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The Microwave Spectrum of Acrylaldehyde Oxime

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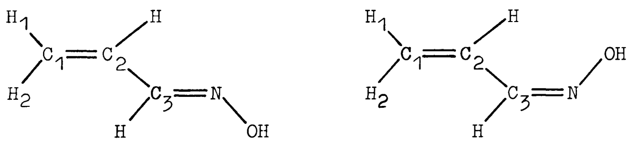
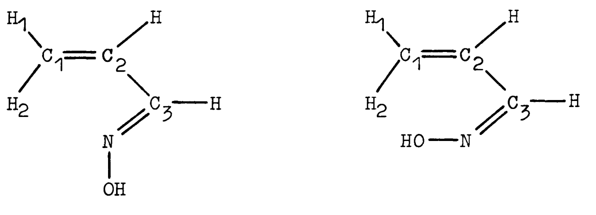
The microwave spectra of acrylaldehyde oxime and its deuterated derivative (CH_2=CH-CH=NOD) were observed in the frequency region from 8.5 to 35 GHz. The several a-type R-branch transitions in the ground vibrational state were identified and the following rotational constants in MHz were determined to be: $A=34117\pm96$, $B=2363.007\pm0.011$, and $C=2210.616\pm0.011$ for normal species and $A=33950\pm103$, $B=2274.301\pm0.010$, and $C=2131.981\pm0.011$ for deuterated species. The most plausible molecular structure to which the spectrum assigned is attributed has been deduced to be a *s-trans syn* geometrical conformer from the rotational constants experimentally determined. The dipole moment component μ_a in the ground vibrational state was determined to be 0.59 D from the Stark effects of $J=2\leftarrow1$ transitions. The r_s coordinates of the OH hydrogen atom have been determined and the orientation of the OH bond in the molecule has been discussed.

Acrylaldehyde oxime has four possible geometrical isomers, as shown in Fig. 1, if this molecule is assumed to be planar. A theoretical study[1] has suggested that the most stable conformation of this molecule is a *s-trans E* form. Wolkowski *et al.*[2] has reported that the proton nuclear magnetic resonance spectrum of acrylaldehyde oxime showed only a *s-trans E* form to exist in a liquid state. However, the gas chromatogram and proton nuclear magnetic resonance spectrum of this molecule have indicated that this molecule has two geometrical isomers[3]: One of these isomers has an *E* form and the other one has a *Z* form. Each of these isomers has two possible rotational conformers with respect to the C-C single bond (See Fig. 1). Masuda *et al.*[3] could not conclude whether a (*Z*)-(acrylaldehyde oxime) molecule has a *s-trans Z* form or a *s-cis Z* form, or both, while the proton nuclear magnetic resonance spectrum of an (*E*)-(acrylaldehyde oxime) could be ascribed to a *s-trans E* form.

It is interesting to determine the molecular conformation of acrylaldehyde oxime, particularly of an anti isomer, in gas phase. We have observed the microwave spectra of acrylaldehyde oxime and its deuterated species and discussed its conformation and the orientation of the OH bond in this molecule.



s-trans E form s-trans Z form



s-cis E form s-cis Z form

Fig. 1. Four possible geometrical isomers and the numbering of carbon and hydrogen atoms of acrylaldehyde oxime.

Experimental

Acrylaldehyde oxime was prepared and purified by Tuerck's[4] and Koral'nik's[5] methods. The deuterated species (CH_2=CH-CH=NOD) was prepared in the absorption cell itself as follows: First, the cell was flushed two or three times with D_2O vapour at room temperature. It was then pumped off for about half an hour. At the end of this time the sample of acrylaldehyde oxime was admitted into the cell. No attempt was made to separate the *E* and *Z* species; therefore, all measurements of the microwave spectrum were made with the equilibrium mixture of geometrical isomers in the absorption cell.

The microwave spectrometer used was of a conventional 100 kHz sinusoidal- and square-wave Stark modulation type with a phase sensitive detector. The spectrum was observed at 0—−10 °C or at room temperature, refreshing the sample about every half an hour.

Results and Discussion

Spectral Assignment and Conformation of Acrylaldehyde Oxime. There are four possible geometrical

Table 1. Structural parameters assumed for (*E*)-(acrylaldehyde oxime)

Bond length	r/Å	Bond angle	θ/°
C=C	1.345[a]	H_1-C=C	121.45[a]
C-C	1.470[a]	H_2-C=C	119.97[a]
C_1-H	1.086[a]	C_1=C_2-H	122.83[a]
C_2-H	1.084[a]	C=C-C	119.83[a]
C=N	1.276[b]	C-C=N(*syn*)	115.55[b]
N-O	1.408[b]	C-C=N(*anti*)	121.77[b]
O-H	0.956[b]	H-C=N(*syn*)	121.77[b]
C_3-H(*syn*)	1.085[b]	H-C=N(*anti*)	115.55[b]
C_3-H(*anti*)	1.086[b]	C=N-O	110.20[b]
		N-O-H	102.68[b]

The numbering of carbon and hydrogen atoms is given in Fig. 1.
a) Cherniak and Costain, *J. Chem. Phys.*, **45**, 101 (1966). See Ref. 6). b) Levine, *J. Chem. Phys.*, **38**, 2326 (1963). See Ref. 7).

isomers of acrylaldehyde oxime if this molecule is assumed to be planar. The assumed structural parameters[6,7] (Table 1) of this molecule showed that three geometrical isomers except for a *s-cis Z* conformer were nearly prolate symmetric rotors. Therefore, it was expected that the a-type R-branch transition lines would be relatively intense.

Table 2. Observed transition frequencies (MHz) of acrylaldehyde oxime

Transition	Normal species		D species	
	Obsd	$\Delta\nu^{a)}$	Obsd	$\Delta\nu^{a)}$
2_{02}-1_{01}	9146.59	−0.10	8812.12	0.05
2_{12}-1_{11}	8994.73	−0.13	8670.51	0.23
2_{11}-1_{10}	9299.28	−0.37	8954.74	−0.15
3_{03}-2_{02}	13718.73	0.09	13217.04	0.13
3_{13}-2_{12}	13491.92	−0.02	13004.95	−0.12
3_{12}-2_{11}	13949.08	−0.03	13432.26	0.24
3_{22}-2_{21}	13721.04	0.07	13218.82	−0.10
3_{21}-2_{20}	13722.98	−0.18	13220.51	−0.33
4_{04}-3_{03}	18288.89	−0.05	17620.35	0.05
4_{14}-3_{13}	17988.44	−0.14	17339.51	0.00
4_{13}-3_{12}	18598.21	0.07	17908.84	0.05
4_{23}-3_{22}	18294.25	0.08	17624.77	−0.08
4_{22}-3_{21}	18299.54	−0.10	17629.65	0.02
4_{32}-3_{31}	18296.11*	0.20	17626.15*	−0.20
4_{31}-3_{30}				
5_{05}-4_{04}	22857.03	0.01	22021.77	−0.01
5_{15}-4_{14}	22484.55	−0.11	21673.42	−0.07
5_{14}-4_{13}	23246.70	0.11	22385.07	0.01
5_{24}-4_{23}	22866.75	−0.22	22030.34	−0.10
5_{23}-4_{22}	22877.75	−0.17	22040.17	0.16
5_{33}-4_{31}	22870.76*	0.42	22033.32*	−0.03
5_{32}-4_{31}		0.42		−0.06
5_{42}-4_{41}	22870.16*	0.08		0.23
5_{41}-4_{40}				
6_{06}-5_{05}	27422.38	0.05	26420.87	0.05
6_{16}-5_{15}	26980.16	0.12	26007.12	0.25
6_{15}-5_{14}	27894.30	−0.01	26860.66	−0.05
6_{25}-5_{24}	27439.20	−0.08	26435.80	0.18
6_{24}-5_{23}	27458.55	0.11	26452.28	−0.08
6_{34}-5_{33}	27445.05*	−0.02	26440.71*	0.07
6_{33}-5_{32}		−0.08		0.02
6_{43}-5_{42}	27444.32*	−0.10	26440.12*	0.10
6_{42}-5_{41}				
6_{52}-5_{51}		−0.21		0.06
6_{51}-5_{50}				
7_{07}-6_{06}	31984.31	−0.02	30816.98	−0.02
7_{17}-6_{16}	31474.65	0.09	30339.44	−0.07
7_{16}-6_{15}	32541.15	0.00	31335.46	−0.15
7_{26}-6_{25}	32010.97	−0.05	30840.38	0.08
7_{25}-6_{24}	32041.66	0.01	30867.04	−0.04
7_{35}-6_{34}	32020.20*	0.06	30848.37*	0.13
7_{34}-6_{33}		−0.10		0.00
7_{44}-6_{43}	32018.89*	−0.05	30847.28*	0.15
7_{43}-6_{42}				
7_{53}-6_{52}		0.02		0.28
7_{52}-6_{51}				
7_{62}-6_{61}	32019.40*	0.08		−0.03
7_{61}-6_{60}				

a) Obsd − Calcd. The calculated transition frequencies were obtained from the rotational constants in Table 3.
* Not resolved.

For normal species, the three J=2←1 transitions with K_{-1}=0, 1 were first observed and identified by their characteristic Stark effects. The other a-type R-branch lines of J=3←2 to J=7←6 transitions with K_{-1}=0, 1 were then observed and assigned on the basis of the result from the J=2←1 transitions. The correction terms, Δ_J, Δ_{JK}, of a first-order centrifugal distortion effect has been taken into account in order to explain the transition lines with high K_{-1} value.

For deuterated species, the observation and assignment of the spectrum were made in the same way as for normal species.

The results of the analyses of the spectra for both normal and deuterated species are in Tables 2 and 3. The small inertia defects (ΔI=I_c−I_a−I_b) of −0.069 and −0.052 amu·Å^2 for normal and deuterated species confirm that this molecule is planar. The comparison between the observed rotational constants and the ones calculated from the molecular models (Table 4) has led to the conclusion that the spectrum assigned in this work is ascribed to an (*E*)-(*s-trans*-acrylaldehyde oxime).

r_s *Coordinates of the Hydroxyl Hydrogen Atom.* Since the acrylaldehyde oxime molecule to which the spectrum identified in this work is ascribed has a planar *s-trans E* form, there are two possible orienta-

Table 3. Observed rotational constants of acrylaldehyde oxime

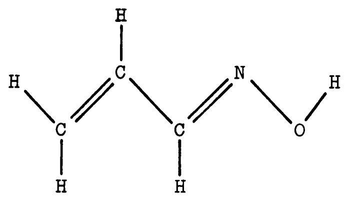
	Normal species	D species
A/MHz	34117±96	33950±103
B/MHz	2363.007±0.011	2274.301±0.010
C/MHz	2210.616±0.011	2131.981±0.011
Δ_J/kHz	0.30±0.09	0.15±0.08
Δ_{JK}/kH$_z$	−5.89±0.25	−4.36±0.78
κ	−0.99045	−0.99105
$\Delta I^{a)}$/amu·Å^2	−0.069	−0.052

a) ΔI=I_c−I_a−I_b.

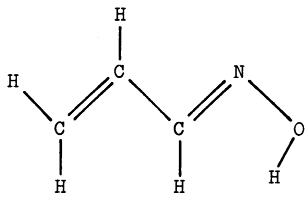
Table 4. Observed and calculated rotational constants (MHz) of acrylaldehyde oxime

Model	A	B	C	κ
Normal species				
s-trans syn				
Model 1*	33902	2390.83	2233.33	−0.99005
Model 2*	31194	2449.22	2270.93	−0.96339
s-cis syn	19130	2989.54	2585.49	−0.95116
s-trans anti	16309	3232.61	2697.87	−0.92143
s-cis anti	9111	6040.54	3632.41	−0.12099
Obsd	34117	2363.007	2210.616	−0.99045
D species				
s-trans syn				
Model 1*	33729	2297.94	2151.37	−0.99072
Model 2*	29335	2407.17	2224.62	−0.98653
Obsd	33950	2274.301	2131.981	−0.99105

* See Fig. 2 and text.



Model 1



Model 2

Fig. 2. Orientation of the OH bond in (*E*)-(acryladehyde oxime).

Table 5. r_s Coordinates of the OH hydrogen atom

Coordinate	Obsd	Calcd	
		Model 1	Model 2
$\|a\|$	2.901±0.005	2.902	1.826
$\|b\|$	0.29±0.06	0.29	1.16

c Coordinate was assumed to be zero.

tions of the hydroxyl group in this molecule: One of the two orientations of OH bond is the trans position with respect to the C=N double bond and another one is the cis position (Fig. 2).

Kraitchman's equation[8] gives the r_s coordinates of the hydroxyl hydrogen atom, using the rotational constants of both the normal and deuterated species in Table 3. The results obtained are given in the second column of Table 5. The third and fourth columns give the coordinates of the hydroxyl hydrogen atom calculated from Models 1 and 2 (Fig. 2). The observed r_s coordinates are in good agreement with the ones calculated from Model 1 in which the OH bond is at the trans position with respect to the C=N double bond. This result is consistent with the orientation of the OH bond in formaldehyde oxime[7] and acetaldehyde oxime.[9,10]

Dipole Moment. The dipole moment of this molecule was determined from measurements of the Stark effects of the $2_{12}\leftarrow 1_{11}$, $2_{02}\leftarrow 1_{01}$, and $2_{11}\leftarrow 1_{10}$ transitions. The electric field in the absorption cell was calibrated by measuring the Stark shifts of the $J=1\leftarrow 0$ and $J=2\leftarrow 1$ transitions of OCS with the dipole moment of 0.715121 D.[11]

Table 6. Stark coefficients (MHz cm^2 V^{-2}) and dipole moment (D) of acrylaldehyde oxime

Transition	$\|M\|$	$(\Delta\nu/E^2)\ 10^6$		
		Obsd	Calcd-1	Calcd-2
2_{12}-1_{11}	1	14.76	14.35	14.32
2_{02}-1_{01}	0	−0.32	−0.32	−0.33
	1	0.26	0.28	0.30
2_{11}-1_{10}	0	0.26	0.24	0.23
	1	−13.62	−14.03	−13.99
$\|\mu_a\|$			0.594±0.009	0.593±0.030
$\|\mu_b\|$			0.7 ±2.9	0.8 ±6.5
$\|\mu_c\|$			0 (assumed)	0.4 ±4.9

The Stark coefficients experimentally determined are given in the third column of Table 6. The fourth column of Table 6 shows the results (Calcd−1) obtained by the least-squares fit, assuming the value of $\mu_c=0$ for this planar molecule. The results given in the fifth column of Table 6 (Calcd −2) were obtained by the least-squares fit, using all three components, μ_a, μ_b, and μ_c, as parameters. Both the Stark coefficients calculated by two assumptions are in good agreement with the ones experimentally obtained (See Table 6). Table 6 shows that the value of μ_a has been determined to be 0.59 D, while the values of μ_b and μ_c are indeterminable because of their large uncertainties.

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