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The Microwave Spectrum of *anti*-Acetaldehyde Oxime-*d*

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The microwave spectrum of *anti*-acetaldehyde oxime-*d* was investigated in the frequency region from 9 to 36 GHz. The rotational transition lines widely split into the A and E species due to the tunneling of the methyl group through the low potential barrier hindering the internal rotation. The transition lines belonging to the A species were fitted to the rigid rotor Hamiltonian, and the following effective rotational constants in MHz were obtained: $A_A=17250$, $B_A=6284.33$, and $C_A=4704.96$. All the observed transition frequencies were fitted to the Hamiltonian containing perturbation terms to the fourth order in order to obtain the internal-rotation parameters using the principal axis method. The potential barrier, V_3, hindering the internal rotation was determined to be 373 cal mol^{-1}. The dipole moment was determined to be 0.828 D from the Stark effect of the transitions belonging to the A species.

Rogowski and Schwendeman¹⁾ studied the microwave spectrum of acetaldehyde oxime and revealed that the potential barrier hindering the internal rotation of the methyl group in the *anti* form is much lower than that in the *syn* form. The microwave spectrum of the deuterated species ($CH_3CH=NOD$) of *syn*-acetaldehyde oxime was investigated, and the orientation of the OH bond in the molecule was determined to be at the *trans* position to the CN bond.²⁾

We have examined the microwave spectrum of *anti*-acetaldehyde oxime-*d* and determined the effective rotational constants, internal-rotation parameters, dipole moment, and r_s coordinates of the hydroxyl hydrogen atom.

Experimental

The sample of acetaldehyde oxime was commercially obtained from the Tokyo Kasei Kogyo Co., Ltd., and purified by trap-to-trap distillation *in vacuo*.

Acetaldehyde oxime in the *anti* form is solid at room temperature (melting point 46.5 °C).³⁾ We obtained the white solid sample of the *anti* form by gradual cooling in the course of distillation.

The deuterated species was prepared by the method used for *syn*-acetaldehyde oxime-*d*.²⁾

The spectrometer used was a conventional 100 kHz sinusoial and square-wave Stark-modulation type with a phase-sensitive detector. The rotational spectrum was observed at 0— —10 °C in order to prevent the decomposition of the sample. The sample gas was renewed about every half hour.

Results and Discussion

Observed Spectrum and Assignment. There are two possible orientations of the OH bond in *anti*-acetaldehyde oxime when the molecule is assumed to have a plane of symmetry. Figure 1 shows the projections of the molecule on its plane of symmetry. In the present analysis, we assumed that the molecule is in the *trans* form (Fig. 1(a)) and predicted the transition frequencies from the structural parameters in Table 1.

From the results for *anti*-acetaldehyde oxime,¹⁾ the following predictions were made: The transition lines of the deuterated species split widely into the A and E members due to the internal rotation of methyl group; the transitions belonging to the A member have little effect on the internal rotation and show the usual second-order Stark effect.

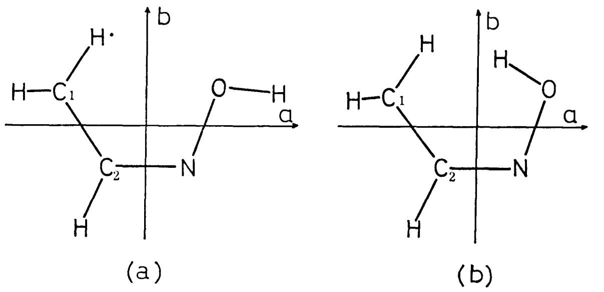

Fig. 1. Projection of *anti*-acetaldehyde oxime in its plane of symmetry.

Table 1. Structural parameters assumed for *anti*-acetaldehyde oxime-*d*

$r(C_2=N)$	1.276Å	$\angle$NOD	102.68°
r(N–O)	1.408	$\angle C_2=N-O$	110.20°
r(O–D)	0.956	$\angle H-C_2=N$	115.6°
$r(C_2-H)$	1.085	$\angle H-C_1-H$	107.6°
$r(C_1-H)$	1.090	$\angle C_1-C_2=N$	126.4°
$r(C_1-C_2)$	1.504		

C_1 = methyl carbon.

In the first place, according to the predictions, the transition lines belonging to the A member were identified and were fitted to the rigid rotor Hamiltonian in order to obtain the effective rotational constants. The results, given in Table 2, show large differences between the observed and calculated frequencies of the 2_{02}-3_{03}, 2_{11}-3_{12}, 2_{21}-3_{22}, and 3_{13}-3_{12} transitions.

If the molecule has a plane of symmetry, only two hydrogen atoms of the methyl group are out of the symmetry plane. Consequently, the inertia defect, $\Delta(=I_\alpha+I_c-I_a-I_b)$, should be zero for the rigid-rotor model, where I_α is the moment of inertia of the methyl top about its rotational axis and where I_a, I_b, and I_c are the moments of inertia about the principal axes. The value of Δ was calculated to be 0.798 amu Å^2 from the effective rotational constants in Table 2, using the assumed value of $I_\alpha=3.1$ amu Å^2. This Δ value deviates greatly from zero. The facts mentioned above indicate

TABLE 2. OBSERVED TRANSITIONS FOR *anti*-ACETALDEHYDE OXIME-*d* (A SPECIES)

Transition	ν_{obsd}(MHz)	$\Delta\nu^{\text{a)}}$(MHz)
$0_{00}\rightarrow1_{01}$ b)	10989.39	0.10
$1_{11}\rightarrow2_{12}$ b)	20399.17	−0.04
$1_{01}\rightarrow2_{02}$ b)	21819.95	−0.02
$1_{10}\rightarrow2_{11}$ b)	23557.88	−0.07
$2_{12}\rightarrow3_{13}$	30503.80	−0.41
$2_{02}\rightarrow3_{03}$	32342.09	−1.70
$2_{11}\rightarrow3_{12}$	35231.37	−0.93
$2_{21}\rightarrow3_{22}$	32965.49	−2.39
$2_{20}\rightarrow3_{21}$	33592.07	0.10
$3_{13}\rightarrow3_{12}$	9464.96	−1.24

a) $\Delta\nu=\nu_{\text{obsd}}-\nu_{\text{calcd}}$, ν_{calcd} obtained using these effective rotational constants; $A_{\text{A}}=$ 17250 MHz, $B_{\text{A}}=6284.33$ MHz, $C_{\text{A}}=$ 4704.96 MHz. b) Used to determine the effective rotational constants.

that the rotational transitions of *anti*-acetaldehyde oxime-*d* are affected by some kind of rotation-vibration interaction.

Using the method described by Rogowski and Schwendeman,[1)] we estimated the barrier height, V_3, hindering the internal rotation of the methyl group, and then predicted the transition frequencies belonging to the E symmetry species. In the vicinity of the predicted transition frequencies, we observed lines which could be attributed to the E member. The lines belonging to the E member exhibited a characteristic first-order Stark effect. The assignment of the transitions was made by observing the Stark effect.

TABLE 3. COMPARISON OF OBSERVED AND CALCULATED TRANSITION FREQUENCIES FOR *anti*-ACETALDEHYDE OXIME-*d*

Transition	ν_{obsd}(MHz)	$\Delta\nu$(MHz)$^{\text{a)}}$ I$^{\text{b)}}$	II$^{\text{c)}}$
	A Species		
$0_{00}\rightarrow1_{01}$	10989.39	−0.99	−0.11
$1_{11}\rightarrow2_{12}$	20399.17	−1.87	−0.29
$1_{01}\rightarrow2_{02}$	21819.95	−0.63	0.11
$1_{10}\rightarrow2_{11}$	23557.88	−1.57	0.13
$2_{12}\rightarrow3_{13}$	30503.80	−2.32	−0.52
$2_{02}\rightarrow3_{03}$	32342.09	1.04	−0.26
$2_{11}\rightarrow3_{12}$	35231.37	−1.89	−0.10
$2_{21}\rightarrow3_{22}$	32965.49	−2.74	−0.81
$2_{20}\rightarrow3_{21}$	33592.07	−5.84	−0.04
$3_{13}\rightarrow3_{12}$	9464.96	0.15	0.32
	E Species		
$0_{00}\rightarrow1_{01}$	10864.60	−5.37	−0.45
$1_{11}\rightarrow2_{12}$	20960.22	3.15	−1.40
$1_{01}\rightarrow2_{02}$	21622.52	−5.85	−0.03
$1_{10}\rightarrow2_{11}$	22880.04	6.19	2.15
$2_{12}\rightarrow3_{13}$	30732.36	5.19	2.50
$2_{02}\rightarrow3_{03}$	32140.50	−0.84	0.43
$2_{11}\rightarrow3_{12}$	34748.08	3.55	−1.36
$2_{21}\rightarrow3_{22}$	33199.51	0.66	0.95
$2_{20}\rightarrow3_{21}$	33132.06	5.74	−1.06

a) $\Delta\nu=\nu_{\text{obsd}}-\nu_{\text{calcd}}$. b) ν_{calcd} obtained using the parameters with $I_\alpha=3.1$ amu Å^2 in Table 4. c) ν_{calcd} obtained using the parameters with I_α $=2.80$ amu Å^2 in Table 4.

TABLE 4. INTERNAL-ROTATION PARAMETERS FOR *anti*-ACETALDEHYDE OXIME-*d*

I$^{\text{a)}}$	II$^{\text{b)}}$
$I_\alpha=3.1$ amu Å^2 (assumed)	$I_\alpha=2.80\pm0.02$ amu Å^2
$A_0=17000\pm42$ MHz	$A_0=17088\pm14$ MHz
$B_0=6254.59\pm0.44$ MHz	$B_0=6255.42\pm0.14$ MHz
$C_0=4704.43\pm0.40$ MHz	$C_0=4704.22\pm0.12$ MHz
$\lambda_a=\cos(52.4\pm0.3°)$	$\lambda_a=\cos(53.4\pm0.1°)$
$s=9.607\pm0.026$	$s=9.453\pm0.014$
$V_3=359$ cal mol^{-1}	$V_3=387$ cal mol^{-1}
$F=173959$ MHz	$F=190956$ MHz

a) Parameters obtained from the least-squares fit, with I_α fixed at 3.1 amu Å^2. b) Parameters obtained from the least-squares fit with I_α varied. The uncertainties are standard deviations.

The hyperfine structure of the absorption lines due to the ^{14}N nuclear quadrupole moment could not be observed.

Barrier to Internal Rotation. All the observed transition frequencies are listed in Table 3. These frequencies were fitted to the internal-rotation parameters, by using the Hamiltonian described by Rogowski *et al.*[1)] except for the denominator correction term, whose matrix elements were given by Stelman.[4)] The internal-rotation parameters obtained are listed in Table 4. The parameters are defined as follows: A_0, B_0, and C_0 are the rotational constants in the absence of internal rotation; λ_g is the cosine of the angle between the axis of the internal top and the principal g axis; s is the dimensionless parameter, the reduced barrier height, and the $s=(4/9)(V_3/F)$ relation holds for a threefold barrier; F is defined by the expression $\hbar^2/(2rI_\alpha)$, where r is equal to the quantity of $1-\sum_g\lambda_g^2(I_\alpha/I_g)$.

In Table 4, Set I is obtained assuming $I_\alpha=3.1$ amu·Å^2, while Set II is obtained with I_α as the fitting parameter. The value of 2.804 amu Å^2 for I_α in Set II is far from the value of 3.0—3.2 amu Å^2 usually found for the methyl top in various molecules. Therefore, the I_α parameter was fixed at 3.1 amu Å^2 in another fitting (Set I). The results of the two fittings are compared in Table 3. The deviations of the calculated frequencies from the observed ones, and the small value of I_α obtained by the least-squares fit in the present work, are comparable with those reported for normal species.[1)] These deviations and the small value of I_α may be ascribed to the facts that the perturbation terms higher than the fourth order for the internal rotation were neglected and that no other rotation-vibration interaction except the methyl torsion was considered.

Although the uncertainty to the value of I_α remains, there is not much difference in the values of V_3 between Set I and Set II, as Table 4 shows. Therefore, it is likely that the value of V_3 for deuterated species is not much different from the values in Table 4. Consequently, the value of V_3 for deuterated species may safely be concluded to be 373±30 cal mol^{-1}. This value is comparable to that of 375 cal mol^{-1} for normal species.[1)]

Dipole Moment. The A species transitions exhibited the usual second-order Stark effect. The dipole moment was determined from measurements of the Stark shifts of the transitions, $J=0\rightarrow1$, $1\rightarrow2$, and $2\rightarrow3$, belonging to the A species. The electric field inside the absorption cell was calibrated by measurements of the Stark shifts of the $J=0\rightarrow1$ and $1\rightarrow2$ transitions of OCS with the dipole moment of 0.71521 D.[5)]

TABLE 5. STARK EFFECT OF *anti*-ACETALDEHYDE OXIME-*d*

Transition	$\lvert M\rvert$	$(\partial\nu/\partial E^2)$[a)] MHz $(\mathrm{V\ cm^{-1}})^{-2}$		
		Obsd	Calcd	
			I	II
$0_{00}\rightarrow1_{01}$	0	7.635×10^{-6}	7.242×10^{-6}	7.240×10^{-6}
$1_{01}\rightarrow2_{02}$	0	−1.889	−1.720	−1.712
	1	2.072	2.251	2.247
$1_{11}\rightarrow2_{12}$	0	1.751	1.648	1.647
	1	22.891	23.313	23.314
$1_{10}\rightarrow2_{11}$	0	1.668	1.617	1.617
	1	−21.464	−21.312	−21.311
$2_{02}\rightarrow3_{03}$	0	−0.410	−0.380	−0.380
	2	1.053	1.113	1.110
$2_{12}\rightarrow3_{13}$	1	0.881	0.763	0.764
	2	3.846	3.590	3.592
$2_{11}\rightarrow3_{12}$	1	−0.601	−0.565	−0.566
	2	−2.889	−2.708	−2.709
$3_{13}\rightarrow3_{12}$	3	2.441	2.456	2.465
		μ_a	0.753 ± 0.004 D	0.753 ± 0.004 D
		μ_b	0.34 ± 0.02 D	0.34 ± 0.03 D
		μ_c	0.02 ± 0.02 D	0 (assumed) D
		μ_{total}	0.828 ± 0.011 D	0.828 ± 0.013 D

a) Based on $\mu(\mathrm{OCS})=0.71521$ D.

The results obtained by the least-squares fit given in Table 5 show good agreements between the observed and calculated Stark coefficients. The fifth column of Table 5 shows the results obtained with the assumed value of $\mu_c=0$. The results given in the fourth column were obtained by the least-squares fit, using all three components, μ_a, μ_b, and μ_c, as parameters. The value of 0.02 D obtained for μ_c is comparable to the uncertainty in this work. Consequently, the value of μ_c is thought to be nearly equal to zero. The values of μ_a and μ_b determined in the fitting (Calcd I) are consistent with those obtained in the other fitting (Calcd II). From the above results, the molecule may reasonably be concluded to have a plane of symmetry.

Orientation of the OH Bond. The rotational constants, A_0, B_0, and C_0, in Table 4 are what the effective rotational constants A_A, B_A, and C_A, would be in the absence of internal rotation.[1)] Consequently, from these rotational constants and the corresponding ones for the normal species,[1)] the r_s coordinates of the hydroxyl hydrogen atom can be calculated using Kraitchman's expressions.[6)] In Table 6, the first column shows the coordinates calculated from the rotational constants with $I_\alpha=3.1$ amu Å^2, while the second column refers to those obtained from the constants with $I_\alpha=2.80$ amu Å^2. The above two sets of results are consistent within the limits of accuracy of the present work. The third and fourth columns show the coordinates of the hydroxyl hydrogen atom calculated from the assumed structures given in Fig. 1(a) and Fig. 1(b) respectively. The coordinates determined experimentally are in good agreement with those calculated from the structure shown in Fig. 1(a). Consequently, it may clearly be concluded that the orientation of the OH bond in the *anti*-acetaldehyde oxime molecule is at the position *trans* to the C–N bond, as is shown in Fig. 1(a). This result is consistent with the orientation of the OH bond in formaldehyde oxime[7)] and *syn*-acetaldehyde oxime.[2)]

TABLE 6. COORDINATES OF THE HYDROGEN ATOM OF THE HYDROXYL GROUP

	Obsd-I[a)]	Obsd-II[b)]	Calcd-I[c)]	Calcd-II[d)]
a	$2.128\pm$ 0.031Å	$2.129\pm$ 0.009Å	2.132Å	0.354Å
b	$0.49\pm$ 0.13	$0.48\pm$ 0.04	0.507	1.152
c	—	$0.14\pm$ 0.19	0 (assumed)	0 (assumed)

a) Using the rotational constants with $I_\alpha=3.1$ amu·Å^2. b) Using the rotational constants with $I_\alpha=2.80$ amu Å. c) Obtained from the assumed structure shown in Fig. 1(a). d) Obtained from the assumed structure shown in Fig. 1(b).

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