April, 1976] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49(4), 891—893 (1976) 891

Microwave Spectrum of *syn*-Acetaldehyde Oxime-*d*

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(Received September 23, 1975)

The microwave spectrum of *syn*-acetaldehyde oxime-*d* was investigated in the frequency region 7.5∼35 GHz. Several a-type R-branch transitions were identified and the following rotational constants in MHz were obtained: $A=45682$, $B=4057.21$, $C=3806.13$. The transitions of *syn*-acetaldehyde oxime-*d* are split into the A and E species by tunneling of the methyl group through the potential barrier hindering the internal rotation. From these separations the height of the barrier was determined to be 1948 cal mol^{-1}. The dipole moment of the molecule was determined to be 0.938 D from the Stark effect.

It has been found that acetaldehyde oxime has α- and β-modifications, which melt at 46.5 °C and 12 °C, respectively.[1)] This molecule also has the two geometrical isomers whose conformations are *syn*- and *anti*-forms. The infrared spectrum of acetaldehyde oxime was investigated with attention to the effects of the geometrical isomerism.[2)] The nuclear magnetic resonance study has revealed that the conformation change from one isomer to another is made easily.[3)] Rogowski and Schwendeman studied the microwave spectrum of acetaldehyde oxime and have shown that the potential barrier hindering the internal rotation of the methyl group is abnormally low in the *anti*-form.[4)]

We examined the microwave spectrum of *syn*-acetaldehyde oxime-*d* ($CH_3CH{=}NOD$) and determined the rotational constants, the potential barrier hindering the internal rotation of the methyl group, and the dipole moment. The orientation of the OH bond and the direction of the dipole moment of the molecule have been discussed, in conjunction with Rogowski's results for the normal species ($CH_3CH{=}NOH$).[4)]

Experimental

Sample of acetaldehyde oxime obtained commercially (Tokyo Kasei Kogyo Co., Ltd.) was purified by trap-to-trap distillations several times *in vacuo*. No attempt was made to separate the *syn* and *anti* species; all the measurements were, consequently, made with the equilibrium mixture of the isomers. The deuterated species was prepared in the absorption cell as follows. First, the cell was filled with D_2O vapor at room temperature. It was then evacuated by vacuum pump for about half an hour. At the end of this time the sample of acetaldehyde oxime purified beforehand was admitted into the cell.

The spectrometer used was a conventional 100 kHz sinusoidal and square wave Stark modulation type with a phase sensitive detector. Because the sample apparently decomposed slowly at room temperature in the sample cell, the spectrum was observed at 0∼−10 °C and the sample was renewed about every half an hour.

Results and Discussion

Observed Spectrum and Assignment. The structure of *syn*-acetaldehyde oxime-*d* was assumed to be the same as that of *syn*-acetaldehyde oxime (normal species) which has been considered to be a planar molecule. This assumption was based on the structural parameters for formaldehyde oxime determined by Levine[5)] and the parameters fitted to the rotational constants *B* and *C* of the normal species.[4)] The bond angles and bond distances assumed are given in Table 1. The projection of the molecule in its plane of symmetry is shown in Fig. 1(a). Although there are two possible orientations of the OH bond in this molecule, as shown in Figs. 1(a) and 1(b), the same orientation as that of formaldehyde oxime was assumed: that is, the OH bond is at the *trans* position relative to the C=N double bond. The assumed orientation of the OH bond will be discussed later. Frequencies of the rotational transitions were predicted from the moments of inertia calculated from the assumed structure. Substitution of a deuterium atom for the hydrogen atom of the hydroxyl group of *syn*-acetaldehyde oxime makes only a small change of the directions of the principal axes of the moment of inertia. Therefore, it was expected that the a-type R-branch transitions would be the most intense, as observed for the normal species.[4)] In fact, only the a-type R-branch transitions have been observed and assigned. They were identified by their Stark effects. The b-type transitions were searched for, but there was no absorption line to be assigned as a b-type transition. This may suggest that the b-type transitions are quite weak because of

TABLE 1. STRUCTURAL PARAMETERS ASSUMED FOR *syn*-ACETALDEHYDE OXIME-d

$r(C_2{=}N)$	1.276 Å	$\angle N{-}O{-}D$	102.68°
$r(N{-}O)$	1.408	$\angle C_2{=}N{-}O$	110.20°
$r(O{-}D)$	0.956	$\angle H{-}C_2{=}N$	121.77°
$r(C_2{-}H)$	1.085	$\angle H{-}C_1{-}H$	108.80°
$r(C_1{-}H)$	1.094	$\angle C_1{-}C_2{=}N$	119.34° [b)]
$r(C_1{-}C_2)$	1.506[b)]		

a) C_1=methyl carbon. b) Fitted to the rotational constants *B* and *C* of the normal species.[4)]

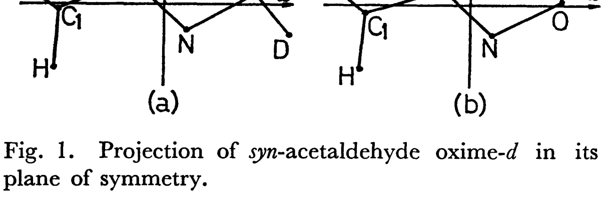

Fig. 1. Projection of *syn*-acetaldehyde oxime-*d* in its plane of symmetry.

TABLE 2. OBSERVED TRANSITIONS FOR *syn*-ACETALDETHYDE OXIME-*d* (A SPECIES)

$J \rightarrow J'$	ν_{obsd} (MHz)	$\Delta\nu$[a] (MHz)
$0_{00} \rightarrow 1_{01}$	7863.36	+0.03
$1_{11} \rightarrow 2_{12}$	15475.71	+0.13
$1_{01} \rightarrow 2_{02}$	15725.69	+0.16
$1_{10} \rightarrow 2_{11}$	15977.28	−0.45
$2_{12} \rightarrow 3_{13}$	23212.37	−0.30
$2_{02} \rightarrow 3_{03}$	23585.68	+0.22
$2_{11} \rightarrow 3_{12}$	23966.40	+0.51
$3_{13} \rightarrow 4_{14}$	30948.86	−0.05
$3_{03} \leftarrow 4_{04}$	31441.96	−0.03
$3_{12} \rightarrow 4_{13}$	31952.82	−0.37

a) $\Delta\nu = \nu_{\mathrm{obsd}} - \nu_{\mathrm{calcd}}$

TABLE 3. OBSERVED AND CALCULATED ROTATIONAL CONSTANTS OF *syn*-ACETALDEHYDE OXIME

	Observed (MHz)	Calculated	
		I[a] (MHz)	II[b] (MHz)
Deuterated species			
A	45682±500	44281	44908
B	4057.20±0.04	4055.56	4334.09
C	3806.13±0.04	3804.51	3952.62
Normal species			
A	44613±385[c]	45511	42661
B	4237.73±0.03[c]	4236.84	4360.06
C	3973.81±0.03[c]	3973.20	4057.06

a) Calculated from the structure in Fig. 1(a).
b) Calculated from the structure in Fig. 1(b).
c) Ref. 4.

their small μ_b components, as described later.

The $K_{-1}=1$ absorption lines were split into A and E members by the internal rotation of the methyl group. The absorption lines of the A member showed the second-order Stark effect, while those of the E member showed the first-order Stark effect. Assuming the rigid rotor Hamiltonian, the rotational constants were fitted to the frequencies of the transitions belonging to the A symmetry species. A comparison of the observed and calculated frequencies is given in Table 2. The effective rotational constants obtained from the rigid rotor fit are in Table 3, together with the rotational constants calculated from the assumed structures.

Splittings of the lines due to the nuclear quadrupole moment of the ^{14}N nucleus were observed in the $1_{10} \rightarrow 2_{11}$ and $1_{11} \rightarrow 2_{12}$ transitions of the A member. Only one quadrupole coupling constant, $\chi_{aa}=3.5 \pm 0.7$ MHz, could be determined.

Barrier to Internal Rotation. The spectra of the A and E species can be treated with the Hamiltonian given by Herschbach.[6] *syn*-Acetaldehyde oxime-*d* is a near prolate symmetric top molecule with the axis of the internal rotation of the methyl group close to the principal a-axis. Therefore, the Hamiltonian for this molecule can be simplified.[4] Using the Hamiltonian including the perturbation terms up to third-order, the A-E splittings of the low J transitions can be fitted to a barrier-dependent parameter from which the barrier height V_3 may be obtained.[4,7]

The A-E splittings of the $K_{-1}=1$ lines were about 1 MHz for $J=2 \rightarrow 3$ transitions and about 4 MHz for $J=1 \rightarrow 2$ transitions. A value of the barrier height, 1948±100 cal mol^{-1}, was obtained by averaging the values of V_3 determined from each of the splittings of the $K_{-1}=1$ lines of the $J=1 \rightarrow 2$ and $J=2 \rightarrow 3$ transitions given in Table 4. The uncertainty, 100 cal mol^{-1}, was estimated by taking account of the uncertainties of the assumed parameters λ_a and I_α. But, because we took no account of the uncertainty of the moment of inertia I_a, the uncertainty obtained may have been underestimated. The barrier height of the deuterated species obtained in this work is higher by about 100 cal mol^{-1} than that of the normal species.

Principal Axis Coordinates of Hydroxyl Hydrogen Atom. The absolute values of the principal axis coordinates of the hydroxyl hydrogen atom were calculated from the moments of inertia of *syn*-acetaldehyde oxime and its deuterated species, using the expressions given by Kraitchman.[8] The conversion factor used was 505376 MHz·amu·Å^2. The value obtained for the a-coordinate is fairly good, while the value for the b-coordinate has a large error. In particular the c-coordinate could not be determined because of the negative square value of the c-coordinate. This may be attributed to the large uncertainty of the rotational constant A. The uncertainties given in Table 5 were calculated from the standard deviations of the rotational constants fitted to the observed frequencies.

From the results given in Tables 3 and 5, it seems reasonable to be led to the following conclusion: The plausible orientation of the OH bond is as shown in Fig. 1(a). The *trans* form as shown in Fig. 1(a) is consistent with the orientation of the OH bond in formalde-

TABLE 4. INTERNAL-ROTATION SPLITTINGS AND BARRIER HEIGHT FOR *syn*-ACETALDEHYDE OXIME-*d*

$J \rightarrow J'$	$(\nu_A - \nu_E)_{\mathrm{obsd}}$ (MHz)	$(\nu_A - \nu_E)_{\mathrm{calcd}}$ (MHz)	V_3 (cal mol^{-1})
$1_{11} \rightarrow 2_{12}$	−3.79	−3.73	1944.7
$1_{10} \rightarrow 2_{11}$	3.83	3.81	1945.8
$2_{12} \rightarrow 3_{13}$	−0.97	−0.94	1941.7
$2_{11} \rightarrow 3_{12}$	0.98	1.04	1958.2

Assumed internal-rotation parameters: $\lambda_a=0.9473$, $\lambda_c=0$, $I_\alpha=3.18$ amu·Å^2.

TABLE 5. PRINCIPAL AXIS COORDINATES OF THE H ATOM OF THE HYDROXYL GROUP

	r_s-Coordinate	Assumed structure	
		III[a]	IV[b]
a	2.379±0.016 Å	2.318 Å	1.515 Å
b	−0.13±0.32	−0.572	1.017
c	——	0	0

Uncertainties were estimated from the standard deviations of the rotational constants. See text.
a) Structure shown in Fig. 1(a). b) Structure shown in Fig. 1(b).

hyde oxime determined by Levine.[5)]

Dipole Moment. The dipole moment was determined by measurements of the Stark shifts of the $0_{00} \rightarrow 1_{01}$, $1_{01} \rightarrow 2_{02}$, $2_{02} \rightarrow 3_{03}$, and $3_{03} \rightarrow 4_{04}$ absorption lines. The electric field in the absorption cell was calibrated by measurements of the Stark shifts of the $J=0 \rightarrow 1$ and $J=1 \rightarrow 2$ absorption lines of OCS. The dipole moment of OCS is 0.71521 D.[9)]

The observed and calculated Stark coefficients are given in Table 6. Assuming that the molecule has a plane of symmetry and the component of the dipole moment along the axis perpendicular to the plane of symmetry is zero, we obtained $\mu_a=0.865\pm0.004$ D, $\mu_b=0.363\pm0.015$ D, and $\mu_{total}=0.938\pm0.009$ D. The uncertainties are the standard deviations obtained by the least square fit. The value of μ_{total} obtained in this work is in good agreement with that of *syn*-acetaldehyde oxime.[4)]

If it is assumed that the structure of the deuterated species is exactly the same as that of the normal species and its structural parameters are as given in Table 1, the orientation of the dipole moment in the molecule can be determined. From the compositions of the dipole moments of normal and deuterated species along the principal axes, the direction of the dipole moment in the molecule was determined as shown with a thick line in Fig. 2. The angle between the dipole moment and the NO bond is 8.09°.

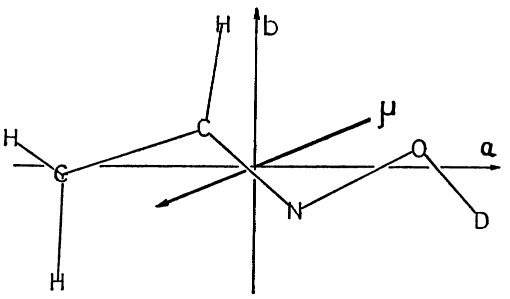

Fig. 2. Orientation of the dipole moment in *syn*-acetaldehyde oxime-*d* molecule.

TABLE 6. STARK EFFECT AND DIPOLE MOMENT OF *syn*-ACETALDEHYDE OXIME-*d*

$J \rightarrow J'$	|M|	$(\partial\nu/\partial E^2)_{obsd}$[a)] MHz(V cm^{-1})$^{-2}$	$(\partial\nu/\partial E^2)_{calcd}$[b)] MHz(V cm^{-1})$^{-2}$
$0_{00} \rightarrow 1_{01}$	0	12.97×10^{-6}	12.97×10^{-6}
$1_{01} \rightarrow 2_{02}$	0	−3.665	−3.645
	1	3.130	3.142
$2_{02} \rightarrow 3_{03}$	0	−0.480	−0.689
	1		−0.219
	2	1.147	1.191
$3_{03} \rightarrow 4_{04}$	1	0.222	0.296

a) Based on μ(OCS)=0.71521 D.[9)] b) Calculated assuming $|\mu_a|=0.865$ D, $|\mu_b|=0.363$ D, and $|\mu_c|=0$.

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