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MICROWAVE SPECTRUM AND DIPOLE MOMENT OF FLUOROALLENE

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The microwave spectrum of $H_2C=C=CHF$ has been studied in the 40 to 45 GHz region and *b*-type *Q*-branch transitions for the ground vibrational state has been assigned. The rotational constants are A=46276.658(10) MHz, B=4300.038(3) MHz, and C=4039.161(3) MHz. The dipole moments are μ_a=1.55(2) D, μ_b=0.835(5) D, and μ_{total}=1.76(2) D. The molecular structure which reproduces the observed moments of inertia is calculated.

The microwave spectrum of fluoroallene has been studied by Ellis et al.[1)] for *a*-type transitions from which the B and C rotational constants were determined. However, the A rotational constant has not been determined. Consequently, no molecular structure has been reported. The dipole-moment components determined using an assumed A rotational constant contains fairly large uncertainties.

In our recent microwave studies, we have reported the structure and dipole moment of trifluoroallene.[2)] The structure was compared with those of other fluorine substituted allenes. To calculate the molecular structure of fluoroallene the rotational constant A was needed. Therefore, we investigated the *b*-type transitions in the microwave spectrum of fluoroallene and determined the A rotational constant. The dipole-moment components of fluoroallene were also recalculated using the newly determined rotational constants.

The sample of fluoroallene was synthesized by the photochemical reaction of carbon suboxide with fluoroethane as described elsewhere.[2,3)] The microwave

Table 1. Rotational transitions (MHz) of fluoroallene in the ground vibrational state

Transition	obsd	obsd-calcd
a-type[a)]		
2,1,2 - 1,1,1	16417.87	0.01
2,1,1 - 1,1,0	16939.58	0.00
3,0,3 - 2,0,2	25012.56	0.00
3,1,3 - 2,1,2	24625.93	-0.01
3,1,2 - 2,1,1	25408.51	0.01
4,1,4 - 3,1,3	32833.02	-0.01
4,1,3 - 3,1,2	33876.37	0.01
10,1,9 -10,1,10	14334.36	0.00
11,1,10-11,1,11	17196.03	0.00
12,1,11-12,1,12	20315.06	0.00
13,1,12-13,1,13	23690.28	0.00
b-type		
1,1,0 - 1,0,1	42237.70	0.01
2,1,1 - 2,0,2	42500.13	0.00
3,1,2 - 3,0,3	42896.05	-0.02
4,1,3 - 4,0,4	43428.19	0.01
5,1,4 - 5,0,5	44100.03	0.00
6,1,5 - 6,0,6	44916.09	0.00

a) Reference 1.

Table 2. Rotational and centrifugal distortion constants of fluoroallene

A = 46276.658 (10) MHz
B = 4300.038 (3) MHz
C = 4039.161 (3) MHz

Δ_J = 0.00168 (10) MHz
Δ_{JK} = -0.0940 (4) MHz
δ_J = 0.0003237 (9) MHz

Standard deviations in parentheses.

Table 3. Stark coefficients and dipole moment of fluoroallene

Transition	M	$\Delta\nu/E^2$ MHz$(\mathrm{kV\cdot cm^{-1}})^{-2}$ observed$^{a)}$	calculated$^{b)}$
$4_{14} - 3_{13}$	1	-20.88	-20.833
	2	-10.46	-10.704
	3	5.93	6.177
$4_{13} - 3_{12}$	1	-2.52	-2.385
	2	-8.66	-8.319

μ_a = 1.55 (2) D
μ_b = 0.835 (5) D
μ_c = 0 (by symmetry)
μ_{total} = 1.76 (2) D

a) Reference 1.
b) Calculated from the dipole-moment components given in this table.

Table 4. Molecular structure of fluoroallene

r(C_1=C_2)	1.307 Å
r(C_2=C_3)	1.308 Å
r(C -F)	1.343 Å
r(C -H)	1.086 Å
<C-C-F	122.78°
<C-C_1-H	122.5 °
<C-C_3-H	123.2 °

spectrometer used was of a conventional Stark modulation type. The microwave radiation from a BWO was phase locked to a synthesizer and was controlled by a microcomputer. Measurements were made at the temperature of dry-ice and the frequency accuracy was estimated to be better than 0.05 MHz.

In order to assign *b*-type transitions, the *A* rotational constant was estimated by using the relation $I_c-I_a-I_b=-m_H r^2_{H...H}$ with the I_b and I_c in fluoroallene[1)] and the $r_{H...H}$ in 1,1-difluoroallene.[4)] The predicted value of *A* was 46766 MHz. The *b*-type transitions were easily assigned by this value as shown in Table 1. The rotational constants and centrifugal distortion constants determined by a least-squares fitting of the observed *a*- and *b*-type transition frequencies are listed in Table 2. The determined *A* rotational constant 46276.658 MHz is much larger than that estimated by Ellis et al.[1)]

The dipole-moment components were recalculated using the rotational constants in Table 2 and are given in Table 3. The μ_b and μ_{total} are quite different from those of Ellis et al.[1)] This is caused by the errors in the Stark coefficients for the 4_{14}-3_{13} transition which are very sensitive to the *A* rotational constant due to the near accidental degeneracy, 857.03 MHz, between 4_{14} and 5_{05} levels.

In order to calculate the molecular structure it is assumed that the bond lengths and bond angles in fluoroallene are changed systematically from those in 1,1-difluoroallene[4)] by the substitution of a fluorine atom with a hydrogen atom, and that all r_{C-H} distances are 1.086 Å. The relation $I_c-I_a-I_b=-m_H r^2_{H...H}$ gives the $r_{H...H}$ distance as 1.8177 Å, which may be compared with 1.7865 Å in 1,1-difluoroallene.[4)] This large difference is probably largely due to change in inertial defect Δ on substitution. The structural parameters in Table 4 are calculated so as to give the observed moments of inertia under above considerations.

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