

# MICROWAVE SPECTRUM, CONFORMATION, INTRAMOLECULAR HYDROGEN BOND, DIPOLE MOMENT, $^{14}\text{N}$ QUADRUPOLE COUPLING CONSTANTS AND CENTRIFUGAL DISTORTION OF 2-FLUOROACETAMIDE

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(Received 5 October 1973)

## ABSTRACT

Microwave spectra of  $\text{CH}_2\text{FCONH}_2$ ,  $\text{CH}_2\text{FCOND}(1)\text{H}(2)$ ,  $\text{CH}_2\text{FCONH}(1)\text{D}(2)$ , and  $\text{CH}_2\text{FCOND}_2$  are reported. The stable form of the molecule is shown to possess a planar FCCONH<sub>2</sub> skeleton with two out-of-plane hydrogens. The C-F and C=O bonds are trans to one another and a weak intramolecular hydrogen bond is formed between the fluorine atom and the nearest amide group hydrogen atom stabilizing the identified rotamer. Other conformations are not present in concentrations exceeding 10 % of the total. Nine vibrationally excited states were assigned. Six of these were attributed to the C-C torsional mode and one to the lowest in-plane bending mode. The first excited state of -NH<sub>2</sub> out-of-plane deformation mode was tentatively assigned. Relative intensity measurements yielded  $114 \pm 14 \text{ cm}^{-1}$  for C-C torsional mode and  $239 \pm 20 \text{ cm}^{-1}$  for the in-plane bending mode. The dipole moment was determined as  $\mu_a = 1.27 \pm 0.01 \text{ D}$ ,  $\mu_b = 1.67 \pm 0.02 \text{ D}$ , and  $\mu_{\text{tot}} = 2.10 \pm 0.02 \text{ D}$ , while the  $^{14}\text{N}$  quadrupole coupling constants were found to be  $\chi_{aa} = 1.6 \pm 0.2 \text{ MHz}$ ,  $\chi_{bb} = 1.6 \pm 0.2 \text{ MHz}$  and  $\chi_{cc} = -3.2 \pm 0.3 \text{ MHz}$ .

## INTRODUCTION

Several conformations are possible for molecules possessing a CH<sub>2</sub>F group attached to a carbonyl group. Fig. 1 illustrates four typical rotameric forms of 2-fluoroacetamide ( $\text{CH}_2\text{FCONH}_2$ ) interchangeable by rotation about the C-C bond. In conformer I the C-F and C=O bonds are cis and eclipsed. This arrangement is the preferred one in free monofluoroacetic acid [1] and in fluoroacetyl fluoride [2]. Rotamers analogous to IV where the C-F and C=O bonds are trans

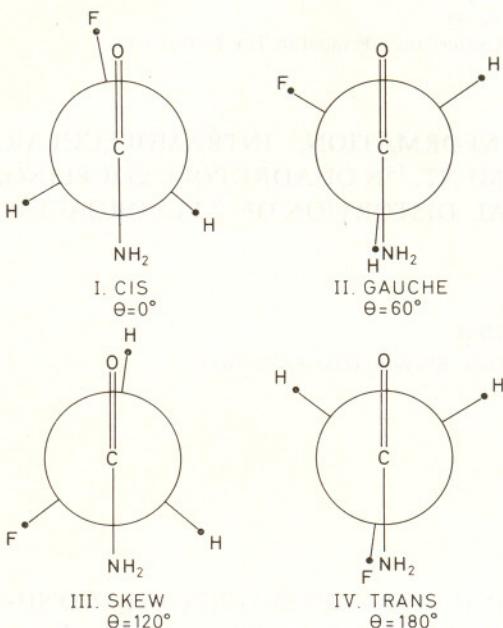


Fig. 1. Four possible conformations of  $\text{CH}_2\text{FCONH}_2$  viewed along the C-C bond. Conformation IV differs from the other three in that an intramolecular hydrogen bond may be formed between the fluorine atom and the nearest amide group hydrogen atom. This kind of interaction is not possible in the other three cases.

with respect to the C-C bond have also been found in the two latter compounds as their less stable forms. Moreover, the preferred conformation of monofluoracetone [3] is the trans. An X-ray structure determination of  $\text{CH}_2\text{FCONH}_2$  by Hughes and Small [4] showed that form IV is present in the crystalline state. Krueger and Smith [5] utilizing infrared spectroscopy found that a similar situation is present in dilute solutions of carbon tetrachloride. No evidence was found for the stable coexistence of more than the trans rotamer [5]. The stability [5] of this conformation was attributed to the formation of an intramolecular hydrogen bond formed between the fluorine atom and the nearest amide group hydrogen atom.

In addition to the conformational behaviour of 2-fluoroacetamide, the planarity of the amide group is currently being debated. Microwave spectroscopy is well suited for the study of this problem, because of the high resolution obtainable. The early microwave investigation of the simplest amide, formamide [6] concluded that this molecule is planar. This was later revised, and the compound was thought to have the two  $\text{NH}_2$  hydrogens slightly out-of-plane [7]. Renewed extensive investigations by Hirota et al. [8] have shown that the equilibrium conformation of formamide is planar or very nearly so. Very recently Steinmetz [9] reported the microwave spectrum of formimide which is also planar.

The present work was undertaken mainly to study the importance of intramolecular hydrogen bonding for the conformational preferences of 2-fluoroacetamide and, moreover, to investigate the amide group planarity problem. It was found that the hydrogen-bonded conformation IV mainly, if not exclusively, exists in the free state. Evidence is presented to show that the amide group of the molecule is planar or very nearly planar.

## EXPERIMENTAL

2-Fluoroacetamide *purum* was purchased from Fluka AG, Buchs, Switzerland and used without further purification.  $\text{CH}_2\text{FCOND}(1)\text{H}(2)$ ,  $\text{CH}_2\text{FCONH}(1)\text{D}(2)$ , (see Fig. 2 for notation) and  $\text{CH}_2\text{FCOND}_2$  were produced by direct

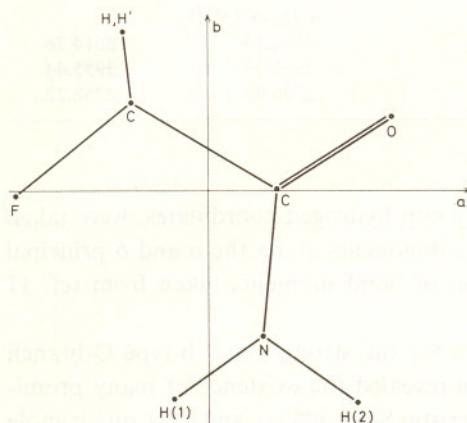


Fig. 2. Projection of stable conformation of 2-fluoroacetamide in the  $a-b$  principal axes plane.

exchange with 99 %  $\text{D}_2\text{O}$  in the cell. Measurements were made at room temperature employing a conventional Stark spectrometer described briefly in ref. 10. This apparatus has no facilities for phase-locking the klystrons. Yet, resolution of better than 0.5 MHz was achieved under favourable conditions. Almost the complete 11.9–29.9 GHz spectral region was searched extensively using recorder presentation of the spectra.

## MICROWAVE SPECTRUM AND ASSIGNMENT OF THE GROUND VIBRATIONAL STATE

Based on the X-ray [4] and infrared findings [5], the trans rotamer depicted in Fig. 2 was expected to be present in the spectrum. Preliminary rotational constants of this form were calculated from the structural parameters of Table 1,

TABLE I

PLAUSIBLE STRUCTURAL PARAMETERS<sup>a</sup> AND OBSERVED AND PREDICTED ROTATIONAL CONSTANTS  
2-FLUOROACETAMIDE

C-O	1.254 Å	∠NCO	124.0°	N-H(1)	1.03 Å	∠H(1)NH(2)	110
C-F	1.406 Å	∠NCC	118.7°	N-H(2)	1.00 Å	∠CCH	109
C-N	1.319 Å	∠CCF	110.0°	C-H	1.093 Å	∠HCH	109
C-C	1.533 Å	∠H(1)NC	124.5°				
<i>Rotational constants (MHz)</i>							
	<i>Observed</i>		<i>Calculated</i>		<i>Observed</i>		<i>Calculated</i>
	CH <sub>2</sub> FCONH <sub>2</sub>				CH <sub>2</sub> FCOND(1)H(2)		
<i>A</i> <sub>0</sub>	9884.358		9754.775		9329.76		9153.58
<i>B</i> <sub>0</sub>	4059.671		4019.236		4055.98		4016.35
<i>C</i> <sub>0</sub>	2932.474		2898.831		2879.88		2841.89
	CH <sub>2</sub> FCONH(1)D(2)				CH <sub>2</sub> FCOND <sub>2</sub>		
<i>A</i> <sub>0</sub>	9293.07		9136.15		8804.18		8614.26
<i>B</i> <sub>0</sub>	3994.87		3957.40		3992.53		3955.44
<i>C</i> <sub>0</sub>	2845.52		2810.60		2796.93		2758.22

<sup>a</sup> Not a derived structure. See text.

which, with the exception of the CH<sub>2</sub>F-group hydrogen coordinates, were taken from ref. 4. The dipole moment and its components along the *a* and *b* principal axes were predicted by vectorial addition of bond moments taken from ref. 1 to be about 0.9 and 1.7 D, respectively.

Search was therefore initially made for the strong low *J* b-type Q-branch transitions. A fairly rich, intense spectrum revealed the existence of many prominent Q-branch transitions. Their characteristic Stark effects and <sup>14</sup>N quadrupole fine structure led to their assignments and the determination of *A*-*C* and *k*. The low *J*, low *K*<sub>-1</sub> a-type transitions were then assigned on the basis of their Stark effects, positions in the spectrum, intensities, and rigid rotor fit. The rotation constants obtained in this manner were used to predict additional low and medium *J* lines, which were subsequently measured, corrected for quadrupole fine structure when necessary and fitted to Watson's first order centrifugal distortion formula:

$$W = W_0 - d_J J^2 (J+1)^2 - d_{JK} J(J+1) \langle P_z^2 \rangle - d_K \langle P_z^4 \rangle - d_{WJ} W_0 J(J+1) - d_{WK} W_0 \langle P_z^2 \rangle \quad (1)$$

utilizing a computer programme [10] based on the perturbation form of eqn. (1).

The improved rotational and centrifugal distortion constants thus obtained were used to predict further high *J* transitions. The assignments of these medium to low intensity lines were made on the basis of their intensities, fit to eqn. (1) and their most useful Stark effects. For the high *J* a-type Q-branch transitions a slow Stark effect towards higher frequencies was observed. The high *J* P- and

TABLE 2

SELECTED TRANSITIONS FOR THE GROUND VIBRATIONAL STATE OF  $\text{CH}_2\text{FCONH}_2$ 

Transition	Observed frequency <sup>a</sup> (MHz)	Obs.-calc. frequency (MHz)	Centrifugal dist. correction (MHz)
<b>a-type</b>			
$1_{0,1} \rightarrow 2_{0,2}$	13835.99	0.03	— 0.02
$1_{1,0} \rightarrow 2_{1,1}$	15111.40	-0.03	— 0.05
$2_{0,2} \rightarrow 3_{0,3}$	20399.46	0.03	— 0.05
$2_{1,2} \rightarrow 3_{1,3}$	19198.27	-0.01	— 0.05
$2_{2,1} \rightarrow 3_{2,2}$	20976.29	0.02	— 0.16
$3_{3,1} \rightarrow 4_{3,2}$	28231.38	0.05	— 0.46
$10_{3,8} \rightarrow 10_{3,7}$	12976.53	0.04	— 2.46
$17_{5,13} \rightarrow 17_{5,12}$	16458.77	0.03	— 11.07
$28_{8,21} \rightarrow 28_{8,20}$	22444.91	-0.04	— 52.24
$48_{14,31} \rightarrow 48_{14,34}$	13571.94	0.06	— 161.65
<b>b-type</b>			
$0_{0,0} \rightarrow 1_{1,1}$	12816.76	-0.06	— 0.01
$1_{0,1} \rightarrow 2_{1,2}$	18681.73	-0.03	— 0.02
$2_{1,1} \rightarrow 2_{2,0}$	17622.27	-0.01	— 0.09
$2_{1,2} \rightarrow 2_{2,1}$	20855.49	-0.03	— 0.13
$2_{1,2} \rightarrow 3_{0,3}$	15553.57	-0.07	— 0.05
$3_{1,2} \rightarrow 3_{2,1}$	16607.99	-0.02	— 0.15
$3_{0,3} \rightarrow 4_{1,4}$	29095.50	-0.01	— 0.12
$4_{0,4} \rightarrow 4_{1,3}$	13663.93	0.03	— 0.27
$4_{1,3} \rightarrow 4_{2,2}$	15923.77	0.08	— 0.24
$5_{1,4} \rightarrow 5_{2,3}$	15965.90	-0.01	— 0.39
$5_{2,3} \rightarrow 5_{3,2}$	28983.37	-0.05	— 0.61
$6_{3,4} \rightarrow 7_{2,5}$	26358.26	0.03	— 0.80
$8_{1,7} \rightarrow 8_{2,6}$	23104.13	0.06	— 1.71
$9_{2,7} \rightarrow 9_{3,6}$	24101.10	-0.05	— 1.74
$11_{2,9} \rightarrow 11_{3,8}$	27921.47	0.07	— 3.78
$21_{12,9} \rightarrow 22_{11,12}$	11927.54	0.08	5.89
$21_{12,10} \rightarrow 22_{11,11}$	11927.54	-0.15	5.89
$25_{15,10} \rightarrow 24_{16,9}$	19039.08	0.09	— 23.84
$25_{15,11} \rightarrow 24_{16,8}$	19039.08	0.09	— 23.84
$30_{17,13} \rightarrow 31_{16,16}$	12744.02	-0.05	19.40
$30_{17,14} \rightarrow 31_{16,15}$	12744.02	-0.05	19.40
$31_{18,13} \rightarrow 30_{19,12}$	14073.14	-0.01	— 38.29
$31_{18,14} \rightarrow 30_{19,11}$	14073.14	-0.01	— 38.29
$40_{22,18} \rightarrow 41_{21,21}$	21227.52	-0.03	40.02
$40_{22,19} \rightarrow 41_{21,20}$	21227.52	-0.03	40.02
$41_{24,18} \rightarrow 40_{25,15}$	19018.54	0.04	— 89.32
$41_{24,17} \rightarrow 40_{25,16}$	19018.54	0.04	— 89.32
$50_{27,23} \rightarrow 51_{26,26}$	29734.15	-0.07	71.33
$50_{27,24} \rightarrow 51_{26,25}$	29734.15	-0.07	71.33
$53_{31,22} \rightarrow 52_{32,21}$	22255.06	0.03	— 188.24
$53_{31,23} \rightarrow 52_{32,20}$	22255.06	0.03	— 188.24

<sup>a</sup>  $\pm 0.10$  MHz.

Transitions are corrected for quadrupole effects.

TABLE 3

MOLECULAR CONSTANTS FOR  $\text{CH}_2\text{FCONH}_2$  IN THE GROUND AND SEVERAL VIBRATIONALLY EXCITED STATE

Vibrational state:	Ground	First ex. C-C tors.	Second ex. C-C tors.	Third ex. C-C
Number of transitions	133	75	31	18
$\sigma$ (MHz)	0.055	0.071	0.149	0.138
$A_v$ (MHz)	$9884.358 \pm 0.004$	$9839.787 \pm 0.007$	$9795.62 \pm 0.04$	$9752.10 \pm 0.07$
$B_v$ (MHz)	$4059.671 \pm 0.002$	$4056.206 \pm 0.003$	$4052.86 \pm 0.02$	$4049.69 \pm 0.04$
$C_v$ (MHz)	$2932.474 \pm 0.001$	$2938.174 \pm 0.002$	$2943.81 \pm 0.02$	$2949.29 \pm 0.04$
$I_a$ ( $\mu\text{\AA}^2$ )	$51.12889 \pm 0.00002$	$51.36046 \pm 0.00004$	$51.5920 \pm 0.0002$	$51.8223 \pm 0.00$
$I_b$ ( $\mu\text{\AA}^2$ )	$124.48694 \pm 0.00006$	$124.59328 \pm 0.00009$	$124.5732 \pm 0.0006$	$124.7937 \pm 0.00$
$I_c$ ( $\mu\text{\AA}^2$ )	$172.33776 \pm 0.00006$	$172.00343 \pm 0.00011$	$171.6741 \pm 0.0011$	$171.3551 \pm 0.00$
$d_J$ (kHz)	$-2.06 \pm 0.05$	$-2.38 \pm 0.11$	$-0.16 \pm 1.25$	$6.1 \pm 3.4$
$d_{JK}$ (kHz)	$-31.2 \pm 1.3$	$-28.8 \pm 2.2$	$-63.4 \pm 26.7$	$-305.8 \pm 66.1$
$d_K$ (kHz)	$-50.7 \pm 2.4$	$-46.3 \pm 4.2$	$-120.0 \pm 44.3$	$-533.5 \pm 111.$
$d_{WJ} \times 10^7$	$8.01 \pm 0.14$	$9.09 \pm 0.30$	$2.9 \pm 3.3$	$-19.7 \pm 8.2$
$d_{WK} \times 10^6$	$8.41 \pm 0.38$	$7.73 \pm 0.66$	$18.4 \pm 7.7$	$88.5 \pm 19.2$
$I_a + I_b - I_c$ ( $\mu\text{\AA}^2$ )	$3.27807 \pm 0.00009$	$3.95031 \pm 0.00015$	$4.4911 \pm 0.0013$	$5.2609 \pm 0.00$

Conversion factor 505376 MHz  $\mu\text{\AA}^2$ .

The uncertainties represent one standard deviation.

 $\sigma$  is the standard deviation of the fit.

R-branch lines exhibit a fast Stark effect due to the near degeneracy of the high  $K_{-1}$  energy levels connected by the a-axis components of the dipole moment. A total of 133 transitions were assigned with a maximum  $J$  value of 53. Table 2 lists 41 selected transitions. The comprehensive list of frequencies for the ground vibrational state as well as for several excited states and the deuterated species available from the authors upon request or from the Microwave Data Center, National Bureau of Standards, Washington, D.C., U.S.A., where it has been deposited.

TABLE 4

CORRELATION MATRIX FOR THE ROTATIONAL AND CENTRIFUGAL DISTORTION CONSTANTS OF THE GROUND VIBRATIONAL STATE OF  $\text{CH}_2\text{FCONH}_2$ 

$A$	$B$	$C$	$d_J$	$d_{JK}$	$d_K$	$d_{WJ}$	$d_{WK}$
1.000							
0.962	1.000						
0.890	0.760	1.000					
-0.073	-0.016	-0.141	1.000				
-0.019	-0.148	0.182	-0.938	1.000			
-0.020	-0.149	0.182	-0.937	1.000	1.000		
0.117	0.095	0.121	-0.987	0.868	0.868	1.000	
0.020	0.149	-0.182	0.937	-1.000	-1.000	-0.867	1.000

TABLE 3 (continued)

<i>Fourth ex. C-C tors.</i>	<i>Fifth ex. C-C tors.</i>	<i>Sixth ex. C-C tors.</i>	<i>First ex. in-plane bend</i>	<i>First ex. in-plane bend + first ex. C-C tors.</i>
13 0.129	8 0.411	7 0.497	15 0.109	5 0.655
9709.14±0.11	9666.18±0.08	9624.44±0.10	9891.93±0.07	9847.3±0.3
4046.61±0.07	4043.57±0.05	4040.69±0.07	4054.75±0.04	4051.0±0.1
2954.93±0.06	2960.42±0.05	2965.92±0.07	2922.70±0.04	2928.9±0.1
52.0516±0.0006	52.2829±0.0004	52.5097±0.0005	51.0897±0.0004	51.321±0.002
124.889±0.002	124.983±0.002	125.072±0.002	124.6380±0.0012	124.753±0.003
171.028±0.003	170.711±0.003	170.394±0.004	172.9141±0.0022	172.548±0.006
-3.1±5.4			5.0±2.3	
20.2±85.3			-168.5±35.3	
-9.4±143.8			-294.4±55.2	
4.3±13.6			-59.1±46.7	
-3.2±25.1			48.5±10.1	
5.913±0.004	6.555±0.004	7.188±0.005	2.8136±0.0025	3.526±0.007

Table 3 gives the result obtained from this analysis. Despite the large number of lines comprising a-type, b-type, P-, Q-, and R-branch transitions used in the least squares procedure, several correlation matrix elements for the centrifugal distortion constants are close to the absolute value of 1 as shown in Table 4. As noted before [12], this seems to be an inherent difficulty with this procedure.

As indicated in Table 3,  $I_a + I_b - I_c = 3.27807 \pm 0.00009 \text{ u}\text{\AA}^2$  which is very close to its counterparts in trans and cis monofluoroacetic acid [1] where the values  $3.2195 \text{ u}\text{\AA}^2$  and  $3.2326 \text{ u}\text{\AA}^2$ , respectively, have been determined. The latter conformers were each proved to possess symmetry planes and two out-of-plane hydrogens.

#### VIBRATIONAL SATELLITE SPECTRA

The ground vibrational state lines were accompanied by a rich satellite spectrum. The strongest of these absorption lines were about 60 % as intense as the corresponding ground state transitions. They are assigned to the first excited state of the C-C torsional mode because  $I_a + I_b - I_c$  increases upon excitation [13] as shown in Table 3. The satellites attributed to its overtone states lie in a series of steadily decreasing intensity. Six excited states of this fundamental mode were assigned. As shown in Table 3 and illustrated in Fig. 3, the variation of the rotational constants and  $I_a + I_b - I_c$  upon excitation is close to linear. This is expected for a very nearly harmonic mode [13].

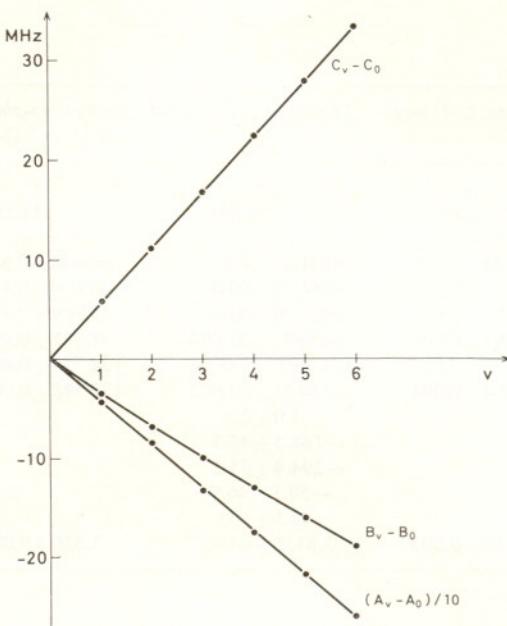


Fig. 3. Variation of the rotational constants upon excitation of the C-C torsional mode.

Another satellite spectrum having about 30 % of the intensity of the ground state is attributed to a low frequency in-plane bending mode because  $I_a + I_b -$  decreases upon excitation [13] as shown in Table 3. The rotational constants of combination mode of the above two fundamental frequencies were also determined (Table 3).

Six Q-branch transitions of about 15 % intensity of the corresponding ground state lines were assigned and  $A - C = 6917.09$  MHz and  $\kappa = -0.6743$  determined. Based on their positions in the spectrum relative to the corresponding ground state lines, this mode is presumably an out-of-plane fundamental which was tentatively assigned as the first excited state of the  $-\text{NH}_2$  group out-of-plane deformation mode. Crude relative intensity measurements suggest that this mode is about  $400 \text{ cm}^{-1}$  above the ground state.

The spectroscopic constants of the excited states appearing in Table 3 were derived by application of Watson's formula (1) in a manner analogous to that described for the ground state when a sufficient number of transitions were available. In the other cases, a rigid rotor fit was performed making no allowance for centrifugal distortion effects. As seen in that table, well determined centrifugal distortion coefficients could only be obtained for the first excited state of the C-C torsional mode, whereas their orders of magnitude were found for other vibrationally excited states.

A total of more than 300 transitions were definitely assigned for the mai-

species. This includes all strong lines present in the spectrum. The great majority of the medium intensity and weak lines were also accounted for. This extensive analysis makes two conclusions possible. Firstly, there is largely one rotameric form of 2-fluoroacetamide, viz. the trans. It is ruled out that further rotamers exist in concentrations exceeding 10 % of the total, because bond moment calculations strongly indicate that additional forms should have sizable dipole moments making their presence readily detectable if this percentage were exceeded.

The Fig. 2 conformer is thus at least 1.0 kcal mole<sup>-1</sup> more stable than any other form of the molecule. Furthermore, the harmonic behaviour of C-C torsional mode through its sixth excited vibrational state is indicative of a deep potential well. Any maximum of the rotational barrier for the torsion about the C-C bond must appear several kcal mole<sup>-1</sup> above the minimum.

The second conclusion possible from the analysis of the vibrationally excited states concerns the amide group planarity problem. If the -NH<sub>2</sub> group out-of-plane deformation mode were governed by a strongly anharmonic double minimum potential, the spectrum normally observed consists of the ground state transitions accompanied by a set of excited state lines of comparable intensities [14, 15]. If observable, the intensities of the transitions of the next two excited states should be greatly reduced compared to those in the first two states. This feature was clearly not present in the spectrum. As discussed above, the only possibility for the first excited state of the deformation mode appears to be about 400 cm<sup>-1</sup> above the ground vibrational state. Thus, the vibrational satellite spectrum strongly tends to refute the existence of any typical anharmonic double minimum potential for the -NH<sub>2</sub> group deformation mode.

TABLE 5

RELATIVE INTENSITIES<sup>a</sup> AND ENERGY DIFFERENCES OF VIBRATIONALLY EXCITED STATES OF 2-FLUOROACETAMIDE

<i>Transition</i>	<i>Relative intensity</i>	<i>Energy difference</i>
C-C tors./ground state		
4 <sub>2,3</sub> → 5 <sub>1,4</sub>	0.58	
8 <sub>1,7</sub> → 8 <sub>2,6</sub>	0.54	
8 <sub>2,6</sub> → 8 <sub>3,5</sub>	0.60	
9 <sub>2,7</sub> → 9 <sub>3,6</sub>	0.65	
10 <sub>2,8</sub> → 10 <sub>3,7</sub>	0.54	
	Av. 0.58 ± 0.04	114 ± 14 cm <sup>-1</sup>
In-plane bend./ground state		
8 <sub>1,7</sub> → 8 <sub>2,6</sub>	0.36	
8 <sub>2,6</sub> → 8 <sub>3,5</sub>	0.31	
9 <sub>2,7</sub> → 9 <sub>3,6</sub>	0.30	
	Av. 0.32 ± 0.03	239 ± 20 cm <sup>-1</sup>

The uncertainties represent one standard deviation.

<sup>a</sup> T = 301 K.

Relative intensity measurements on the first excited states of the C torsional and the in-plane bending modes were performed. Most, but not all the precautions of ref. 16 were observed. The results are presented in Table 3. The energy difference between states were derived by assuming that relative intensity is proportional to the Boltzman factor. The torsional frequency was determined to be  $114 \pm 14 \text{ cm}^{-1}$  and the in-plane bending mode was  $239 \pm 15 \text{ cm}^{-1}$ . The torsional frequency may be approximated [13] from  $\omega(\text{cm}^{-1}) = 67.5 \Delta$ , where  $\Delta = I_a^1 + I_b^1 - I_c^1 - (I_a^0 + I_b^0 - I_c^0)$ . Substituting  $\Delta = 0.672 \text{ u}\text{\AA}^2$  taken from Table 3,  $\omega = 100 \text{ cm}^{-1}$  is calculated which compares well to  $114 \pm 10 \text{ cm}^{-1}$  obtained by the relative intensity method.

#### DEUTERATED SPECIES AND MOLECULAR STRUCTURE

The spectra of  $\text{CH}_2\text{FCOND}(1)\text{H}(2)$ ,  $\text{CH}_2\text{FCONH}(1)\text{D}(2)$ , and  $\text{CH}_2\text{FCOND}_2$  were measured in order to obtain additional information about the structural and conformational properties of the amide. The spectra were assigned in a straight forward manner and the evaluated spectroscopic constants are listed in Table 6. The values derived for  $I_a + I_b - I_c$  in the three cases are very close to the main species counterpart. This is strong evidence for the presence of a plane of symmetry and two out-of-plane hydrogens which must belong to the  $\text{CH}_2\text{F}$  part of the molecule.

TABLE 6

MOLECULAR CONSTANTS FOR THE GROUND VIBRATIONAL STATE OF DEUTERATED SPECIES OF 2-FLUOROACETIC ACID

<i>Isotopic species</i>	<i>CH<sub>2</sub>FCOND(1)H(2)</i>	<i>CH<sub>2</sub>FCONH(1)D(2)</i>	<i>CH<sub>2</sub>FCOND<sub>2</sub></i>
Number of transitions	24	24	24
$\sigma$ (MHz)	0.088	0.115	0.115
$A_0$ (MHz)	$9329.76 \pm 0.03$	$9293.07 \pm 0.04$	$8804.18$
$B_0$ (MHz)	$4055.98 \pm 0.03$	$3994.87 \pm 0.02$	$3992.53$
$C_0$ (MHz)	$2879.88 \pm 0.03$	$2845.52 \pm 0.02$	$2796.93$
$I_a$ ( $\text{u}\text{\AA}^2$ )	$54.1682 \pm 0.0002$	$54.3820 \pm 0.0002$	$57.4018$
$I_b$ ( $\text{u}\text{\AA}^2$ )	$124.6002 \pm 0.0009$	$126.5062 \pm 0.0006$	$126.5804$
$I_c$ ( $\text{u}\text{\AA}^2$ )	$175.4851 \pm 0.0017$	$177.6041 \pm 0.0011$	$180.6895$
$d_J$ (kHz)	$-2.4 \pm 1.1$	$-1.0 \pm 1.0$	$-1.2$
$d_{JK}$ (kHz)	$-45.5 \pm 11.8$	$-54.4 \pm 19.1$	$-57.4$
$d_K$ (kHz)	$-82.5 \pm 17.9$	$-96.1 \pm 28.6$	$-48.5$
$d_{WJ} \times 10^7$	$6.9 \pm 1.9$	$7.0 \pm 2.9$	$5.8$
$d_{WK} \times 10^6$	$13.3 \pm 3.4$	$15.7 \pm 5.6$	$15.7$
$I_a + I_b - I_c$ ( $\text{u}\text{\AA}^2$ )	$3.2833 \pm 0.0019$	$3.2841 \pm 0.0013$	$3.2927$

Conversion factor  $505376 \text{ MHz u}\text{\AA}^2$ .

The uncertainties represent one standard deviation.

 $\sigma$  is the standard deviation of the fit.

TABLE 7

SUBSTITUTION COORDINATES FOR 2-FLUOROACETAMIDE

Atom	Principal axes		
	$ a $ ( $\text{\AA}$ )	$ b $ ( $\text{\AA}$ )	$ c $ ( $\text{\AA}$ )
H(1)	$0.3268 \pm 0.0002$	$1.7497 \pm 0.0002$	$0.0546 \pm 0.0119$
H(2)	$1.3928 \pm 0.0001$	$1.8335 \pm 0.0002$	$0.0568 \pm 0.0100$

 $\text{CH}_2\text{FCONH}_2$  is the parent molecule.

The uncertainties represent one standard deviation calculated from the standard deviations of the rotational constants.

Kraitchman's coordinates [17] of the amide group hydrogens may be calculated from the rotational constants of Tables 3 and 6. Any of the four isotopic species studied can be employed as the parent molecule. Table 7 shows the result obtained with  $\text{CH}_2\text{FCONH}_2$  as the basis molecule. As expected, the  $c$ -axis coordinates are very small and not significantly different from zero. This, of course, supports the idea of the presence of a plane of symmetry.

Assuming appropriate signs for the principal axes coordinates of Table 7 and putting  $c = 0.0$ , the non-bonded  $\text{H} \cdots \text{H}$  distance of the  $-\text{NH}_2$  group was calculated to be  $1.7216 \pm 0.0002$   $\text{\AA}$ . The corresponding distance in formamide [7] is 1.735  $\text{\AA}$ , and the X-ray value of 2-fluoroacetamide [4] is 1.668  $\text{\AA}$ .

The rotational constants of the main and the three deuterated species furnish insufficient information for a detailed structure determination. However, the structure of Table 1 reproduces the rotational constants and the principal axis coordinates of Table 7 reasonably well. This, perhaps, indicates that there is no great difference between the solid state and the free molecule geometry.

## DIPOLE MOMENT

Stark coefficients of the  $6_{1,5} \rightarrow 6_{2,4}$  and  $6_{2,4} \rightarrow 6_{3,3}$  transitions were used to determine the dipole moment. A d.c. voltage was applied between the Stark septum and the cell with the modulating square wave voltage superimposed. The d.c. voltage was measured with a digital voltmeter having an accuracy of 0.025 %. The electric field was calibrated using the OCS  $1 \rightarrow 2$  transition with  $\mu_{\text{OCS}} = 0.71521$  D (ref. 18). A least squares fit using a diagonal weight matrix was performed. The weights were chosen as the inverse squares of the experimentally determined standard deviations of the coefficients appearing in Table 8. From the fit,  $\mu_a = 1.267 \pm 0.006$  D,  $\mu_b = 1.67 \pm 0.01$  D, and  $\mu_{\text{tot}} = 2.10 \pm 0.01$  D were determined. However, taking possible systematic errors into account, the latter standard deviations are probably too small, possibly by a factor of 2. As the final result  $\mu_a = 1.27 \pm 0.01$  D,  $\mu_b = 1.67 \pm 0.02$  D, and  $\mu_{\text{tot}} = 2.10 \pm 0.02$  D are given.

The uncertainties quoted represent one standard deviation. The total dip moment determined in a benzene solution [19] was  $2.64 \pm 0.04$  D.

TABLE 8

STARK COEFFICIENTS AND DIPOLE MOMENT OF 2-FLUOROACETAMIDE

Transition	$ M $	$ \Delta\nu/E^2 $	$(MHz/(V/cm)^2 \times 10^5)$	$Obs.$	$Calc.$
		$(MHz/(V/cm)^2 \times 10^5)$			
$6_{1,5} \rightarrow 6_{2,4}$	$ M  = 4$	0.858 $\pm$ 0.008	0.862		
	$ M  = 5$	1.38 $\pm$ 0.01	1.37		
	$ M  = 6$	2.00 $\pm$ 0.01	2.00		
$6_{2,4} \rightarrow 6_{3,3}$	$ M  = 4$	2.46 $\pm$ 0.02	2.40		
	$ M  = 5$	4.26 $\pm$ 0.03	4.26		
	$ M  = 6$	6.28 $\pm$ 0.06	6.53		
	$\mu_a =$	1.27 $\pm$ 0.01 D			
	$\mu_b =$	1.67 $\pm$ 0.02 D			
	$\mu_{tot} =$	2.10 $\pm$ 0.02 D			

The uncertainties represent one standard deviation.

TABLE 9

14N NUCLEAR QUADRUPOLE SPLITTINGS OF 2-FLUOROACETAMIDE MICROWAVE LINES USED TO DETERMINE THE QUADRUPOLE COUPLING CONSTANTS

Transition	$F \rightarrow F'$	Frequency (MHz)		
		$Obs.$	$Calc.$	$Centre$
$0_{0,0} \rightarrow 1_{1,1}$	$1 \rightarrow 1$	12817.29	12817.16	12816.76
	$1 \rightarrow 2$	16.73	16.68	
$4_{0,4} \rightarrow 4_{1,3}$	$4 \rightarrow 4$	13662.92	13662.97	12663.93
	$5 \rightarrow 5$	64.58	64.28	
	$3 \rightarrow 3$		64.59	
$5_{0,5} \rightarrow 5_{1,4}$	$5 \rightarrow 5$	18110.61	18110.58	18111.58
	$6 \rightarrow 6$	12.14	11.97	
	$4 \rightarrow 4$		12.25	
$6_{0,6} \rightarrow 6_{1,5}$	$6 \rightarrow 6$	23589.66	23589.65	23590.64
	$7 \rightarrow 7$	91.42	91.04	
	$5 \rightarrow 5$		91.27	
$7_{0,7} \rightarrow 7_{1,6}$	$7 \rightarrow 7$	29760.52	29760.52	29761.46
	$8 \rightarrow 8$	62.20	61.85	
	$6 \rightarrow 6$		62.04	
$2_{1,2} \rightarrow 2_{2,1}$	$2 \rightarrow 2$	20854.41	20854.29	20855.49
	$3 \rightarrow 3$	55.82	55.83	
$3_{1,3} \rightarrow 3_{2,2}$	$3 \rightarrow 3$	22632.60	22632.64	22633.57
	$4 \rightarrow 4$	33.88	33.88	
$4_{1,4} \rightarrow 4_{2,3}$	$4 \rightarrow 4$	25034.22	25034.35	25035.17
	$5 \rightarrow 5$	35.50	35.47	
	$5 \rightarrow 5$	28056.75	28056.69	28057.46
$5_{1,4} \rightarrow 5_{2,3}$	$6 \rightarrow 6$	58.05	7.76	
	$4 \rightarrow 4$		7.97	

## <sup>14</sup>N QUADRUPOLE COUPLING CONSTANTS

Several of the observed lines were split due to quadrupole coupling of the <sup>14</sup>N nucleus with the molecular rotation. Nine transitions of which splittings were resolved are listed in Table 9. The diagonal elements of the quadrupole coupling tensor were determined from these transitions as  $\chi_{aa} = 1.6 \pm 0.2$  MHz,  $\chi_{bb} = 1.6 \pm 0.2$  MHz, and  $\chi_{cc} = -3.2 \pm 0.3$  MHz. Computer programme [20] MB09 was used to evaluate these parameters. The above values were also used to calculate the centre frequencies of the split excited state lines.

$\chi_{cc}$  is close to  $-3.6$  MHz determined for formamide [6] and  $-3.41 \pm 0.07$  MHz obtained for formimide [9].

## DISCUSSION

2-fluoroacetamide exists as the trans form in the crystalline state [4], in solution [5], and in the gas phase. The remarkable stability of this conformer in the latter state can be mainly ascribed to two different intramolecular forces, viz. the five-membered intramolecular hydrogen bond and the electrostatic interaction of the bond dipoles.

The hydrogen bond geometry is probably unfavourable for the formation of a strong intramolecular bond. Utilizing the plausible structure of Table 1, the non-bonded H(1) ··· F distance is computed to be about 2.31 Å which is approximately 0.25 Å shorter than the sum of the pertinent Van der Waals' radii [21]. The N ··· F distance is roughly 2.65 Å compared to 2.85 Å which is the sum of the N and F Van der Waals' radii [21]. The N–H(1) ··· F angle is far from linear. The plausible structure yields 98°. Moreover, the  $\angle$ H(1) ··· F–C is about 89° and the N–H(1) and C–F bonds are approximately 7° from being parallel. These values are hopefully correct to within a few hundredths of an Å and a few degrees. It is difficult to estimate quantitatively how large the hydrogen bond stabilisation energy is, but the 1–3 kcal mole<sup>-1</sup> range appears reasonable.

The identified rotamer has a geometry which is very favourable for electrostatic bond dipole stabilisation. The C=O and C–F bonds are trans and there is thus a minimum of bond dipole repulsion. There should also be considerable attraction between the C–F and the two N–H bond dipoles. Moreover, the N–H(1) and the C–F bonds are close to being parallel which is the most favourable arrangement. The electrostatic stabilisation energy is perhaps as important as hydrogen bonding in this case. It is difficult to estimate quantitatively its contribution, but an interaction energy in the 1–3 kcal mole<sup>-1</sup> range is expected.

The two effects discussed above both tend to stabilize the Fig. 2 form, possibly by several kcal mole<sup>-1</sup>, and largely explain the infrared and microwave evidence for the non-existence of additional rotamers.

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