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Study of Rotational Isomerism in Fluoroacetyl Fluoride by Microwave Spectroscopy*

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Fluoroacetyl fluoride has been found to have two distinct sets of pure rotational transitions in the microwave region 8 to 36 kMc/sec, which have been identified as arising from two rotamers, one with the two fluorine atoms trans to one another and the other in which they are in the cis position. These spectra have been analyzed and moments of inertia obtained. The Stark effect gives the dipole-moment components: $trans \mu_a = 0.456 \pm 0.010 \text{ D}, \mu_b = 2.63 \pm 0.05 \text{ D}, \mu = 2.67 \pm 0.05 \text{ D}; cis \mu_a = 1.18 \pm 0.03 \text{ D}, \mu_b = 1.68 \pm 0.04 \text{ D}, \mu = 1.68 \pm 0.04 \text{ D},$ 2.05 ± 0.06 D; $\mu_e=0$ for both forms. Several sets of satellite lines were observed and assigned to torsionally excited trans molecules, to a skeletal bending mode, and to a combination of these. Relative intensities then gave trans frequencies near 127 cm⁻¹ for the torsion and 265 cm⁻¹ for the bending. Intensities also gave an energy difference, Ecia-Etrans, of 910±100 cal/mole. The available data do not completely define the torsional potential function but suggest that the threefold component may be in the range 1000-1300 cal/mole as in acetyl derivatives. The twofold component must be dominant to produce the cis instead of gauche minimum.

I. INTRODUCTION

WHEN both groups attached to a central single bond of a molecule are server. bond of a molecule are asymmetric, the molecule may exist in two or more different stable configurations corresponding to different rotational orientations of the two groups. These rotational isomers have been studied extensively by Mizushima and co-workers using infrared and Raman spectroscopy, electron diffraction, and dielectric-constant measurements.¹

Recently, the microwave spectra of two rotational isomers have been assigned for several molecules. Hirota demonstrated that normal propyl fluoride² and butyronitrile³ exist in trans and gauche forms and that 3-fluoropropene⁴ has stable *cis* and *gauche* forms. Sarachman studied the trans and gauche forms of normal propyl chloride.⁵ Butcher has observed microwave spectra due to the cis and gauche isomers of propionaldehyde,⁶ and Michielsen-Effinger has assigned rotational transitions to trans and gauche isomers of ethyl alcohol.7 In addition, Mukhtarov identified the microwave spectrum of one of the isomers of 1-fluoro-2chloroethane⁸ and of 1, 1, 2-trifluoroethane.⁹ So far only

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⁷ J. Michielsen-Effinger, Ann. Soc. Sci. Bruxelles, Ser. I 78, 223 (1964).
⁸ I. A. Mukhtarov, Doklady Akad. Nauk SSSR 115, 486 (1957); Izv. Akad. Nauk SSSR Ser. Fiz. 22, 1154 (1958); Opt. i Spektroskopiya 6, 260 (1959); Izv. Akad. Nauk Azerb. SSR Ser. Fiz. Mat. i Tekhn. Nauk 6, 37 (1964).
⁹ I. A. Mukhtarov, Doklady Akad. Nauk SSSR 148, 566 (1963); 151, 1076 (1963); Opt. i Spektroskopiya 14, 728 (1963); 16, 360 (1964); 16, 910 (1964).

the trans form has been found for acrolein¹⁰ and for butadiene derivatives,¹¹ in which the central single bond is adjacent to two double bonds.

The microwave spectrum of fluoroacetyl fluoride was investigated to see how interactions between the fluorine atom on the CH₂F group and the COF group affect the stable structures and the barrier to internal rotation between them. A comparison is made with acetyl fluoride.12

No previous structural study of fluoroacetyl fluoride has been reported, but the infrared and Raman spectra of chloroacetyl chloride, bromoacetyl chloride, and bromoacetyl bromide have been measured by Nakagawa et al.13 These authors concluded that there are two rotational isomers of each of these molecules in the gaseous state. A normal vibration calculation for chloroacetyl chloride and bromoacetyl chloride indicates that the more stable isomer has the two halogen atoms in a trans configuration. The electron-diffraction investigation of Morino et al. also established that the more stable form of chloroacetyl chloride is the trans.¹⁴ The best agreement between the observed vibrational frequencies of the less stable isomer of chloroacetyl chloride and bromoacetyl chloride and the calculated normal frequencies is obtained for a dihedral angle of about 150° from the trans position.^{13,15} The two carbonyl stretching frequencies observed by Bellamy and Williams in the infrared spectrum of chloroacetyl

⁽¹⁵⁾ J¹⁴ Y. Morino, K. Kuchitsu, and M. Sugiura, J. Chem. Soc. Japan **75**, 721 (1954).
 ¹⁵ S. Mizushima, T. Shimanouchi, I. Nakagawa, and A. Miyake, J. Chem. Phys. **21**, 215 (1953).

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¹ S. Mizushima, Structure of Molecules and Internal Rotation</sup> (Academic Press Inc., New York, 1954).
² E. Hirota, J. Chem. Phys. **37**, 283 (1962).
³ E. Hirota, J. Chem. Phys. **37**, 2918 (1962).
⁴ E. Hirota, J. Chem. Phys. **42**, 2071 (1965).
⁵ T. N. Sarachman, J. Chem. Phys. **39**, 469 (1963).
⁶ S. S. Butcher and E. B. Wilson, Jr., J. Chem. Phys. **40**, 1671 (1964).

¹⁰ E. A. Cherniak and C. C. Costain, J. Chem. Phys. 45, 104 (1966).

¹¹ D. R. Lide, Jr., J. Chem. Phys. **37**, 2074 (1962); D. R. Lide, Jr., and M. Jen, *ibid.* **40**, 252 (1964); R. A. Beaudet, *ibid.* **42**, 2770 (1967). 3758 (1965).

¹² L. Pierce and L. C. Krisher, J. Chem. Phys. 31, 875 (1959).

¹³ I. Nakagawa, I. Ichishima, K. Kuratani, T. Miyazawa, T. Shimanouchi, and S. Mizushima, J. Chem. Phys. 20, 1720 (1952).

chloride are in accord with the existence of two rotational isomers in the gaseous state.¹⁶

A check of the infrared and nuclear-magneticresonance spectra of the sample of fluoroacetyl fluoride used in this work was made at the E. I. du Pont Company.¹⁷ It was noted that fluoroacetyl fluoride has

TABLE I. Assigned transitions^a of the trans isomer of fluoroacetyl fluoride in the ground vibrational state.

Transition	Obs frequency	Obs-calc frequency
a Type		
$1_{01} \rightarrow 2_{02}$	13 350.17	-0.01
$1_{10} \rightarrow 2_{11}$	14 435.79	0.00
$3_{30} \rightarrow 4_{31}$	27 126.07	-0.44
$3_{13} \rightarrow 4_{14}$	24 749.72	-0.27
$3_{22} \rightarrow 4_{23}$	26 823.73	-0.27
b Type		
0 ₀₀ →1 ₁₁	13 379.67	0.11
1 ₁₁ →2 ₂₀	35 482.82	-0.01
$1_{01} \rightarrow 2_{12}$	19 121.04	0.02
$1_{10} \rightarrow 2_{21}$	34 397.16	-0.06
$2_{12} \rightarrow 3_{03}$	14 008.04	-0.01
$2_{02} \rightarrow 3_{13}$	24 411.20	-0.09
$3_{13} \rightarrow 4_{04}$	21 316.03	-0.02
$3_{03} \rightarrow 4_{14}$	29 382.04	-0.35
4 ₁₄ →5 ₀₅	28 427.85	-0.19
$4_{04} \rightarrow 5_{15}$	34 221.44	-0.42
5 ₁₅ →6 ₀₆	35 234.80	-0.48
5 ₂₄ →6 ₁₅	27 753.51	-0.21
$7_{35} \rightarrow 8_{26}$	28 497.79	-0.32
$2_{02} \rightarrow 2_{11}$	8 723.87	0.16
$3_{03} \rightarrow 3_{12}$	10 531.80	0.23
$4_{04} \rightarrow 4_{13}$	13 231.50	0.30
$5_{05} \rightarrow 5_{14}$	16 943.95	0.18
$7_{07} \rightarrow 7_{16}$	27 208.99	-0.09
$8_{08} \rightarrow 8_{17}$	33 309.90	-0.36
$2_{11} \rightarrow 2_{20}$	20 062.78	0.03
$3_{12} \rightarrow 3_{21}$	19 051.52	-0.08
9 ₁₈ →9 ₂₇	25 456.05	-1.43
$10_{19} \rightarrow 10_{28}$	30 255.52	-2.09
$2_{12} \rightarrow 2_{21}$	22 914.18	-0.12
$3_{13} \rightarrow 3_{22}$	24 451.13	0.03
$4_{14} \rightarrow 4_{23}$	26 525.14	0.04
$5_{15} \rightarrow 5_{24}$	29 140.85	-0.13
$6_{16} \rightarrow 6_{25}$	32 287.89	-0.32
$3_{21} \rightarrow 3_{30}$	35 296.81	-0.22
$4_{22} \rightarrow 4_{31}$	34 644.91	-0.44
$5_{23} \rightarrow 5_{32}$	33 524.93	-0.87
7 ₂₅ →7 ₃₄	30 191.62	-1.61
$8_{26} \rightarrow 8_{35}$	28 517.89	-1.83
$9_{27} \rightarrow 9_{36}$	27 334.57	-2.20
$10_{28} \rightarrow 10_{37}$	26 993.26	-2.67
$11_{29} \rightarrow 11_{38}$	27 765.06	-3.28
$12_{2,10} \rightarrow 12_{39}$	29 831.89	-4.27

^a In megacycles per second.

 ¹⁶ L. J. Bellamy and R. L. Williams, J. Chem. Soc. 1958, 3465.
 ¹⁷ F. S. Fawcett, Central Research Department, E. I. du Pont Company, Wilmington, Del. (private communication).

TABLE II. Ground-state rotational constants^a and moments of inertia^b of the *trans* isomer.

A B	10 508.83	
C C	2 870.73	
κ	-0.742268	
I_A	48.1054°	
I_B	131.1358°	
10	170.0984	
$I_A + I_B - I_C$	3.1428	

* In megacycles per second.

^b In (atomic mass units) (angstroms)².

^c Conversion factor 505 531 amu · Å²·Mc/sec.

a rather high carbonyl absorption frequency (1905, 1890 cm^{-1}) which is comparable to that of trifluoroacetyl fluoride (1901 cm⁻¹). Fluoroacetyl fluoride also showed an unusually high F-F spin-spin coupling constant (J = 42-44 cps). These values suggested that the fluorine atoms are in a trans position in the more stable form of this compound.

This paper reports the microwave spectra of the trans isomer of fluoroacetyl fluoride and of another, less stable isomer in which the fluorine atoms are in a cis position.

Concurrently with this microwave work, the infrared spectrum of the same sample of fluoroacetyl fluoride was studied in the gas phase by Loos.¹⁸ Evidence for the existence of a second isomer in addition to the trans was obtained.

II. EXPERIMENTAL

The sample of fluoroacetyl fluoride was obtained from F. S. Fawcett of the E. I. du Pont Company and was used without further purification. It was prepared by the reaction of sodium fluoroacetate with sulfur tetrafluoride at $120^{\circ}C/6$ h under autogenous pressure.¹⁷ These conditions are similar to those used for related compounds by Hasek, Smith, and Engelhardt.¹⁹ Fluoroacetyl fluoride is very toxic.²⁰

The microwave spectra were observed in the frequency region 8 to 36 kMc/sec using conventional Stark modulation spectrometers.²¹ Spectral frequencies were measured using either a conventional frequency standard or a Gertsch FM-4A frequency multiplier stabilized with a Gertsch FM-6 frequency meter. The basic crystal oscillator of the frequency standard was monitored with the 100-kc/sec standard signal from the Cruft Laboratory at Harvard University. The frequency measurements were reproducible to ± 0.1 Mc/sec and were made at dry-ice temperature. Relative

¹⁸ K. R. Loos, Ph.D. thesis, Massachusetts Institute of Tech-

¹⁹ W. R. Hasek, W. C. Smith, and V. A. Engelhardt, J. Am. Chem. Soc. 82, 543 (1960).

²⁰ B. C. Saunders and G. J. Stacey, J. Chem. Soc. **1948**, 1773. ²¹ K. B. McAfee, R. H. Hughes, and E. B. Wilson, Jr., Rev. Sci. Instr. 20, 821 (1949).



FIG. 1. Variation of the asymmetry parameter and $I_B + I_C - I_A$ with dihedral angle.

intensities of absorption lines were determined by the technique developed by Esbitt.²²

III. GROUND-STATE ROTATIONAL SPECTRUM OF THE trans ISOMER

Preliminary rotational constants for the trans isomer were calculated from the structure (hereafter called the "basic" structure) obtained by combining the COF parameters of acetyl fluoride,12 the CH2F parameters derived from the ethyl fluoride²³ and 3-fluoropropene⁴ structures, and the C-C distance for acetyl fluoride.¹² See Table XI. The conformation about the C-C bond was chosen so that the heavy atoms are in a plane and the fluorine atom of the CH₂F group eclipses the oxygen.

A strong b-type spectrum was found close to the predicted one. The low J lines were first identified on the basis of their very clear Stark patterns and a rigid-rotor frequency fit. Subsequently, higher Jb-type lines were measured. Individual Stark lobes could be resolved for most of these lines, even for the $12_{2,10} \rightarrow 12_{39}$, so that their assignment is definite. A double-resonance signal²⁴ for the lines assigned to the $4_{14} \rightarrow 5_{05}$ and $5_{05} \rightarrow 5_{14}$ transitions was also observed, in agreement with the previous assignment of these transitions. Several of the much weaker *a*-type *R*-branch lines were assigned by making use of their predicted frequencies and qualitative Stark effects.

The observed transition frequencies are listed in Table I. The rotational constants given in Table II were used to obtain the calculated frequencies. These rotational constants were determined from the transitions with $J \leq 2$ and are probably accurate to ± 0.1 Mc/sec.

Table XII and Figs. 1 and 2 indicate the agreement between the preliminary and experimental moments of inertia. The observed value of $I_A + I_B - I_C$ provides experimental evidence for the planarity of the heavy atoms. If the only out-of-plane atoms are the pair of hydrogen atoms, the relation

$$I_A + I_B - I_C = 4m_{\rm H}c_{\rm H}^2 - \Delta \tag{1}$$

holds, where $c_{\rm H}$ is the equilibrium out-of-plane hydrogen distance and Δ is a constant arising mostly from lowfrequency vibrations of the heavy in-plane atoms.²⁵ For $c_{\rm H} = 0.890_8$ Å,⁴ $4m_{\rm H}c_{\rm H}^2 = 3.200$ amu·Å². Comparing this with the experimental value, $I_A + I_B - I_C = 3.143$ amu·Å², gives $\Delta \cong 0.057$ amu·Å² which is similar in magnitude to the values observed for completely planar molecules.

IV. VIBRATIONAL SATELLITE SPECTRA OF THE trans ISOMER

Several sets of satellite lines were found accompanying the ground-state transitions of the trans isomer. As shown in Table III, these satellites have been assigned to excited states of the two lowest normal vibrational modes, the C-C torsion and the skeletal bending mode. Only b-type transitions were assigned for the vibrational satellites. All of the observed



FIG. 2. Variation of other second moments with dihedral angle.

²⁵ V. W. Laurie, J. Chem. Phys. 28, 704 (1958).

²² A. S. Esbitt and E. B. Wilson, Jr., Rev. Sci. Instr. 34, 901

¹⁹ A. S. Esoret and L. L. (1963).
²⁸ B. Bak, L. Hansen-Nygaard, J. Tormod Nielsen, and J. Rastrup-Andersen, Spectrochim. Acta 16, 376 (1960).
²⁴ A. P. Cox, G. W. Flynn, and E. B. Wilson, Jr., J. Chem. Phys. 42, 3094 (1965); R. C. Woods III, A. M. Ronn, and E. B. Wilson, Jr., Rev. Sci. Instr. 37, 927 (1966).

Transition	Obs Obs-calc frequency frequency	Obs Obs-calc frequency frequency	Transition	Obs Obs-calc frequency frequency	Obs Obs-calc frequency frequency
	Excited states of the C-	C torsion		Third excited state	Fourth excited state
	First excited state	Second excited state	312-322	23 925 86 -0 02	
0 ₀₀ →1 ₁₁	13 332.72 0.15	13 291.03 0.06	515→594	28 492.70 -0.27	
$1_{11} \rightarrow 2_{20}$	35 321.95 -0.02		615→695	31 557.72 - 0.42	
$1_{01} \rightarrow 2_{12}$	19 083.79 0.04		321	34 565.71 0.24	
$1_{10} \rightarrow 2_{21}$	34 246.45 -0.08		4 ₂₂ →4 ₂₁	$33 \ 933.32 \ -0.54$	
$2_{12} \rightarrow 3_{03}$	14 054.27 0.09	14 098.02 0.00	$5_{22} \rightarrow 5_{22}$	32 845.70 - 0.89	32 618.99 -0.92
$2_{02} \rightarrow 3_{13}$	24 387.81 0.00	24 368.67 0.00	6 ₂₄ →6 ₃₃		31 121.67 -0.89
$3_{13} \rightarrow 4_{04}$	21 359.00 0.02		$7_{95} \rightarrow 7_{34}$	29 597.65 -1.44	0
$3_{03} \rightarrow 4_{14}$	29 375.18 -0.12	29 371.48 -0.07	895-35	27 957.28 - 1.72	
$4_{14} \rightarrow 5_{05}$	28 470.21 -0.09		1048	$26\ 428.42\ -2.55$	
$4_{04} \rightarrow 5_{15}$	34 231.57 -0.22	34 243.79 -0.22	1170	27 148.42 - 3.15	
515-→606	35 279.88 -0.17	$35 \ 324.27 \ -0.44$	12, 10-1230	29 125.94 - 4.00	
5 ₂₄ →6 ₁₅	27 836.29 -0.08				
7 ₃₅ →8 ₂₆		28 814.40 -0.91	Fr.	cited states of the skaletal	bending mode
$2_{02} \rightarrow 2_{11}$	8 657.00 0.17	8 596.90 0.14		The states of the skeletar	
$3_{03} \rightarrow 3_{12}$	10 447.58 0.10	10 372.17 0.07		First excited state	Second excited state
$4_{04} \rightarrow 4_{13}$	13 121.22 0.07		$1_{01} \rightarrow 2_{12}$	19 147.85 0.05	
$5_{05} \rightarrow 5_{14}$		16 667.85 -0.25	$2_{12} \rightarrow 3_{03}$	13 976.65 0.02	
$7_{07} \rightarrow 7_{16}$	$26\ 968.04\ -0.49$	26 752.96 -0.97	$2_{02} \rightarrow 3_{13}$	$24 \ 427.24 \ -0.02$	
$2_{11} \rightarrow 2_{20}$	19 918.73 0.08	19 788.81 0.03	$3_{13} \rightarrow 4_{04}$	21 287.29 -0.01	
$3_{12} \rightarrow 3_{21}$	18 915.64 -0.30		$3_{03} \rightarrow 4_{14}$	$29 \ 385.40 \ -0.12$	29 387.93
$9_{18} \rightarrow 9_{27}$		25 033.21 -2.22	$2_{02} \rightarrow 2_{11}$	8 774.03 0.09	
10 ₁₉ ↔10 ₂₈		29 737.99 -3.23	$3_{03} \rightarrow 3_{12}$	10 596,44 0.10	
$2_{12} \rightarrow 2_{21}$	$22\ 744.12\ -0.05$	22 591.06 -0.05	4 ₀₄ →4 ₁₃	$13 \ 317.90 \ -0.08$	
$3_{13} \rightarrow 3_{22}$	24 266.57 -0.16	24 100.90 -0.10	7 ₀₇ →7 ₁₆	27 404.30 - 0.79	
$5_{15} \rightarrow 5_{24}$	$28 \ 912.80 \ -0.34$	$28\ 708.17\ -0.54$	$2_{11} \rightarrow 2_{20}$	$20\ 166.25\ -0.05$	
$6_{16} \rightarrow 6_{25}$	$32 \ 030.77 \ -0.55$	31 800.24 - 0.78	$3_{12} \rightarrow 3_{21}$	19 148.29 -0.19	
$3_{21} \rightarrow 3_{30}$	35 040.54 - 0.32	34 809.78 - 0.33	$4_{14} \rightarrow 4_{23}$	26 677.87 -0.25	
$4_{22} \rightarrow 4_{31}$	$34 \ 395.61 \ -0.54$		$5_{15} \rightarrow 5_{24}$		29 477.47
$5_{23} \rightarrow 5_{32}$	$33\ 287.29\ -0.78$		6 ₁₆ →6 ₂₅	$32 \ 484.90 \ -0.73$	
6 ₂₄ →6 ₃₃		31 548.42 - 0.95	$4_{22} \rightarrow 4_{31}$	34 824.12 - 0.47	
8 ₂₆ →8 ₃₅	$28 \ 322.09 \ -1.64$	$28 \ 145.22 \ -1.45$	$5_{23} \rightarrow 5_{32}$	33 694.22 - 0.82	
9 ₂₇ →9 ₃₆	27 142.88 - 2.06	$26\ 969.90\ -2.01$	10 ₂₈ →10 ₈₇	$27 \ 138.01 \ -2.68$	
$10_{28} \rightarrow 10_{37}$	$26\ 795.14\ -2.63$	$26 \ 616.83 \ -2.62$	$12_{2,10} \rightarrow 12_{39}$	$30\ 028.46\ -4.85$	30 214.96
11 ₂₉ →11 ₃₈	27 548.12 - 3.26	$27 \ 353.31 \ -3.55$	ĺ		
$12_{2,10} \rightarrow 12_{39}$	29 582.64 - 4.39	$29 \ 359.57 \ -4.79$	ł	Lowest combination	state
	Third excited state	Fourth excited state		C-C torsion+skeletal	bending
1→2aa		34 881 22 0 00	0→1	13 362 20 -0.06	
$1_{10} \rightarrow 2_{20}$		33 833.34 0.00	312→404"	21 333.58 0.03	
$2_{09} \rightarrow 3_{12}$	24,350,24,-0,04		211→200	20 008.82 0.04	
414-→505	28559.42 - 0.22		5 ₁₅ →5 ₂₄	$29\ 064.90\ -0.38$	
4 ₀₄ →5 ₁₅	$34\ 259.67\ -0.28$		616→69K	32 204.30 -0.68	
735→826	28 984.21 - 0.60		321→330	$35\ 202.17\ -0.28$	
3 ₀₃ →319	10 292.74 0.11		4 ₉₉ -→4 ₂₁	34 551.65 -0.54	
8 ₀₈ →817	32 477.50 -0.52		5 ₂₂ →5 ₃₂	33 434.50 -0.66	
10 ₁₉ →10 ₂₈	29 483.56 -2.07		12 _{2.10} →12 ₃₀	29 756.48 -4.51	

TABLE III. Assigned transitions^a of the trans isomer of fluoroacetyl fluoride in excited vibrational states.

^a In megacycles per second.

satellite lines are narrow, unsplit lines, and they fit rigid-rotor patterns. The calculated frequencies of Table III were obtained from the rotational constants given in Table IV. The rotational constants for the stronger satellites were determined from low J transitions. For the weaker satellites, where somewhat higher J transitions had to be used, the centrifugal distortion correction for a transition was set equal to the correction for the corresponding transition in the ground and lower vibrational states.

The strongest satellite, about two-fifths as intense as the ground-state line, is assigned to the first excited state of the C-C torsion. The satellites attributed to its overtone states lie in a series of steadily decreasing

	Excited states of the C–C torsion			
	First	Second	Third	Fourth
	excited	excited	excited	excited
	state	state	state	state
A	10 456.98	10 410.67	10 362.02	10 314.10
B	3 850.83	3 847.48	3 844.31	3 841.70
C	2 875.59	2 880.30	2 885.59	2 891.04
I _A	48.3439	48.5589	48.7869	49.0136
I _B	131.2785	131.3928	131.5011	131.5904
I _C	175.8008	175.5133	175.1916	174.8613
$I_A + I_B - I_C$	3.8216	4.4384	5.0964	5.7427

TABLE IV. Rotational constants^a and moments of inertia^b of the *trans* isomer in excited vibrational states.^a

First excited state of the skeletal bending mode

A	10 546.80	
B	3 858.81	
l	2 807.00	
I.	47.9322	
I_B	131,0070	
Ĩc	176.3275	
$I_A + I_B - I_C$	2.6117	
Lowest con	nbination state	
C–C torsion+	-skeletal bending	
А	10 490.04	
B	3 854.15	
С	2 872.22	
Ι	48.1915	
I_R^{-n}	131.1654	
I_c	176.0071	
$I_A + I_B - I_C$	3.3498	

^a In megacycles per second.

^b In (atomic mass units) (angstroms)².

⁶ Conversion factor 505 531 amu · Å² · Mc/sec is used to calculate moments of inertia.

intensity. To the first approximation, the inertial defect Δ depends on the vibrational state according to

$$\Delta = \sum_{s} \Delta_{s}(v_{s} + \frac{1}{2}).$$
 (2)

The observed change in $\Delta = 4m_{\rm H}c_{\rm H}^2 - (I_A + I_B - I_C)$ indicates that the contribution of the vibration to the inertial defect is negative, $\Delta_s = -0.6_8$ amu·Å². This is consistent with the assignment of this vibration as the lowest out-of-plane mode,²⁶ i.e., presumably the torsional mode.

Another satellite, which has about the same intensity as that due to the second excited state of the C-C torsion, is assigned to the first excited state of the skeletal bending mode. In this case $I_A+I_B-I_C$ is smaller for the excited state than for the ground state. Therefore, the contribution of this vibration to the inertial defect is positive, $\Delta_s = +0.5_3$ amu·Å², in agreement with its assignment to a low-frequency in-plane mode.²⁶ A few lines assigned to the second excited state of this mode were also observed, but the rotational constants for this state were not obtained.

The final satellite observed is about as intense as that attributed to the third excited state of the C-C torsion. On the basis of its intensity and its position, this satellite is assigned to the combination state for which $v_{\text{torsion}}=1$ and $v_{\text{bend}}=1$.

The relative intensities of pairs of transitions in different vibrational states were measured.²² All the measurements were carried out with dry ice packed around the waveguide. Since the ends of the waveguide cell are located outside the dry-ice trough, the temperature was measured at various points along the waveguide, and the effective temperature of the gas was calculated.²⁷ The various precautions of Ref. 22

 TABLE V. Relative intensities of ground and excited state transitions of the *trans* isomer.

Transition	T _{eff}	Intensity ratio	Derived energy difference between the states
	Excited s	states of the C-C to	rsion
	Ground	state/first excited st	tate
$\begin{array}{c} 2_{02} \longrightarrow 2_{11} \\ 3_{03} \longrightarrow 3_{12} \\ 6_{16} \longrightarrow 6_{25} \end{array}$		2.21 2.42 2.98	
	200°K	Av: 2.54 ± 0.46	$130 \pm 30 \text{ cm}^{-1}$
	First excited	I state/second excite	ed state
$\begin{array}{c} 2_{02} \longrightarrow 2_{11} \\ 3_{03} \longrightarrow 3_{12} \end{array}$		2.80 2.25	
	202°K	Av: 2.53 ± 0.46	$130\pm30 \text{ cm}^{-1}$
	Second excit	ed state/third excite	ed state
$3_{03} \rightarrow 3_{12}$	203°K	2.47 ± 0.46	$128 \pm 30 \text{ cm}^{-1}$
	Third excite	d state/fourth excite	ed state
5 ₂₃ →5 ₃₂	205°K	2.61 ± 0.46	$137 \pm 30 \text{ cm}^{-1}$
Firs	st excited sta Ground	te of the skeletal be state/first excited st	nding mode ate
$6_{16} \rightarrow 6_{25}$	201°K	6.66 ± 1.0	265±30 cm ⁻¹
Lowest o	combination Ground	state C-C torsion+ state/combination s	skeletal bending tate
$4_{22} {\longrightarrow} 4_{31}$	202°K	16.8±2.5	$396 \pm 30 \text{ cm}^{-1}$

 $^{^{27}}$ A. S. Esbitt, Ph.D. thesis, Harvard University, 1961, and Ref. 2. The effective temperature of the gas $T_{\rm eff}$ is calculated from the relation

$$\exp[h(\nu_2 - \nu_1) k T_{\text{eff}}]$$

$$=\sum_{i}T_{i}^{-n}l_{i}\exp(-h\nu_{1}/kT_{i})/\sum_{i}T_{i}^{-n}l_{i}\exp(-h\nu_{2}/kT_{i}),$$

where l_i and T_i are the length and temperature of the *i*th section of the waveguide. The numerator and denominator of the righthand side of the equation are proportional to the intensities of the lines due to the vibrational states of energy hv_1 and hv_2 , respectively, above the ground state. If one of the lines is a groundstate line, $hv_1=0$. The exponent *n* is assumed to be 4.

²⁶ D. R. Herschbach and V. W. Laurie, J. Chem. Phys. 40, 3142 (1964).

were observed but the scatter from transition to transition was somewhat large.

Table V summarizes the results of the relative intensity measurements. The energy differences between states are derived by assuming that the relative intensity is proportional to the Boltzmann factor. For the C-C torsion the equal spacing between successive energy levels indicates that this vibration is essentially harmonic. The fundamental frequency of 130 ± 15 cm⁻¹ is in excellent agreement with the infrared value of 127 cm⁻¹.¹⁸ The frequency obtained for the skeletal bending mode, 265 ± 30 cm⁻¹, also agrees within experimental error with the infrared value of 252 cm⁻¹.¹⁸ The energy of the combination state is equal to the sum of these two fundamental frequencies.

The regular change in the rotational constants for the excited torsional states with vibrational quantum number also supports the conclusion that the C-C torsion is quite harmonic. For example, the differences, $A_v - A_{v-1}$, between the A rotational constants for successive states are -51.85, -46.31, -48.65, and -47.92 Mc/sec. The variation in these values is small, but is outside experimental error. Some of this variation is a "Fermi resonance" perturbation effect,²⁸ arising from the fact that the fundamental frequency of the bending mode is about twice that of the torsion, so that the second, third, and fourth excited torsional states each have almost the same energy as other vibrational states. The effect of this perturbation is also observed in the states for which the bending mode is excited. The A rotational constant for the combination state, for instance, has nearly, but not exactly, the value predicted by the simple formula²⁹

$$A_{v} = A_{e} - \sum_{s} \alpha_{s}(v_{s} + \frac{1}{2}).$$
 (3)

V. DIPOLE MOMENT OF THE trans ISOMER

The dipole moment of the trans isomer was determined by measuring the Stark coefficients of the

TABLE VI. Stark effect and dipole moment of the trans isomer. *

		$\Delta u/E^{2{ m b}}$	
Transition	М	Obs	Calc
$1_{11} \rightarrow 2_{20}$	0 1	-0.526 ± 0.026 10.26 ±0.51	-0.549 10.23
$2_{02} \rightarrow 2_{11}$	1 2	1.87 ± 0.09 12.27 ± 0.61	$\begin{array}{c}1.85\\11.84\end{array}$
$3_{03} \rightarrow 3_{12}$	2 3	4.64 ± 0.28 9.19 ± 0.55	4.48 8.68
$5_{23} \rightarrow 5_{32}$	5	5.22 ± 0.21	5.23

^a $\mu_a = 0.456 \pm 0.010$ D, $\mu_b = 2.63 \pm 0.05$ D, $\mu = 2.67 \pm 0.05$ D.

^b In $[10^{-5}(Mc/sec)(V/cm)^{-2}]$.

 ²⁸ C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill Book Co., New York, 1955), pp. 35-40.
 ²⁹ D. R. Herschbach and V. W. Laurie, J. Chem. Phys. 37, 1668 (1962).



FIG. 3. Diagram of trans isomer of fluoroacetyl fluoride. The arrowheads indicate the negative end of the dipole moment.

 $1_{11} \rightarrow 2_{20}$, $2_{02} \rightarrow 2_{11}$, $3_{03} \rightarrow 3_{12}$, and $5_{23} \rightarrow 5_{32}$ transitions.³⁰ The $0 \rightarrow 1$ transition of OCS was used to calibrate the electric field.³¹ The results are listed in Table VI.

The most reasonable orientation of the dipole moment is shown in Fig. 3, where the signs assumed for μ_a and μ_b are those indicated by a bond moment calculation. Since the contributions from the two C-F bonds practically cancel, the total dipole moment is directed nearly along the C=O bond, the actual angle between the dipole moment and the C=O bond being about 5°.

The value of the total dipole moment (2.67 D) is close to the dipole moments of acetaldehyde $(2.69 D)^{32}$ and the cis rotamer of propionaldehyde (2.52 D).⁶

VI. ASSIGNMENT OF THE GROUND-STATE SPECTRUM OF THE LESS STABLE ISOMER

Using the basic structure, the moments of inertia and rotational constants were calculated for various values of the dihedral angle, which describes the relative orientation of the CH2F and COF groups about the C-C bond. This angle is taken to be 0° for the trans isomer and 180° at the position with the two fluorine atoms eclipsed. The dependence of the second moments P_A , P_B , and P_C $(2P_A = I_B + I_C - I_A = 2\sum_i m_i a_i^2$, etc.) and the asymmetry parameter κ on the dihedral angle is shown in Figs. 1 and 2. Assuming that the dipole moment arises entirely from the three highly polar bonds, the components of the dipole moment along the principal axes were calculated as a function of dihedral angle. The bond-moment values, C=O 2.97 D, C-F (COF group) 1.95 D,33 and C-F (CH₂F group) 1.70 D, were used together with the basic structure. Figure 4 shows the results.

The $6_{24} \rightarrow 6_{33}$ transition of the less stable isomer was first observed as a low J line which could not reasonably be assigned to a vibrationally excited state or a carbon-

³⁰ S. Golden and E. B. Wilson, Jr., J. Chem. Phys. 16, 669

^{(1948).} ³¹ S. A. Marshall and J. Weber, Phys. Rev. 105, 1502 (1957). ³² D. W. Kilb, C. C. Lin, and E. B. Wilson, Jr., J. Chem. ³² R. W. Kilb, C. C. Lin, and E. B. Wilson, Jr., J. Chem. Phys. 26, 1695 (1957).
 ³³ L. C. Krisher and E. B. Wilson, Jr., J. Chem. Phys. 31, 882

^{(1959).}



FIG. 4. Variation of the squares of the dipole-moment components with dihedral angle.

13 species of the trans form. The relative intensities of its four observable high-frequency Stark components indicated that this was a Q-branch transition. From measurements of the frequency displacements of these components the J value of this transition was determined to be in the range 5 to 7.30,34 The $1_{10} \rightarrow 2_{21}$ transition with one high-frequency Stark component and one fast low-frequency component was next observed. The Stark coefficient of the low-frequency component is about three times larger in magnitude than the coefficients of the fast M = 1 components of the trans $1_{10} \rightarrow 2_{21}$ and $1_{11} \rightarrow 2_{20}$ transitions. For an asymmetry parameter κ of about -0.7, the 2₂₀ and 2₂₁ energy levels are close together, so that these Stark coefficients are sensitive to the *a* component of the dipole moment. Since μ_a is expected to be larger for the second isomer than for the trans isomer, it was reasonable to assign this new transition to a second rotational isomer. The $1_{11} \rightarrow 2_{20}$ transition of the second isomer was found at a low Stark voltage, and its fast high-frequency Stark component was measured. At a higher voltage this line is overlapped by other lines. The assignment was confirmed by the observation of the nearby $4_{04} \rightarrow 5_{15}$ transition with resolved high-frequency Stark components. The $1_{10}\rightarrow 2_{21}$, $1_{11}\rightarrow 2_{20}$, and $6_{24}\rightarrow 6_{33}$ transitions of the less stable isomer are slightly stronger than the corresponding transitions in the fourth excited torsional state of the trans isomer.

Other transitions were readily identified on the basis

of a rigid-rotor frequency fit, Stark effects, and qualitative relative intensities. The frequencies of the assigned transitions are given in Table VII. These transitions are narrow, single lines. The *a*-type transitions are much stronger relative to the *b*-type than for the *trans* form. In addition, the *a*-type $3_{03}\rightarrow 4_{04}$ transition of the less stable form is just 0.62 Mc/sec below the $3_{30}\rightarrow 4_{31}$ transition in the ground state of the *trans* form. At dry-ice temperature the transition of the less stable form is approximately 1.5 times as strong as that of the *trans* form. This result agrees with the conclusion from the Stark effect that the *a* component of the dipole moment is larger for the less stable form than for the *trans* form.

Table VIII lists the rotational constants used to obtain the calculated frequencies of Table VII. These rotational constants were determined from transitions with $J \leq 4$. The differences between the observed and calculated frequencies of the higher J lines, attributed to centrifugal distortion, are the same order of magnitude as those for the *trans* isomer.

As shown in Fig. 2, the observed value of $I_A+I_B-I_C$ indicates that the dihedral angle of the less stable isomer is large—180° or close to 180°. The experimental values of $I_C+I_A-I_B$ and $I_B+I_C-I_A$ also agree quite well with those calculated from the preliminary structure for a dihedral angle of about 180°. See Figs. 1 and 2.

VII. DIPOLE MOMENT OF THE LESS STABLE ISOMER

The Stark coefficients of the $1_{10}\rightarrow 2_{21}$, $1_{11}\rightarrow 2_{20}$, $4_{04}\rightarrow 5_{15}$, and $6_{24}\rightarrow 6_{33}$ transitions of the less stable isomer were measured.³⁰ The electric field was calibrated using the OCS $0\rightarrow 1$ transition.³¹ Table IX gives the results

TABLE VII. Assigned transitions^a of the less stable isomer of fluoroacetyl fluoride in the ground vibrational state.

Transition	Obs frequency	Obs-calc frequency
a Type		
$3_{03} \rightarrow 4_{04}$	27 125.45	0.01
$3_{12} \rightarrow 4_{13}$	30 331.60	-0.10
$3_{22} \rightarrow 4_{23}$	28 300.52	-0.13
b Type		
$1_{11} \rightarrow 2_{20}$	34 921.69	0.02
$1_{10} \rightarrow 2_{21}$	33 663.24	-0.01
$3_{08} \rightarrow 4_{14}$	29 843,00	-0.02
$4_{04} \rightarrow 5_{15}$	34 925.29	-0.17
7 ₀₇ →7 ₁₆	29 817.23	-1.39
5 ₁₅ →5 ₂₄	28 826,62	-0.64
$6_{24} \rightarrow 6_{33}$	28 731.33	-1.06
7 ₂₅ →7 ₃₄	26 927.47	-1.40
$11_{29} \rightarrow 11_{38}$	28 219.00	-4.34
12 _{2,10} →12 ₃₉	32 082.08	-5.85

^a In megacycles per second.

³⁴ D. R. Lide, Jr., Ph.D. thesis, Harvard University, 1952, Sec. V.C.

along with the derived dipole moment. The most consistent fit to the observed Stark coefficients is obtained with $\mu_c = 0$, and the Stark-effect data on the $4_{04} \rightarrow 5_{15}$ transition limits μ_c to less than 0.08 D.

The value of μ_e was independently determined from a study of the $7_{07} \rightarrow 7_{16}$ transition of the second isomer. For this transition the contribution of the a and bcomponents of the dipole moment to the Stark coefficients is negative, but a c component would give a positive contribution. The strongest Stark component would be positive for $\mu_c > 0.12$ D. However, the observed transition has a negative, unresolved Stark effect. In order to quantitatively compare the observed and calculated Stark effects, the line shape was synthesized using an IBM 1620 computer. A Lorentz function was assumed for the zero-field line, and Lorentz functions of opposite phase were used for the Stark components. These functions were added, and the total absorption curve was plotted for several values of the electric field and various values of μ_c . At each value of the field the separation of the peak of the Stark lobe and the

TABLE VIII. Ground-state rotational constants^a and moments of inertia^b of the less stable isomer.

A B C	10 223.76 4 110.50 2 991.97
к	-0.690663
I _A I _B I _C	49.4467° 122.9853° 168.9626°
$I_A + I_B - I_C$	3.4694

^a In megacycles per second.

^b In (atomic mass units) (angstroms)².

^o Conversion factor 505 531 amu · Å² · Mc/sec.

peak of the zero-field line calculated for $\mu_c = 0$ agrees well with the measured separation. Comparison of the measured peak separations with those calculated for larger values of μ_c definitely limits μ_c to less than 0.05 D.

The absence of a c component of the dipole moment is consistent with a dihedral angle of 180° for the less stable isomer. The observed values of μ_a and μ_b are also in good agreement with those calculated for a dihedral angle of 180°. They are inconsistent with a smaller angle around 135° where the calculated curves for μ_a^2 and μ_b^2 given in Fig. 4 cross.

The most reasonable orientation of the dipole moment in the structure with the fluorine atoms in a *cis* position is shown in Fig. 5. The total dipole moment of the less stable isomer (2.05 D) is smaller than that of the *trans* isomer (2.67 D).

VIII. ENERGY DIFFERENCE BETWEEN THE ISOMERS

The relative intensities of the $6_{16} \rightarrow 6_{25}$ transition (32 287.89 Mc/sec) in the ground state of the *trans*

TABLE IX. Stark effect and dipole moment of the less stable isomer.^a

		$\Delta u / E^2$ b	
Transition	М	Obs	Calc
$1_{10} \rightarrow 2_{21}$	0 1	0.506 ± 0.027 -34.4 \pm 4.0	0.496 -37.9
$1_{11} \rightarrow 2_{20}$	1	35.8 ± 4.0	37.3
$4_{04} {\rightarrow} 5_{15}$	2 3	0.390 ± 0.010 0.730 ± 0.033	0.388 0.757
6 ₂₄ →6 ₃₃	3 4 5 6	$\begin{array}{c} 1.21 \pm 0.10 \\ 2.57 \pm 0.08 \\ 4.26 \pm 0.13 \\ 6.32 \pm 0.19 \end{array}$	$1.25 \\ 2.55 \\ 4.22 \\ 6.26$

^a $\mu_a = 1.18 \pm 0.03$ D, $\mu_b = 1.68 \pm 0.04$ D, $\mu_c = 0 \pm 0.05$ D, $\mu = 2.05 \pm 0.06$ D. ^b In $[10^{-6}(Mc/sec)(V/cm)^{-2}]$.

isomer and the $12_{2,10} \rightarrow 12_{39}$ transition (32 082.08) Mc/sec) of the second isomer were measured at room and dry-ice temperatures.22 The intensity ratios obtained are given in Table X. The energy difference between the ground states of the two isomers was derived independently from the intensity ratio at each temperature. In this calculation the half-widths of the two lines were assumed to be the same. The experimental traces support this assumption. If a statistical weight of 1 for both forms is used, the two values of the energy difference obtained agree very well. These values also agree within experimental uncertainty with the value determined directly from the temperature dependence of the relative intensity. If the second isomer existed in two equivalent forms with a high potential barrier between them at the 180° position, the ground state of this isomer would have a statistical weight of 2. Table X shows that this assumption leads to inconsistent results. Therefore, if there is a barrier at 180°, it is low enough so that the ground state of the second isomer is not degenerate. The absence of a c component of the dipole moment for the second isomer is independent evidence for this conclusion.

The second rotational isomer was found to be $910\pm$ 100 cal/mole less stable than the *trans* isomer. This



FIG. 5. Diagram of cis isomer of fluoroacetyl fluoride. The arrowheads indicate the negative end of the dipole moment.

TABLE X. Relative intensity ratio of the ground-state $6_{16} \rightarrow 6_{25}$ transition of the trans isomer to the $12_{2,10} \rightarrow 12_{39}$ transition of the less stable isomer.

		$E_{\text{less stab}}$	E_{trans}
Temperature	Intensity ratio	If $g_1/g_2 = 1$	If $g_1/g_2 = \frac{1}{2}$
202°K	7.22 ± 0.50	319±20 cm ⁻¹	$417 \pm 20 \text{ cm}^{-1}$
297°K	3.58 ± 0.50	332±35 cm ⁻¹	475±35 cm ⁻¹
Ratio (202°K)/	/Ratio (297°K)	$E_{\rm less\ stab}$	$le - E_{trans}$
$2.02\pm$	0.30	293±6	55 cm ⁻¹
Over-al	l mean	319±35 cm ⁻ cal/mole	$-1 = 910 \pm 100$

value is in good agreement with the value of 1000 ± 300 cal/mole for the energy difference between the isomers obtained from the temperature dependence of the relative intensity of two infrared absorption bands.¹⁸ In addition, the qualitative temperature dependence of the intensity of the $3_{30} \rightarrow 4_{31}$ transition (27 126.07 Mc/sec) of the trans isomer relative to the nearby $3_{03} \rightarrow 4_{04}$ transition (27 125.45 Mc/sec) of the second isomer is consistent with this value of the energy difference.

IX. STRUCTURE

It is certain that the microwave spectrum attributed to the less stable isomer is correctly assigned to a second rotational isomer of fluoroacetyl fluoride. From the temperature dependence of the relative intensity, the molecule giving rise to this spectrum has an energy 293 ± 65 cm⁻¹ above the *trans* ground state. Therefore, it cannot be an isotopic species of the trans isomer. The large difference between both its a and b dipolemoment components and those of the trans form rules out the possibility that this molecule is in a vibrationally excited state of the trans form. In addition, the infrared spectrum indicates that the lowest normal vibrational mode of the trans isomer for which vibrational satellites have not been assigned has a funda-

TABLE XI. Plausible molecular structure of fluoroacetyl fluoride.ª

С-С	1.502 Å	СН	1.094 Å
C=0	1.185	∠CCH	111°17′
C-F (COF group)	1.343	∠HCH	108°55′
C-F (CH ₂ F group)	1.379		
	Basic structure	Refined structure of <i>trans</i> form	Refined structure of less stable form
∠CCO	127°54′	130°21′	124°55′
∠CCF (COF group)	110°44′	108°17′	113°43′
$\angle CCF$ (CH ₂ F group)	111°	110°	112°20′
Dihedral angle		0°	180°

^a Not a derived structure. See text.

mental frequency of 455 cm^{-1,18} Consequently, all the excited states of the trans isomer which could have the appropriate energy have been accounted for by other spectra. Finally, the observed moments of inertia and dipole-moment components for the spectra assigned to both isomers are in good agreement with values calculated from the original basic structure.

The observed value of I_B is smaller for the less stable isomer than for the trans isomer. Table XII shows that the calculated values have the same trend. The values of the a and b dipole-moment components clearly differentiate the two rotational orientations and establish that the more stable isomer has the fluorine atoms in a trans configuration.

The fact that the C-C torsion for the trans isomer is very nearly a harmonic vibration indicates that there is a simple minimum in the potential function for internal rotation at 0° . The heavy atoms of the trans isomer are then planar.

TABLE XII. Comparison of observed and calculated moments of inertia^a of fluoroacetyl fluoride.

	Observed	Calculated from refined structure	Calculated from basic structure ^b
	tro	ans Isomer	
I_A	48.1054	48.1063	47.0704
I_B	131.1358	131.1422	133.1832
I_{C}	176.0984	176.0529	177.0580
	Less	stable isomer	
I_A	49.4467	49.4310	48.0590
IR	122.9853	122.9944	121.7459
I_c	168.9626	169.2297	166.6090

^a In (atomic mass units) (angstroms)².

 $^{\rm b}$ The CH2F group is oriented so that the fluorine atom of this group eclipses the oxygen for the trans isomer and the two fluorine atoms are eclipsed for the less stable isomer.

With the present data a small barrier at 180° cannot be ruled out. However, if there is such a barrier, it must be quite low. It has already been pointed out that the ground state of the less stable isomer is not degenerate. If the first excited state of the C-C torsion were close to the ground state, large deviations from a rigid-rotor pattern resulting from vibration-rotation interaction could occur.^{35,36} The fact that a good rigidrotor fit is obtained for the less stable isomer therefore indicates that the ground and first excited torsional states are quite well separated. If the ground state is above the top of the barrier, the less stable isomer would be vibrating about the 180° position. From Eq. (1) the inertial defect would then be negative, $\Delta \cong -0.27$ amu \cdot Å². This value is reasonable if this isomer has a

 ³⁵ D. R. Lide, Jr., J. Mol. Spectry. 8, 142 (1962).
 ³⁶ S. S. Butcher and C. C. Costain, J. Mol. Spectry. 15, 40 (1965).

low torsional vibration frequency.²⁶ In the infrared spectrum a band which has been assigned to the C-C torsion of the second isomer is observed at $49.5 \text{ cm}^{-1.18}$

The structures of the two isomers were refined to obtain better agreement between the calculated and observed moments of inertia. The dihedral angle of the less stable isomer was taken to be 180°. For each isomer the CCO angle, keeping the OCF angle constant, and the CCF (CH₂F group) angle were changed in order to fit I_A and I_B . The values obtained are given in Table XI. Changing the calculated I_A and I_B by ± 0.5 amu·Å² changes these angles by less than 1.5°. Therefore the tilt of the COF group with respect to the C-C bond may be different for the two isomers. The moments of inertia calculated from the refined structures are listed in Table XII.

X. POTENTIAL FUNCTION FOR ROTATION ABOUT THE C-C BOND

The information available is unfortunately not quite sufficient to yield an accurate potential function but it is possible to give arguments leading to a plausible form. The microwave and infrared¹⁸ spectra provide the following information:

(1) There is a real minimum, nearly harmonic, at the *trans* position $(\theta=0^\circ)$.

(2) There is a general minimum at the *cis* position $(\theta = 180^{\circ})$, although a small bump there cannot be completely excluded.

(3) The lowest torsional transitions are at $127 \pm 15 \text{ cm}^{-1}$ (trans) and $\sim 49 \text{ cm}^{-1}$ (cis).

(4) Relative intensities place the lowest *cis* level 910 ± 100 cal/mole above the lowest *trans* level.

(5) Since nearly harmonic *trans* torsional excited states were observed up to ~ 1600 cal/mole above the *trans* minimum, the *cis-trans* barrier must be higher than this value and probably considerably higher.

(6) The statistical weights and absence of a c component of the dipole moment makes it certain that



FIG. 6. A reasonable form for the potential function for internal rotation. Microwave spectra have been assigned for the levels indicated by solid lines. Based on $V_1 = -0.72$ kcal, $V_2 = 4.32$ kcal, $V_3 = 1.95$, kcal $V_4 = -0.01$, kcal $V_5 = -0.18$ kcal. See text.

 TABLE XIII. Distances between nonbonded atoms in fluoroacetyl fluoride.

	F(CH ₂ F group) 0 distance	FF distance
Refined structure of trans form	2.77 Å	3.51 Å
Refined structure of less stable (cis) form	3.52	2.57
Basic structure—dihedral angle 0° 90° 120° 150° 180°	2.75 3.15 3.34 3.47 3.52	3.55 3.06 2.78 2.56 2.47
Sum of van der Waal's radiiª	r ^F +r ⁰ 2.75 Å	<i>r</i> ^F + <i>r</i> ^F 2.70 Å

^a Reference 40.

the non*trans* form does not exist in two equivalent nontunneling forms.

(7) The absence of visible "hot" bands in the infrared for the *cis* form limits the likelihood of there being a bump at 180° .

(8) Relative intensities give very rough limits for the anharmonicity of the *trans* form.

(9) With certain assumptions the variation of A, B, and C with torsional excitation (*trans*) can be used to limit the *trans* anharmonicity to a small value.

(10) The inertial defects are known to be relatively independent of anharmonic potential constants. In the present cases there is not enough information about the other quadratic force constants to calculate the necessary Coriolis terms in the expression for the contribution of the torsion to the inertial defect.^{26,29} But it appears that the inertial defect data is at least not in conflict with the infrared values of the torsional frequencies: 127 cm⁻¹ for the *trans* form and 49.5 cm⁻¹ for the *cis*.

It is clear that this information defines reasonably well the shape and relative positions (in angle and in energy) of the two minima but does not give good direct information about the way the two wells are connected, i.e., the barrier region. It is, however, expected that the Fourier-series representation,

$$V(\theta) = \frac{1}{2} \sum_{n} V_{n} (1 - \cos n\theta), \qquad (4)$$

will converge rapidly³⁷ and that V_n will be negligible for n>5 and perhaps small for n=5. With these assumed constraints, it was hoped that the two potential wells could be connected in an approximate way. See Fig. 6.

If there is no bump at 180° , the energy difference between *cis* and *trans* forms, when corrected for the

³⁷ E. Tannenbaum, R. J. Myers, and W. D. Gwinn, J. Chem. Phys. 25, 42 (1956); R. E. Naylor, Jr., and E. B. Wilson, Jr., *ibid.* 26, 1057 (1957).

zero-point effects, gives the relation $V_1+V_3+V_5=1020\pm100$ cal/mole. The two vibration frequencies together with the reduced moments of inertia for the torsion, $(G^{-1})_{tt}$, give the curvatures in the wells. The values of $(G^{-1})_{tt}$, calculated by the method of Polo,³⁸ are 10.54 amu·Å²/rad² for the *trans* form and 10.86 amu·Å²/rad² for the *cis* form. The two relationships obtained can be combined to yield: $V_1+9V_3+25V_5=12\ 160\pm2420\ cal/mole; V_2+4V_4=4170\pm600\ cal/mole.$

If V_5 could be assumed small then V_3 would come out from these equations to be not very far from its value in the related molecules: CH₃COF, 1041±20 cal/mole;¹² CF₃COF, 1390±210 cal/mole.³⁹ V_1 would be of moderate size and negative. V_2 must obviously be rather large and positive in order to produce the minimum in the *cis* position.

In principle, one additional piece of information is available, namely the anharmonicity in the *trans* well. This can be roughly obtained from the intensity measurements on the excited states which suggest that it is quite small. A more refined value, although a less certain one, can be obtained from the change of moments of inertia with torsional state, using the one vibration approximation. However, the difficulty here is that the anharmonicity is considerably affected by V_6 even if V_6 is only 10 cal, because of the large coefficient which occurs. It does not seem safe therefore to introduce this additional piece of information into our calculations.

XI. DISCUSSION

This investigation demonstrates that the replacement of one hydrogen of acetyl fluoride by a fluorine atom has a drastic effect on the stable configurations and the barrier to internal rotation. Because of the threefold symmetry of the methyl group, the potential function for internal rotation in acetyl fluoride has minima at 120° intervals. The potential function for fluoroacetyl fluoride, however, has two wells separated by 180°. Since the *cis*, rather than the *gauche*, configuration of fluoroacetyl fluoride is stable, the V_2 term of the potential function dominates the V_3 term. This result accounts for the higher barrier in fluoroacetyl fluoride.

The interaction of an atom A on the CH_2F group of fluoroacetyl fluoride with an atom B on the COF group can be written as the Fourier series

$$v^{AB}(\theta) = v_1^{AB} \cos\theta + v_2^{AB} \cos2\theta + \cdots$$
 (5)

The onefold term is expected to be the leading term. Then the interaction of the fluorine atom on the CH_2F

group with the COF group is given by

$$v^{\text{F}\cdots\text{COF}}(\theta) = v^{\text{FO}}(\theta) + v^{\text{FF}}(\theta + \pi)$$
$$= (v_1^{\text{FO}} - v_1^{\text{FF}})\cos\theta + (v_2^{\text{FO}} + v_2^{\text{FF}})\cos2\theta + \cdots.$$
(6a)

Similarly,

$$v^{\text{H}\cdots\text{COF}}(\theta) = v^{\text{HO}}(\theta) + v^{\text{HF}}(\theta + \pi)$$
$$= (v_1^{\text{HO}} - v_1^{\text{HF}})\cos\theta$$
$$+ (v_2^{\text{HO}} + v_2^{\text{HF}})\cos2\theta + \cdots (6b)$$

The total contribution of the nonbonded interactions to the potential function is

$$V(\theta) = v^{\text{F}\cdots\text{COF}}(\theta) + v^{\text{H}\cdots\text{COF}}(\theta + \frac{2}{3}\pi) + v^{\text{H}\cdots\text{COF}}(\theta - \frac{2}{3}\pi)$$
$$= \left[(v_1^{\text{FO}} - v_1^{\text{FF}}) - (v_1^{\text{HO}} - v_1^{\text{HF}}) \right] \cos\theta$$
$$+ \left[(v_2^{\text{FO}} + v_2^{\text{FF}}) - (v_2^{\text{HO}} + v_2^{\text{HF}}) \right] \cos2\theta + \cdots .$$
(7)

Except for an arbitrary constant, this equation has the same form as Eq. (4). The large value obtained for V_2 indicates that the F····COF and the H····COF interactions are different. Then the small value of V_1 suggests that v^{FO} is about the same as v^{FF} and that v^{HO} and v^{HF} are either small or nearly equal. This conclusion seems reasonable since oxygen and fluorine are nearly the same size and are both very electronegative.⁴⁰ V_3 probably depends on the nature of bonds to the axial atoms. It may have a value near that of V_3 in CH₃COF or CF₃COF.

The $F(CH_2F \text{ group})$ O and FF distances for several configurations of fluoroacetyl fluoride are given in Table XIII. The FF distance in the *cis* form is slightly smaller than the sum of the van der Waals radii.

The changes in angles which were made in order to fit the observed rotational constants increased this distance by 0.1 Å. However, steric hindrance between the fluorine atoms is not great enough to rotate the CH_2F group so that the fluorine is out of the plane of the COF group. Steric hindrance between two chlorine atoms in the *cis* position would be larger. Hence it is reasonable that the less stable isomer of chloroacetyl chloride could have a different dihedral angle.^{13,15}

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³⁸ S. R. Polo, J. Chem. Phys. 24, 1133 (1956).

³⁹ K. R. Loos and R. C. Lord, Spectrochim. Acta 21, 119 (1965).

⁴⁰ L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, N.Y., 1960), pp. 88-91, 257-264.