpha})_{eff}$ was calculated from Eq. (1a). The structure parameters determined by microwave spectroscopy[1] and the force constants determined by Cossee and Schachtschneider, the VF3 set,[14] were used in this calculation. The same force constants were assumed for all the isotopic species. Although there are, for some reason, slight discrepancies between the vibrational frequencies calculated in the present study and those reported

TABLE 3. OBSERVED AND CALCULATED NORMAL FREQUENCIES OF ACETALDEHYDE (IN cm^{-1})

	CH_3CHO			CD_3CDO		
	obsd[a]	calcd	calcd[a]	obsd[a]	calcd	calcd[a]
In-plane modes						
1	3010	3008	3007	2265	2247	2247
2	2967	2961	2961	2130	2139	2139
3	2822	2802	2801	2060	2098	2098
4	1743	1769	1762	1737	1701	1700
5	1441	1440	1455	1151	1165	1164
6	1400	1409	1402	1045	1033	1044
7	1352	1307	1329	1028	955	1016
8	1113	1127	1089	938	941	930
9	919	931	917	747	752	720
10	509	511	510	436	454	456
Out-of-plane modes						
11	3010	3004	3003	2225	2236	2236
12	1420	1426	1426	1028	1029	1029
13	867	863	863	—	672	672
14	763	762	761	573	620	620
15	150	145	148	116	109	113

a) Reported by Cossee and Schachtschneider.[14]

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[11] D. Kivelson and E. B. Wilson, Jr., *ibid.*, **20**, 1575 (1952).

[12] D. R. Herschbach and V. W. Laurie, *ibid.*, **37**, 1661 (1962).

[13] V. W. Laurie and D. R. Herschbach, *ibid.*, **37**, 1687 (1962).

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

orignally by Cossee and Schachtschneider, as is shown in Table 3, no further refinement of the force constants was made. The mean-square amplitudes of vibration calculated by use of the force constants were in good agreement with those observed by electron diffraction (*cf.* Table 4 in Ref. 2).

The effects of the slipping rotation of the π-electrons of a C=O bond and the lone-pair electrons of the oxygen atom were corrected for in the case of formaldehyde by Oka.(3) His corrections were -0.003 amu.Å^2 at most. Although the effects are expected to be of a similar magnitude for acetaldehyde, the corrections are only a few in ten thousand or less since the moments of inertia of acetaldehyde are much greater than those of formaldehyde. Therefore, the corrections for these effects were ignored in the present study.

Isotope Effect on Zero-point Structure

In order to determine the r_z-structures from the moments of inertia, $I_\alpha^{(z)}$, of several isotopic species, the primary and secondary isotope effects*[2] on r_z distances should be estimated. By defining the local Cartesian coordinates, x, y, and z, for a particular pair of atoms with a z axis taken in the direction of their equilibrium positions, r_z is expressed as:

$$r_z = r_e + \langle \Delta z \rangle_0 \tag{4}$$

in terms of the equilibrium distance, r_e, and the average increment of the distance along the z-axis, $\langle \Delta z \rangle_0$. The average is taken at 0°K, or for the ground vibrational state. By the diatomic approximation(8,15) $\langle \Delta z \rangle_0$ is given by:

$$\langle \Delta z \rangle_0 = (3/2)a_3 l_0^2 - K_0 \tag{5}$$

and:

$$K_0 = [\langle \Delta x^2 \rangle_0 + \langle \Delta y^2 \rangle_0]/2r_e\,, \tag{6}$$

where a_3 is the Morse anharmonicity parameter of the bond-stretching; l_0^2, the mean-square amplitude of vibration at 0°K, and $\langle \Delta x^2 \rangle_0$ and $\langle \Delta y^2 \rangle_0$, the perpendicular mean-square amplitudes of vibration at 0°K.

The anharmonicity parameters for C–H, C–C, and C=O bonds were assumed to be 1.98 Å^{-1}, 2.1 Å^{-1}, and 2.4 Å^{-1}, respectively.(15) The mean-square amplitudes and the perpendicular amplitudes needed for the estimation of K_0 were calculated by the use of l-matrix elements, which were obtained simultaneously with a computing program for the calculation of the I_{eff} values. The numerical values of $\langle \Delta z \rangle_0$ calculated for the bonded distances of several isotopic species are tabulated in Table 4.

TABLE 4. ISOTOPE EFFECTS ON r_z PARAMETERS. CALCULATED VALUES OF $\langle \Delta z \rangle_0$ (IN Å UNITS)

	C–H$_{\text{Me}}$	C–H$_{\text{Ald}}$	C–C	C=O
CH_3CHO	-0.005	0.001	0.0059	0.0026
CD_3CDO	-0.002	0.001	0.0056	0.0028
CD_3CHO	0.000	-0.001	a	0.0024
$^{13}CH_3{}^{13}CHO$	-0.005	a	0.0056	a
$CH_3CH^{18}O$	a	a	a	0.0025

a) Not calculated. This does not necessarily mean that the values are negligibly small.

The relatively large negative values of $\langle \Delta z \rangle_0$ for the methyl C–H distances are caused by the large perpendicular amplitudes due to the torsional motion of the methyl top. For the C–C and C=O distances, the differences in $\langle \Delta z \rangle_0$ for different isotopic species are negligibly small, as had been expected.

The values of $\langle \Delta z \rangle_0$ in the table might include large systematic errors, caused mainly by assuming the values of a_3.(9,16,17) Kuchitsu estimated an uncertainty of $+0.002$ Å for the difference between the $\langle \Delta z \rangle_0$ values of the C–C bonds in C_2H_6 and C_2D_6.(9) This amount of uncertainty in the isotope effect sometimes leads to large errors in the structure parameters determined by the least-squares adjustment, especially when the adjustment is made under the circumstances that a strong correlation exists among some of the parameters.(7) In the present study, the correlation between r_{C-C} and $r_{C=O}$ was very strong when only spectroscopic data were used, as will be shown in the following section. Therefore, the uncertainties in the parameters are expected to be yet larger than those listed in Table 6, column I, which appears later. When diffraction data are used cooperatively, however, the influence of the possible systematic errors in $\langle \Delta z \rangle_0$ would be unimportant. The isotope effect for bond angles was ignored in the present study.

Zero-point Structure from $I_\alpha^{(z)}$

The seven parameters shown in Fig. 1 determine the structure of acetaldehyde when C_{3v} symmetry is assumed for the methyl top. In the final results, the parameters h and x shown in the figure are converted into r_{C-H} and ∠HCH respectively. It was confirmed by Kilb, Lin, and Wilson(1) that one of the three hydrogen atoms of the methyl top is opposed by the oxygen atom.

By a simple geometrical consideration, the following equation is obtained:

$$I_a^{(z)} + I_b^{(z)} - I_c^{(z)} = 3m_H h_z^2\,, \tag{7}$$

where:

$$h_z = (2/\sqrt{3})r_z \sin(\alpha_z/2)\,, \tag{8}$$

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*[2] Primary and secondary isotope effects have the meaning defined in Ref. 17.

15) K. Kuchitsu and Y. Morino, This Bulletin, **38**, 805, 814 (1965).

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

17) L. S. Bartell, *ibid.*, **42**, 1681 (1965).

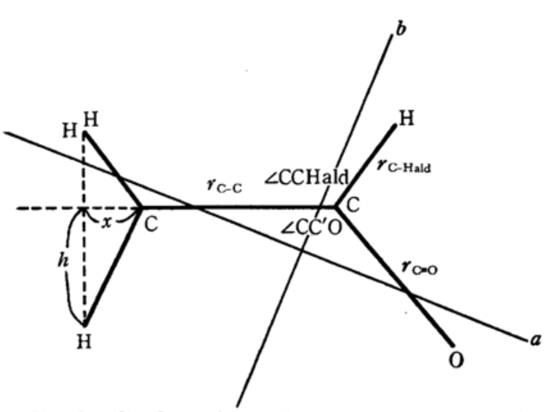

Fig. 1. Configuration and structure parameters of acetaldehyde.

and where r_z and α_z designate r_z(C–H) and ∠HCH respectively. From the observed $I_\alpha^{(z)}$ values of CH_3CHO, CD_3CDO, and CD_3CHO, the best-fit value of h_z, or the product of the parameters r_z and $\sin(\alpha_z/2)$, was determined, where slight differences in the h_z values of the three isotopic species were taken into consideration. The right-hand side of Eq. (7), calculated from the determined value of h_z, is compared with the observed value of the left-hand side for each isotopic species in Table 5. As may be seen in the table, the agreement is quite satisfactory. This is one of the cases in which an isotope effect of r_z estimated on the basis of the mass difference accounts for the observed results. In this stage, r_z(C–H) and α_z were not determined separately.

TABLE 5. COMPARISONS OF $I_a^{(z)}+I_b^{(z)}-I_c^{(z)}$ (IN amu.Å^2)

	obsd[a]	calcd[b]
CH_3CHO	3.071	3.072
CD_3CDO	6.176	6.170
CD_3CHO	6.192	6.196

a) Observed by microwave spectroscopy. Ref. 1.
b) Calculated by use of the adjusted parameters. (Eq. (7)).

The Jacobian matrix elements of twelve moments of inertia (two from each of the six isotopic species)[*3] with regard to six in-plane parameters were calculated. The Jacobian matrix showed that $I_\alpha^{(z)}$'s were quite insensitive to ∠CCH(ald); hence, this angle was fixed at the value reported by Kilb, Lin, and Wilson,[1)] and five parameters, r_{C-C}, $r_{C=O}$, ∠CCO, x, and $r_{C-H(ald)}$, were adjusted by the standard least-squares procedure. The parameters derived are listed in the column I of Table 6, along with their limits of error. The twelve observed $I_\alpha^{(z)}$'s are not independent enough to alleviate the strong correlation between the increase in r_{C-C} and the decrease in $r_{C=O}$; the correlation factor estimated from the elements of the error matrix[*4] amounted to 100 percent. This is more

TABLE 6. ADJUSTED r_z PARAMETERS OF CH_3CHO WITH LIMITS OF ERROR (IN Å UNITS)[a)]

	I	II
C-C	1.504±0.012	1.515±0.005
C=O	1.217±0.011	1.207±0.004
∠CCO	124°3′±25′	123°48′±9′
C-H(Me)	1.074±0.004	1.073±0.002
∠HCH	108°43′±34′	108°52′±17′
C-H(ald)	1.114±0.012	1.114±0.011
∠CCH(ald)	117°29′ (ass'd)	117°29′ (ass'd)

I. Obtained by using spectroscopic moments of inertia $I_{obs}^{(z)}$ only. The uncertainties should be larger if systematic errors in $\langle \Delta z\rangle_0$ are also taken into consideration.
II. Obtained by using r_z-values from electron diffraction in addition to the spectroscopic data.
a) 2.5 times standard deviation obtained by the least-squares procedure.

TABLE 7. COMPARISON OF MOMENTS OF INERTIA[a)] (IN amu. Å^2)

		I		II	
		$I_{calc}^{(z)}$	dev.[b)]	$I_{calc}^{(z)}$	dev.[b)]
CH_3CHO	a	8.903	−0.016	8.900	−0.013
	b	49.760	0.013	49.758	0.015
	c	(55.590	−0.001)	(55.586	0.003)
CD_3CDO	a	14.383	0.004	14.376	0.011
	b	58.945	0.012	58.956	0.001
	c	(67.152	0.016)	(67.155	0.013)
CD_3CHO	a	12.040	0.013	12.029	0.024
	b	58.852	0.016	58.850	0.018
	c	(64.691	0.038)	(64.684	0.035)
$^{13}CH_3{}^{13}CHO$	a	—	—	—	—
	b	51.332	0.020	51.343	0.009
	c	57.368	0.002	57.375	−0.005
$^{13}CH_3CHO$	a	—	—	—	—
	b	51.313	0.015	51.321	0.007
	c	57.168	0.000	57.172	−0.004
$CH_3CH^{18}O$	a	—	—	—	—
	b	52.267	0.015	52.249	0.033
	c	58.199	−0.003	58.183	0.013

a) Calculated values of $I_\alpha^{(z)}$ by using the structure parameters adjusted by the least-squares procedure. See Table 6 for specifications I and II.
b) dev.$=I_{obs}^{(z)}-I_{calc}^{(z)}$.

[*3] The moments of inertia of $CH_3{}^{13}CHO$ were not included, because they probably depend more strongly on those of the other isotope species.

[*4] A matrix $\boldsymbol{B}$ is defined in terms of the Jacobian matrix $\boldsymbol{J}$ and a diagonal weight matrix $\boldsymbol{W}$ as $\boldsymbol{B}=\boldsymbol{JW\tilde{J}}$. The inverse of B is called an error matrix. According to the theory of errors, a correlation factor between the ith and jth parameters which have been adjusted by the least-squares method is given by

$$\text{correlation factor}=(B^{-1})_{ij}/[(B^{-1})_{ii}(B^{-1})_{jj}]^{1/2}.$$

easily seen in Fig. 2, where the process of solving the normal equation in the least-squares adjustment is reduced to the determination of the cross point of two straight lines drawn on the r_{C-C} *versus* $r_{C=O}$ plane. However, because of the strong correlation between r_{C-C} and $r_{C=O}$ the two lines are almost identical. Large standard errors result from this correlation making the error matrix nearly singular.

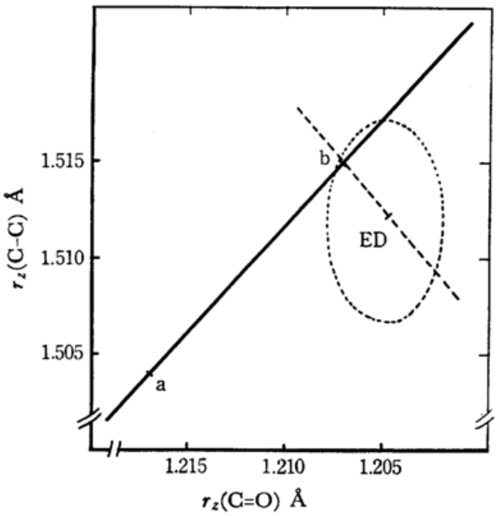

Fig. 2. Relation between r_z(C–C) and r_z(C=O). The cross point a of the two straight lines, indistinguishable in this figure, indicates the most probable values of r_z(C–C) and r_z(C=O) determined for spectroscopic moments of inertia. The point b indicates the most probable values determined by using electron diffraction data in addition to the spectroscopic data. The point ED indicates the results of electron diffraction for r_z(C–C) and r_z(C=O). The contour shows the limits of error of the diffraction data. The dashed line shows possible variation of r_z(C–C) and r_z(C=O) when a systematic error is allowed for in the scale factor of the diffraction data.

The moments of inertia, $I_a^{(z)}$, calculated from the most probable values of the parameters are listed in Table 7, together with deviations from the observed moments of inertia. A deviation as large as 0.03 amu.Å^2 can originate from possible systematic errors in the isotope effects estimated for $\langle \Delta z \rangle_0$ and from the ignorance of anharmonicity in the deformation of bond angles, as has been mentioned in the preceding sections. Fractional deviations, however, are as small as a few parts per thousand or less. Therefore, uncertainties in the structure parameters due to these origins may also be expected to be a few parts per thousand unless correlations between parameters are as strong as in this case.

Zero-point Average Distance from Electron Diffraction

The distances, r_g(C–C) and r_g(C=O), determined by electron diffraction at room temperature were converted to r_z distances by the following equation;[9,10]

$$r_z = \lim_{T \to 0^\circ\mathrm{K}} r_g{}^T - K_0$$
$$\cong r_g{}^T - (3/2)a_3(l_T{}^2 - l_0{}^2) - \delta r_{cent} - K_0 \qquad (9)$$

where $l_T{}^2$ is the mean-square amplitudes and δr_{cent} the centrifugal stretching, both at room temperature, and where the other notations are as specified in Eqs. (5) and (6). This process is based on the assumption that a potential function associated with a bonded distance is well approximated by the Morse-type potential if the net distance between the two atoms, not the distance projected onto the equilibrium direction, is taken as a parameter of the potential function.[15] The non-bonded distances were not converted, for the uncertainties in their values are larger and, also, the anharmonicities for non-bonded atom pairs are not well known. The C–H distances were not determined with sufficient accuracy by electron diffraction.

The centrifugal stretching corrections were roughly estimated to be 0.000_4 Å for C–C and 0.000_2 Å for C=O by referring to the C=O bond of CO$_2$ calculated rigorously at room temperature, 0.0003 Å.[18] The numerical values for this conversion are summarized in Table 8. A comparison of the r_z-values in Table 8 with those in Table 6 reveals no inconsistency between the spectroscopic and diffraction r_z values; any inconsistency would be obscured by the large limits of error in the spectroscopic values.

TABLE 8. CONVERSION FROM r_g TO r_z

	$r_g{}^T$ (Å)	$l_T{}^2$ (Å^2)	$l_0{}^2$ (Å^2)	a_3 (Å^{-1})
C–C	1.514	0.00244	0.00237	2.1
C=O	1.209	0.00151	0.00150	2.4

	K_0 (Å)	δr_{cent} (Å)	r_z (Å)
C–C	0.0016	0.0004	1.512
C=O	0.0018	0.0002	1.205

T=300°K

Zero-point Structure with Additional r_z's Observed by Electron Diffraction

The strong correlation between the r_{C-C} and $r_{C=O}$ values was dissolved by a cooperative use of the r_z distances observed by electron diffraction

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18) Y. Murata, K. Kuchitsu and M. Tanimoto, This Bulletin, to be published.

and the moments of inertia observed by microwave spectroscopy. The least-squares procedure was straightforward, and the two observed quantities, r_z^{ED}(C–C) and r_z^{ED}(C=O), were added to the twelve $I_\alpha^{(z)}$'s. Thus, five parameters were adjusted to fourteen observations. Obviously, the additional part of the Jacobian matrix had only two non-vanishing elements, one between the parameter r_{C-C} and the observed r_z^{ED}(C–C), and the other between r_{C-O} and r_z^{ED}(C=O). The relative weighting factors for observed quantities were identified as being inversely proportional to the square of the error of each observed value. The limits of error (99% confidence interval) in electron diffraction were reported to be ±0.005 Å for r_z^{ED}(C–C) and ±0.003 Å for r_z^{ED}(C=O). The errors arising from the conversion from r_g to r_z were ignored because they were considered to be less important. For the $I_\alpha^{(z)}$'s determined by microwave spectroscopy, the errors from which the weighting factors should be estimated are not only the original experimental errors in the moments of inertia, but also those including uncertainties in the conversion from I_{eff} to $I_\alpha^{(z)}$. However, most of the errors may be considered to arise from the conversion process. Therefore, these uncertainties are represented by the deviations of $I_\alpha^{(z)}$(obs) from $I_\alpha^{(z)}$(calc) calculated by use of the most probable values of the parameters. Corresponding to the 99% confidence interval in electron diffraction, the maximum deviation of $I_\alpha^{(z)}$(calc), ±0.03 amu.Å^2, was taken as an error for $I_\alpha^{(z)}$.

The results of the least-squares adjustment are summarized in the second column of Tables 6 and 7. The adjusted values of r_{C-C} and $r_{C=O}$ are also indicated in Fig. 2 by the b point. Although there might be additional systematic errors which do not appear as a mutual inconsistency between the $I_\alpha^{(z)}$'s of several isotopically-substituted species, they were not taken into consideration, for their amounts are not well known. In the present case, however, even if the weighting factor for $I_\alpha^{(z)}$ were reduced to a quarter of the values used in view of the possible systematic error, the final set of parameters would remain almost unchanged, for the b point in Fig. 2 is the nearest point to the ED point on the solid line. The authors' view is that better estimates of errors for $I_\alpha^{(z)}$ will be established gradually through the further application to other molecules of the method of the cooperative use of diffraction and spectroscopic data.

Another method of this cooperative use is to eliminate a systematic error in the scale factor for diffraction results by the use of the spectroscopic moments of inertia, as was applied to the cyanogen molecule by Morino *et al.*⁷⁾ and to ethane by Kuchitsu.⁹⁾ In the present study this corresponds to finding a cross point of the two lines in Fig. 2: a dashed line passing the ED point so as to represent a proportional variation in r_{C-C} and $r_{C=O}$ according to a small deviation in the scale factor, and a solid line which represents the values of r_{C-C} and $r_{C=O}$ satsifying the least-squares condition for $I_\alpha^{(z)}$. Fortuitously, the cross point was very close to the b point, so the parameter values were identical with those obtained by the least-squares adjustment. Thus, the structure parameters listed in column II of Table 6 are considered to give the most reliable average structure of acetaldehyde.

From the values of $\langle\Delta z\rangle_0$ shown in Table 4 and the r_z values determined in the present study, an approximate value of r_e was estimated by the use of Eq. (4), although it might include a large systematic error. The value of r_e obtained for the C–H bond of the methyl group was 1.078 Å, showing fair agreement with the 1.085 Å of $CH_4$¹⁹⁾ and the 1.080 Å of CH_3X.²⁰⁾ When the r_z-value of the C–H(Me) of acetaldehyde, 1.073 Å, is compared with the r_z-value of the C–H in CH_4, 1.100 Å, one might erroneously conclude that there is a remarkable difference in the nature of the C–H bonds in acetaldehyde and methane. However, it must be noted that the r_z value depends not only on the nature of the bond but also on the environment of the bond in a molecule and the isotope effect. Judging from the agreement of the approximate r_e-values, it is probable that the C–H bonds in these molecules are similar in nature and that the difference between r_z-values arises mainly from the environment effect, *e.g.*, the torsional motion of the methyl top in acetaldehyde.

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