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The Microwave Spectrum of (*E*)-(Propinaldehyde Oxime)

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Synopsis. Microwave spectra of propionaldehyde oxime and its deuterated derivatives ($CH_3CH_2CH{=}NOD$) were observed in the frequency region from 10 to 35 GHz. Several a-type R-branch transitions were identified and the following rotational constants(MHz) in the vibrationally ground state were determined to be: $A=19400\pm400$, $B=2278.16\pm0.03$, and $C=2204.09\pm0.03$ for the normal species, and $A=19000\pm400$, $B=2194.31\pm0.02$, and $C=2128.40\pm0.02$ for the deuterated species. The spectrum analyzed in this work has been concluded from the rotational constants to be due to a *ac*,*E*-conformer.

From its rotational spectrum propionic acid (CH_3CH_2COOH) has been shown to exist predominantly in a *sp*-conformation in which the methyl group eclipses the carbonyl bond and the hydroxyl hydrogen is located between the two oxygen atoms.[1] Acrylaldehyde oxime has been reported to exist predominantly in a *s-trans* form for both *E*- and *Z*-forms.[2,3]

Propionaldehyde oxime[4] has been reported by nuclear magnetic resonance spectroscopic study to exist in two stereoisomeric forms, termed *E*- and *Z*-forms with respect to the C=N bond, each form of which has four possible rotational conformations with respect to the C_2–C_3 bond if the OH bond is assumed to be at the trans position to the CN bond just as it has been found in such molecules as acrylaldehyde oxime[2,3] and acetaldehyde oxime,[6,7] as shown in Fig. 1.

Experimental

Propionaldehyde oxime was produced by reacting propionaldehyde with hydroxylamine hydrochloride according to Dunstan and Dymond's method.[5]

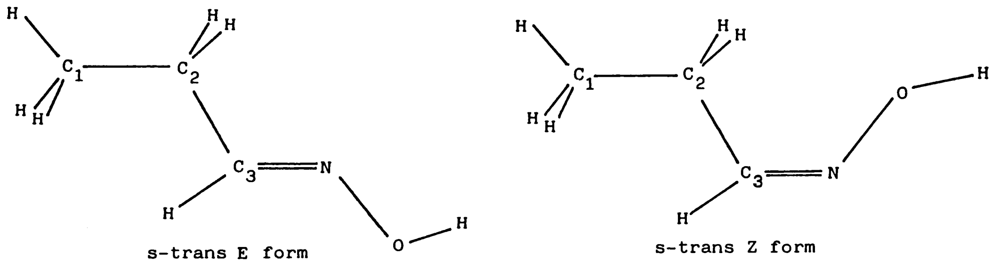
Deuterated species of propionaldehyde oxime ($CH_3CH_2CH{=}NOD$) was prepared in the absorption cell itself in the same way as that for acetylaldehyde oxime-d.[6,7]

The microwave spectrometer used was a conventional 100 KHz sinusoidal- and square-wave Stark modulation type with a phase sensitive detector. The spectra were observed at room temperature.

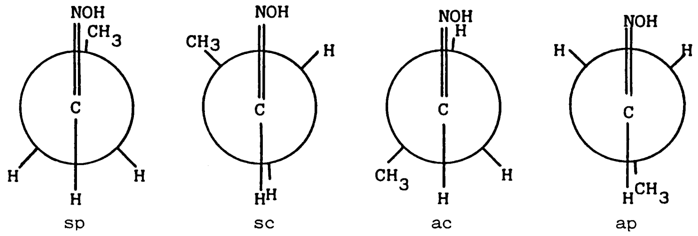
Results and Discussion

The rotational constants calculated from the assumed structural parameters as listed in Table 1 suggests that seven conformers of eight possible rotational conformers were near prolate symmetric top molecules in whose spectra bunches of the absorption lines are expected with the frequency interval of about ($B+C$).

A survey of the spectrum was made in frequency region of 8.5 to 32 GHz at the Stark fields between 200 and 300 V cm^{-1}. Groups of the absorption lines were found with the frequency interval of about 4500 MHz. The frequencies of the absorption lines which were assigned on the basis of their characteristic Stark effects are listed in Table 2 together with



s-trans E form s-trans Z form



sp sc ac ap

Fig. 1. Four possible rotational conformers and the numbering of carbon atoms of a *ap*-(*E*)-(propionaldehyde oxime) and a *ap*-(*Z*)-(propionaldehyde oxime).

the differences between the observed and calculated frequencies which were obtained by the least squares fitting. These lines should be attributable to a ground vibrational state because of their strong intensities, some of which were accompanied by relatively weak satellites in their vicinity and they might be ascribed to a vibrationally excited state.

The values of the rotational and centrifugal distortion constants were obtained from the least squares fit of all the assigned lines in which the Watson type Hamiltonian including the centrifugal distortion terms of $\varDelta_J$ and $\varDelta_{JK}$ was used and the results are listed in Table 3.

The spectrum of the deuterated species was analyzed with the same way as the normal species and its results are listed in Tables 2 and 3.

The derived values of the rotational constants and the values of $\Delta I = I_c - I_a - I_b$ have close correspondence with the values calculated for the *ac,E*-conformer as shown in Table 4.

The r_s coordinates of the hydroxyl hydrogen atom were calculated from the rotational constants of the normal and deuterated species, using the Kraitchman's equations,[8] as follows: $|a|=2.84\pm0.06$ Å, $|b|=0.3\pm0.5$ Å, and $|c|=0.7\pm0.3$ Å. These values are consistent with the values calculated for the *ac,E*-conformer which are $|a|=2.7$ Å, $|b|=0.06$ Å, and $|c|=0.53$ Å. Above discussion leads to the conclusion that the spectrum analyzed in this work is due to an *ac,(E)*-(propionaldehyde oxime).

Table 1. Structural Parameters Assumed for Propionaldehyde Oxime

Bond length	r/Å	Bond angle	θ/°
C_1-C_2	1.536	HC_1H	109.5
C_2-C_3	1.493	HC_2H	105.7
C_1-H	1.095	$C_1C_2C_3$	112.1
C_2-H	1.095	HC_1C_2	110.3
C_3-H	1.086	HC_2C_3	109.8
C_3=N	1.276	C_2C_3=N	125.4
N-O	1.408	HC_3=N	121.8
O-H	0.956	C_3=NO	110.2
		NOH	102.7

Table 2. Observed Transition Frequencies (MHz) of Propionaldehyde Oxime

Transition	Normal		Deuterated	
	Obsd	$\Delta\nu$[a)]	Obsd	$\Delta\nu$[a)]
3_{13}—2_{12}	13335.67	0.16	12869.42	0.24
3_{03}—2_{02}	13445.73	0.04	12967.33	0.04
3_{12}—2_{11}	13557.74	0.00	13066.77	−0.16
4_{14}—3_{13}	17780.43	0.11	17158.65	0.04
4_{04}—3_{03}	17926.33	−0.06	17288.71	0.04
4_{23}—3_{22}	17929.37	0.10		
4_{22}—3_{21}	17931.42	−0.24		
4_{13}—3_{12}	18076.51	−0.10	17422.30	0.03
5_{15}—4_{14}	22224.76	−0.04	21447.75	−0.04
5_{05}—4_{04}	22406.09	0.06	21609.26	−0.11
5_{24}—4_{23}	22411.36	0.22	21613.58	0.04
5_{23}—4_{22}	22415.78	−0.14	21617.44	0.04
5_{14}—4_{13}	22595.07	−0.09	21777.32	−0.04
6_{16}—5_{15}	26668.87	−0.03	25736.52	−0.13
6_{06}—5_{05}	26884.47	0.08	25928.99	0.04
6_{25}—5_{24}	26892.59	−0.12	25935.64	−0.09
6_{24}—5_{23}	26901.13	0.05	25942.45	−0.03
6_{15}—5_{14}	27113.30	−0.02	26132.25	0.12
7_{17}—6_{16}	31112.44	−0.09	30025.13	−0.01
7_{07}—6_{06}	31361.12	−0.09	30247.37	0.08
7_{26}—6_{25}	31373.97	0.04	30257.63	0.00
7_{25}—6_{24}	31387.36	0.04	30268.49	0.05
7_{16}—6_{15}	31631.11	0.13	30486.46	−0.05

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

Table 3. Observed Rotational Constants of Propionaldehyde Oxime

	Normal	Deuterated
A/MHz	194000 ±400	19000 ±400
B/MHz	2278.16± 0.03	2194.31± 0.02
C/MHz	2204.09± 0.03	2128.40± 0.02
$\varDelta_J$/kHz	0.8 ± 0.2	0.6± 0.2
$\varDelta_{JK}$/kHz	21 ± 5	18 ± 5
κ	−0.9914	−0.9922
ΔI/amu·Å^2	−18.5 ± 0.5	−19.4 ± 0.5

$\varDelta I = I_c - I_a - I_b$, Conversion factor: 505376 MHz·amu·Å^2

Table 4. Observed and Calculated Rotational Constants of Propionaldehyde Oxime

	A/MHz	B/MHz	C/MHz	κ	ΔI/amu·Å^2
Obsd	19400	2278.16	2204.09	−0.9914	−18.5
E-form					
sp	15142	3076.49	2641.09	−0.9303	−6.3
sc	16458	2830.04	2582.00	−0.9642	−13.5
ac	21125	2487.06	2407.51	−0.9915	−17.2
ap	25342	2409.59	2262.37	−0.9872	−6.3
Z-form					
sp	9715	5519.52	3681.10	−0.3906	−6.3
sc	10493	4386.31	3506.58	−0.7482	−19.3
ac	14623	3215.38	2990.05	−0.9613	−22.7
ap	19361	2959.99	2652.29	−0.9632	−6.3

$\Delta I = I_c - I_a - I_b$

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