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The Microwave Spectrum of (*Z*)-(Propionaldehyde Oxime)

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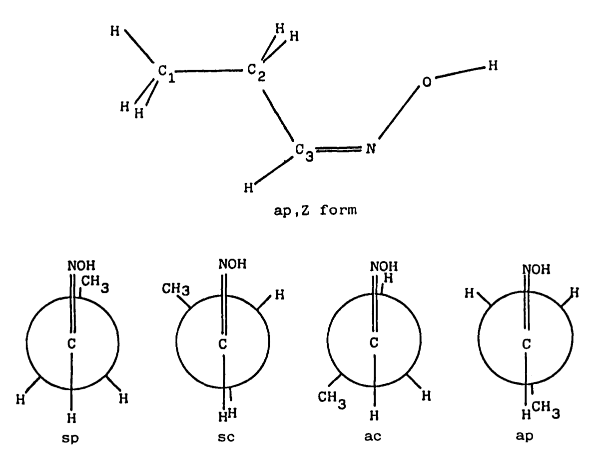
Synopsis. The microwave spectrum of (*Z*)-(propionaldehyde oxime) was observed in the frequency region of 10 to 30 GHz. The rotational constants (MHz) for the ground vibrational state were determined to be A=15453.95±0.20, B=2733.60±0.03, and C=2394.85±0.02. The conformation has been plausibly deduced to be the *ap*, *Z*-form from the rotational constants. The dipole moments were determined by the Stark effect: μ_a=0.889±0.010 and μ_b=0.364±0.025 *D*.

From its rotational spectrum propionic acid has been shown to exist predominantly in *sp*-conformation in which the methyl group eclipses the carbonyl bond and the hydroxyl hydrogen is located between the two oxygen atoms.[1] Nuclear magnetic resonance spectroscopic study[2] of propionaldehyde oxime has suggested that this molecule exists in two stereoisomeric forms, termed *E* and *Z* forms with respect to the C=N bond. Each of the conformers has four possible rotational conformations with respect to the C_2–C_3 single bond if the OH bond is assumed to be at the trans position to the C=N bond just as in acetaldehyde oxime[3,4] and acrylaldehyde oxime,[5,6] as shown in Fig. 1. The microwave spectroscopic study[7] has revealed that (*E*)-(propionaldehyde oxime) exists in an *ac*, *E*-conformation (See Fig. 1).



	sp	sc	ac	ap
A/MHz	7954.8	8514.4	11838	15658
B/MHz	5618.3	4321.4	3062.7	2773.5
C/MHz	3434.9	3264.4	2740.3	2418.1
ΔI/amu·Å²	-6.35	-21.5	-23.3	-6.35

Fig. 1. Four possible rotatonal conformers, their calculated rotational constants, and the numbering of carbon atoms of an *ap*, (*Z*) -(propionaldehyde oxime)

Experimental

Propionaldehyde oxime was prepared by the method described elsewhere.[7]

The microwave spectrometer employed was the same one as described elsewhere.[7] The spectrum was observed at room temperature.

Results and Discussion

A survey of the spectrum was made in the frequency region of 19 to 22 GHz in which the J=4—3 transition lines were expected to be observed from the molecular model calculation of the rotational constants.

The six absorption line frequencies of the J=4—3 transtions led to the preliminary rotational constants which were employed to predict the other transition lines. The assignments of the transition lines were made on the basis of their characteristic Stark effects. The frequencies of the transitions assigned to the

Table 1. Rotational Transition Frequencies (MHz) of (*Z*)-(Propionaldehyde Oxime) in the Ground Vibrational State

Transition	Obsd	$\Delta\nu^{a)}$	Transition	Obsd	$\Delta\nu^{a)}$
	a-Type R-branch		5_{15}—4_{14}	24766.63	−0.32
2_{12}—1_{11}	9918.21	0.03	5_{05}—4_{04}	25509.59	0.20
2_{02}—1_{01}	10250.25	0.02	5_{24}—4_{23}	25627.49	−0.01
2_{11}—1_{10}	10596.01	0.34	5_{23}—4_{22}	25760.37	0.13
3_{13}—2_{12}	14873.01	−0.10	5_{14}—4_{13}	26458.98	0.01
3_{03}—2_{02}	15358.64	−0.01		b-Type Q-branch	
3_{22}—2_{21}	15385.27	−0.19	4_{13}—4_{04}	14665.65	−0.07
3_{21}—2_{20}	15412.11	−0.04	5_{14}—5_{05}	15615.12	−0.18
3_{12}—2_{11}	15889.19	−0.09	6_{15}—6_{06}	16806.89	0.18
4_{14}—3_{13}	19823.05	−0.13	7_{16}—7_{07}	18265.27	0.13
4_{04}—3_{03}	20447.18	0.03	8_{17}—8_{08}	20016.18	0.18
4_{23}—3_{22}	20508.82	0.10	9_{18}—9_{09}	22084.18	−0.18
4_{22}—3_{21}	20575.41	0.08	10_{19}—10_{010}	24488.40	−0.07
4_{13}—3_{12}	21177.73	0.04			

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

Table 2. Rotational Transitions of (Z)-(Propionaldehyde Oxime) in the Excited States (MHz)

Transition	$v=1$		$v=2$	
	Obsd	$\Delta\nu$[a]	Obsd	$\Delta\nu$[a]
2_{02}—1_{01}	10311.97	0.26	10376.34	−0.34
2_{12}—1_{11}	9998.82	0.27	10075.82	0.49
2_{11}—1_{10}	10637.27	−0.13	10689.33	−0.09
3_{03}—2_{02}	15452.25	0.05	15549.95	−0.08
3_{13}—2_{12}	14994.03	0.02	15209.26	−0.03
3_{12}—2_{11}	15952.36	0.15	16030.50	0.13
3_{22}—2_{21}	15477.40	−0.03	15572.07	−0.07
3_{21}—2_{20}	15501.39	−0.64		
4_{04}—3_{03}	20574.31	−0.02	20705.56	0.07
4_{14}—3_{13}	19984.75	−0.25	20138.83	−0.11
4_{13}—3_{12}	21262.11	−0.14	21366.74	0.06
4_{23}—3_{22}	20632.08	0.30		
4_{22}—3_{21}	20693.43	0.26		

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

Table 3. Rotational Constants of (Z)-(Propionaldehyde Oxime)

	Ground state	Excited state	
	$v=0$	$v=1$	$v=2$
A/MHz	15453.95(20)	15014(155)	14354(180)
B/MHz	2733.60(3)	2739.18(14)	2749.19(12)
C/MHz	2394.85(2)	2419.76(14)	2442.15(11)
κ	−0.948120(37)	−0.949(24)	−0.948(29)
ΔI/amu·Å^2	−6.552(4)	−9.3(4)	−12.1(5)

$\Delta I=I_c-I_a-I_b$

Table 4. Structural Parameters Assumed for (Z)-(Propionaldehyde Oxime)

Bond length	r/Å	Bond angle	θ/°
C_1-C_2	1.525	HC_1H	109.5
C_2-C_3	1.510	HC_2H	109.5
C_1-H	1.087	HC_1C_2	109.5
C_2-H	1.087	HC_2C_3	109.5
C_3-H	1.086[a]	$C_1C_2C_3$	109.5
C_3=N	1.276[a]	HC_3=N	122.0[a]
N-O	1.408[a]	C_2C_3=N	126.0[a]
O-H	0.956[a]	C_3=NO	110.2[a]
		NOH	102.7[a]

Structural parameters of ethyl group were estimated from mono-substituted ethyl derivatives.

a) See Ref. 7: K. Yoshida et al., *Bull. Chem. Soc. Jpn.*, **59**, 1620 (1986).

Table 5. Stark Coefficients (Hz/(V/cm)^2) and Dipole Moments (D) of (Z)-(Propionaldehyde Oxime)

Transition	|M|	Obsd	Calcd
3_{13}—2_{12}	1	5.493	5.499
	2	21.50	21.81
3_{12}—2_{11}	1	−4.665	−4.716
	2	−17.59	−17.12
	$\mu_a=0.889\pm0.010$		
	$\mu_b=0.364\pm0.025$		
	$\mu_c=0$(assumed)		
	$\mu_t=0.961\pm0.019$		

ground vibrational state of (Z)-(propionaldehyde oxime) are listed in Table 1.

From comparison between the observed and calculated rotational constants and values of $\Delta I(=I_c-I_a-I_b)$ listed in Table 3 and Fig. 1, it has been reasonably concluded that the conformation of (Z)-(propionaldehyde oxime) with respect to the C_2–C_3 bond is an *ap* form in contrast to the *ac* form for (E)-(propionaldehyde oxime).[7] Table 4 shows the structural parameters of this molecule used for a model calculation of the rotational constants.

Two satellite lines which could be attributable to vibrationally excited states were observed in the vicinity of the ground state lines. The results of the least squares analysis of data are given in Tables 2 and 3. From the trends of changes in the rotational constants and values of ΔI given in Table 3, these two satellites should be ascribed to one vibrational mode that may be the torsional motion around the C_2–C_3 bond.

The dipole moments were determined by the measurements of the Stark effects of the 3_{13}—2_{12} and 3_{12}—2_{11} transition lines. The electric field in the absorption cell was calibrated with OCS[8] as a standard. The observed and calculated Stark coefficients are given in Table 5 together with the dipole moments experimentally determined.

Table 5 shows that the observed Stark coefficients are in good agreement with the ones calculated from the dipole moments determined by the least squares analysis assuming $\mu_c=0$. The above fact is consistent with that the conformation of (Z)-(propionaldehyde oxime) is an *ap*, Z-form.

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