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CONFORMATIONAL STABILITY, BARRIERS TO INTERNAL ROTATION, AB INITIO CALCULATIONS AND VIBRATIONAL ASSIGNMENT OF FLUOROACETYL FLUORIDE*

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ABSTRACT

The far infrared spectrum (350 to 35 cm^{-1}) of gaseous fluoroacetyl fluoride has been recorded at a resolution of 0.10 cm^{-1}. The fundamental asymmetric torsion of the more stable *trans* conformer where the two fluorine atoms are *trans* to one another has been observed at 118.90 cm^{-1} with twelve upper state transitions falling to lower frequency. Additionally, the fundamental torsional transition of the *cis* conformer has been observed at 52.06 cm^{-1} with five excited states falling to lower frequency. From these data, the asymmetric torsional potential coefficients have been determined to be: $V_1 = 86 \pm 11$; $V_2 = 946 \pm 33$; $V_3 = 407 \pm 4$; $V_4 = 138 \pm 20$ and $V_6 = -14 \pm 7$ cm^{-1}. The *trans* to *cis* and *cis* to *trans* barriers were calculated to be 1297 ± 26 (3.71 ± 0.07 kcal mol^{-1}) and 803 ± 26 cm^{-1} (2.30 ± 0.07 kcal mol^{-1}), respectively, with the energy difference being 494 ± 48 cm^{-1} (1.41 ± 0.14 kcal mol^{-1}). From the temperature dependence of the Raman spectra the enthalpy difference between the conformations has been determined to be 456 ± 32 cm^{-1} (1.30 ± 0.09 kcal mol^{-1}) and 695 ± 8 cm^{-1} (1.99 ± 0.02 kcal mol^{-1}) for the gas and liquid, respectively. The structural parameters, conformational stabilities, barriers to internal rotation, and fundamental vibrational frequencies which have been determined experimentally, are compared to those obtained from ab initio Hartree–Fock gradient calculations employing both the 3-21G and 6-31G* basis sets, and to the corresponding quantities obtained for some similar molecules.

INTRODUCTION

The microwave spectrum of fluoroacetyl fluoride has been the subject of two previously reported studies [1,2]. From the first of these [1] experimental moments of inertia and dipole moments were found to be consistent with the

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*Dedicated to Professor W.J. Orville-Thomas.

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***Taken in part from the thesis of H.V. Phan which will be submitted to the Department of Chemistry in partial fulfilment of the Ph.D. degree.

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existence of both a *trans* conformation where the two fluorine atoms are *trans* to one another and a *cis* conformation where they eclipse one another. From relative intensity measurements the energy difference between the two forms was determined to be 318±35 cm^{-1} (909±100 cal mol^{-1}) and frequencies near 127 and 265 cm^{-1} were determined for the asymmetric torsion and a skeletal bend, respectively, for the *trans* conformer. These data were not sufficient to yield an accurate potential function governing internal rotation about the C–C bond; however, a plausible form of the potential function could be obtained from which it was concluded that there was a minimum at the *trans* position with the potential nearly harmonic for this conformer although the possibility of a slight "bump" in the bottom of the *cis* well could not be excluded.

The more recently published [2] investigation of the microwave spectrum included five isotopically substituted derivatives which allowed for the determination of mixed r_0/r_s structures for both conformations. Particular attention was given to the transitions arising from the *cis* conformer from which it was concluded that the torsional motion for this form was also essentially harmonic. Furthermore, in this latter study [2] it is suggested that if the *cis* to *trans* conversion is a semi-rigid rotation followed by geometry changes in the internal coordinates, then ab initio calculations may give a good estimate of the energy changes involved with the geometry relaxation.

The vibrational spectra of fluoroacetyl fluoride have also been the subject of two previous investigations [3,4]. The fundamental torsional frequencies for the *trans* and high energy conformer were assigned [3] to features observed at 127 and 49.5 cm^{-1}, respectively, in the far infrared spectrum of the gas; however, the absence of transitions arising from upper state torsional transitions precluded the determination of the torsional potential function. From an investigation of the mid-infrared spectra of the gas and liquid to 500 cm^{-1} and the Raman spectrum of the liquid to 200 cm^{-1}, an approximate Urey–Bradley force field for both conformations has been reported [4]; however, this force field was not intended to reproduce the experimental frequencies, and little attention was given to the asymmetric torsional potential function.

Therefore, we have reinvestigated the far infrared spectrum of the gas for the purpose of determining the asymmetric potential function. Also, in order to provide a more complete study of the vibrational spectrum, we have reinvestigated the mid-infrared spectra of the gaseous and solid phases along with the Raman spectra of the gas and liquid. We have also carried out ab initio calculations in order to provide information on the energy involved in geometry relaxation, the force field and torsional potential barriers for comparison with the experimentally determined values. The results of this study are reported herein.

EXPERIMENTAL

A sample of fluoroacetyl chloride was purchased from Alfa Products, Milwaukee, WI, and fluoroacetyl fluoride was synthesized by reacting the chloride with freshly sublimated antimony trifluoride under reduced pressure. Purification was carried out with a low-temperature vacuum fractionation column and the pure fluoroacetyl fluoride was stored under vacuum and in a slush of n-propanol and Dry Ice.

The far infrared spectrum of gaseous fluoroacetyl fluoride from which the torsional transitions were obtained (Figs. 1A and 2) was collected with a Ni-

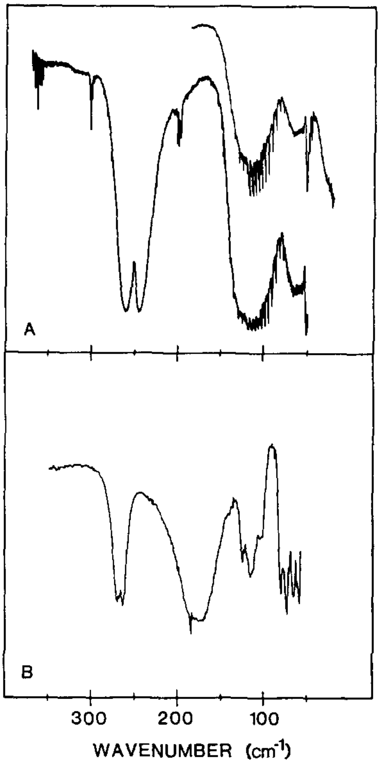

Fig. 1. Far infrared spectra of fluoroacetyl fluoride: (A) gas and (B) annealed solid.

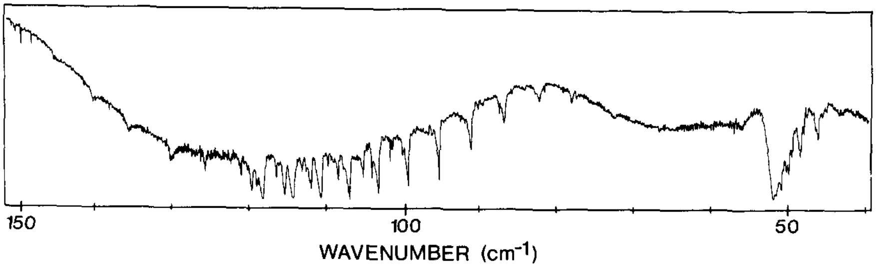

Fig. 2. Far infrared spectrum of gaseous fluoroacetyl fluoride in the region of the asymmetric torsional mode.

colet model SVX 200 Fourier transform interferometer from the sample contained in a one meter cell fitted with polyethylene windows. This instrument is equipped with a vacuum bench and a liquid helium cooled Ge bolometer containing a wedged sapphire filter and a polyethylene window. Spectra were collected at 0.10 cm^{-1} resolution with both 12.5 and 6.25 μm Mylar beamsplitters. The far infrared spectra of the annealed solid (Fig. 1B) was obtained with a Digilab model FTS-15B Fourier transform interferometer equipped with a 6.25 μm Mylar beamsplitter and a TGS detector. The sample was deposited onto a silicon window cooled by boiling liquid nitrogen and contained in a cell fitted with polyethylene windows. A spectrum of the amorphous solid was recorded immediately following sample deposition and following several cycles of warming and cooling the spectrum of the annealed solid was obtained.

Mid-infrared spectra of the gas and solid phases (Fig. 3) were recorded on a Digilab model FTS-14C Fourier transform interferometer equipped with a Ge/KBr beamsplitter and a TGS detector. For the spectrum of the gas the sample was contained in a 12 cm cell fitted with CsI windows. The spectrum of the solid was obtained by depositing the sample onto a CsI plate cooled by boiling liquid nitrogen and housed in a cell fitted with CsI windows. The data were collected following several cycles of warming and cooling of the sample.

The Raman spectra (Fig. 4) were recorded on a Cary model 82 spectrophotometer equipped with a Spectra-Physics model 171 argon ion laser operating on the 5145 Å line. The spectrum of the gas, as well as the variable temperature study of the vapor, was recorded by using a standard Cary multipass accessory. The spectrum of the liquid was obtained from the sample sealed in a glass

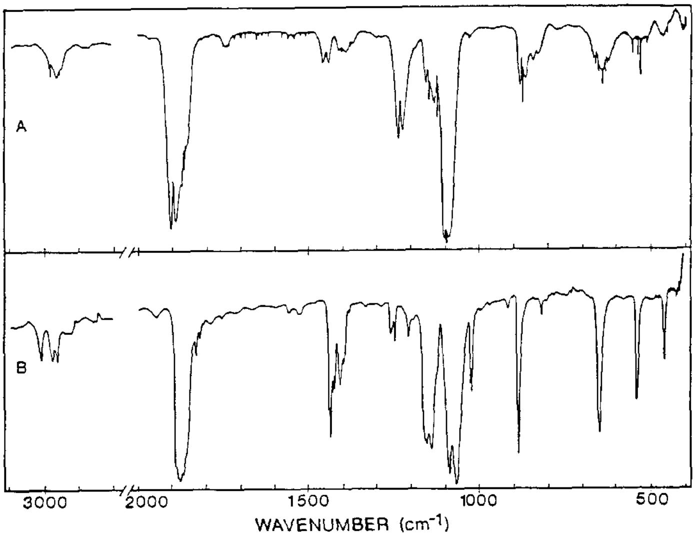

Fig. 3. Mid-infrared spectra of fluoroacetyl fluoride: (A) gas and (B) annealed solid.

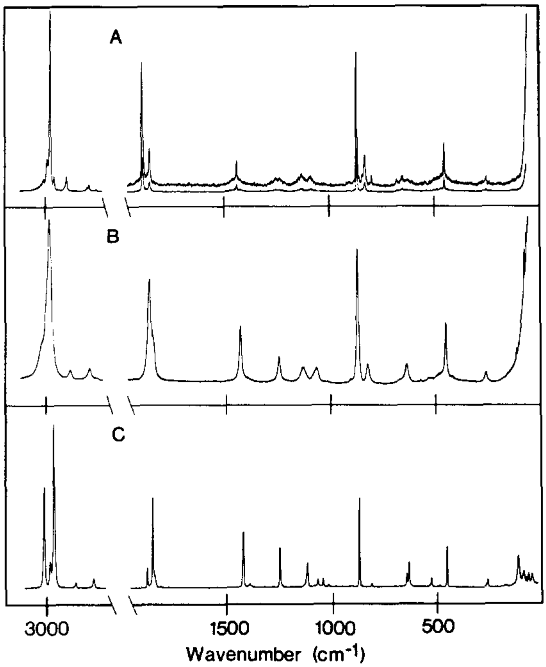

Fig. 4. Raman spectra of fluoroacetyl fluoride: (A) gas, (B) liquid and (C) annealed solid.

capillary. The variable temperature study of the liquid was carried out by the method of Miller and Harney [5]. The Raman spectrum of the annealed solid was obtained by depositing the sample onto a blackened brass block which was housed in a cell fitted with quartz windows and cooled by boiling liquid nitrogen. The annealing process was the same as that used for the infrared experiments.

CONFORMATIONAL ENTHALPY DIFFERENCE

The enthalpy difference between the low energy *trans* and high energy *cis* conformations of fluoroacetyl fluoride can be determined by applying the van 't Hoff isochore, $-\ln K = (\Delta H/RT) - (\Delta S/R)$ and measuring the relative intensity of the 872 and 833 cm^{-1} lines in the Raman spectrum of the gas and the corresponding lines observed at 874 and 828 cm^{-1} in the spectrum of the liquid. The absence of the 833 cm^{-1} line and persistence of the 872 cm^{-1} line in the spectrum of the solid indicate that these lines arise from the *cis* and *trans* conformations, respectively.

Five sets of spectral data (Table 1) were obtained with a gaseous sample at various temperatures ranging from 23 to 67°C. The natural logarithm values of the relative intensities of the aforementioned two lines were plotted against

TABLE 1

Temperature and intensity ratios (833/872 and 1865/1899 cm^{-1}, vapor and 828/874 cm^{-1}, liquid lines) for the conformational study of gaseous and liquid fluoroacetyl fluoride

T (°C)	1000 $(1/T)$ K^{-1}	$K=I_c/I_t$[a]	$-\ln K$[a]
Gas			
23	3.38	0.228(0.269)	1.48(1.31)
31	3.29	0.244(0.290)	1.41(1.24)
43	3.16	0.266(0.307)	1.32(1.18)
53	3.07	0.280(0.329)	1.27(1.11)
67	2.94	0.311(0.356)	1.17(1.03)
Liquid			
−32	4.15	0.058	2.85
−21	3.96	0.069	2.67
−10	3.80	0.082	2.50
10	3.53	0.107	2.23
23	3.38	0.125	2.08

[a] The values in parentheses are those obtained from the 1865/1899 cm^{-1} "conformer pair".

the reciprocal of the absolute temperatures. Similarly, the relative intensities of the two lines centered at 1899 and 1865 cm^{-1}, which have been assigned to the C=O stretch of the *trans* and *cis* conformers, respectively, were also measured as a function of temperature and these data were treated as for the 872/833 cm^{-1} pair. All of these data gave average values of ΔH and ΔS for the gas phase of 456 ± 32 cm^{-1} (1.30 ± 0.09 kcal mol^{-1}) and 1.64 ± 0.50 cal mol^{-1} K^{-1}, respectively.

For the determination of the enthalpy difference between the two conformers in the liquid phase five sets of spectral data were taken at different temperatures ranging from −32 to 23°C. These data were treated as for the gas and values for ΔH and ΔS of 695 ± 8 cm^{-1} (1.99 ± 0.02 kcal mol^{-1}) and 2.57 ± 1.00 cal mol^{-1} K^{-1}, respectively, were obtained.

The increase in the value of the enthalpy difference obtained for the gas, 456 ± 32 cm^{-1}, to that of the liquid, 695 ± 8 cm^{-1} can be attributed to dipole–dipole interactions in the liquid phase [6–8]. This observation is in agreement with the early work of Mizushima and others [9–11] where, in the liquid phase, a stabilizing effect was found for the rotamer having the larger total dipole moment. Thus, the increased stability of the *trans* ($\mu_t=2.67\pm0.05$ D) relative to the *cis* conformer ($\mu_t=2.05\pm0.06$ D) as one proceeds from the gas to the liquid is consistent with the values of the total dipole moments which were previously reported [1] for the two conformers.

TORSIONAL POTENTIAL FUNCTION

The direct observation of the torsional fundamentals and numerous associated "hot band" transitions originating from both conformers allows for the determination of the asymmetric torsional potential function. The assignments of the observed torsional transitions (Fig. 2) for the *trans* and *cis* conformers are summarized in Table 2. The large number of observed upper level transitions allows for the almost complete definition of both the *trans* and *cis* potential energy wells and, thus, adds to the reliability of the barrier height determinations.

The torsional dihedral angular dependence of the internal rotation constant, $F(\phi)$, can be represented as a Fourier series:

$$F(\phi)=F_0+\sum_{i=1}^{6} F_i \cos i\,\phi$$

The relaxation of the structural parameters, $B(\phi)$, during the internal rotation can be incorporated into the above equation by assuming them to be small periodic functions of the torsional angle of the general type

$$B(\phi)=a+b\cos\phi+c\sin\phi$$

Initially, the structural parameters reported in the microwave investigation [2], for both the *trans* and *cis* conformers, were used to calculate the kinetic constants. Subsequent calculations employing structures presently determined from ab initio methods showed insignificant differences. The choice of the former "F-series" to be used for the calculation of the kinetic term for the potential function calculations was arbitrary.

The torsional potential is also represented as a Fourier cosine series in the internal dihedral torsional angle (ϕ):

$$V(\phi)=\sum_{i=1}^{6} (V_i/2)\,(1-\cos i\,\phi)$$

The kinetic terms, the asymmetric torsional frequencies given in Table 2, and the experimentally obtained energy difference for the gas phase were then used to calculate the torsional potential function. The computer program employed was recently developed in our laboratory [12].

The series coefficients for the rigid rotation of the CH_2F moiety as presently determined are listed in Table 3. The first two torsional transitions for each conformer along with the experimentally determined energy difference for the gas phase were used to calculate initial values for the potential constants V_1, V_2, and V_3. Additional torsional transitions were added and these data allowed for the calculation of two additional potential constants, V_4 and V_6. At this point the value of the energy difference was allowed to vary until the differences between the observed and calculated frequencies as well as the dispersions in the potential constants were minimized. From the calculated potential function the energy difference between the two conformers is determined to be 494 ± 48 cm^{-1} (1.41 ± 0.14 kcal mol^{-1}). The calculated potential function is

TABLE 2

Observed and calculated (cm^{-1}) asymmetric torsional transitions for fluoroacetyl fluoride

Transition	Obs.	Max.	Calc.[a]	Δ
Trans				
	127.50			
	121.71			
	120.35			
	119.52			
1←0	118.90	118.90	118.47	0.43
	117.09			
	115.03			
2←1	114.95	114.95	115.18	−0.23
	113.73			
	113.16			
	112.75			
	112.56			
3←2	111.29	111.29	111.75	−0.46
	110.34			
	109.92			
	109.59			
	109.00			
	108.30			
	107.79			
4←3	107.52	107.52	108.15	−0.63
	105.74			
	105.54			
5←4	103.75	103.75	104.36	−0.61
	103.03			
	102.16			
	101.91			
	100.57			
6←5	99.85	99.85	100.36	−0.51
	95.73			
7←6	95.35	95.35	96.09	−0.74
8←7	91.72	91.72	91.50	0.22
9←8	87.43	87.43	86.50	0.93
10←9	82.87	82.87	80.95	1.92
11←10	78.51	78.51		
12←11	72.91	72.91		
13←12	67.05	67.05		
Cis				
1←0	52.06	52.06	51.76	0.30
	51.80			

TABLE 2 (continued)

Transition	Obs.	Max.	Calc.[a]	Δ
2←1	51.04	51.04	50.91	0.13
	50.75			
	50.40			
3←2	50.09	50.09	49.73	0.36
	49.70			
	49.35			
	48.75			
4←3	48.59	48.59	48.31	0.28
	48.20			
	47.84			
	47.20			
	46.60			
5←4	46.35	46.35	46.76	−0.41
	45.82			
	45.28			
6←5	43.68	43.68	45.17	−1.49

[a] Calculated using the potential constants given in Table 3 and $F_0=1.48065$, $F_1=0.01656$, $F_2=0.09671$, $F_3=0.00140$, $F_4=0.00472$, $F_5=0.00009$, and $F_6=0.00024$ cm^{-1}.

TABLE 3

Comparison of energy parameters (cm^{-1}) as determined for fluoroacetyl fluoride by ab initio calculations and microwave and infrared spectroscopy

	Microwave[a]	Infrared[c]	Infrared[d]	Ab initio[d]	
				3-21G	6-31G*
Torsional frequency (*trans*)	130 ± 15	127	118.90	127	
Torsional frequency (*cis*)	~49 (assumed)	49.5	52.06	34	
	60 ± 10[b]				
V_1 potential constant	−252	−277	86 ± 11		
V_2 potential constant	1511	1067	946 ± 33		
V_3 potential constant	682	661	407 ± 4		
V_4 potential constant	−3		138 ± 20		
V_5 potential constant	−63				
V_6 potential constant			−14 ± 7		
trans to *cis* barrier	> 879	1329	1297 ± 26	1533 (1502)[f]	1446 (1435)
cis to *trans* barrier	> 560	~1000	803 ± 26	1057 (886)	1264 (1130)
Enthalpy difference	318 ± 35	350 ± 105	494 ± 48[e]	476 (616)	182 (305)

[a] Values taken from ref. 1. [b] Values taken from ref. 2. [c] Values taken from ref. 3. [d] This study. [e] Value is from the potential function. The experimentally determined value is 456 ± 32 cm^{-1}. [f] Values in parentheses refer to parameters calculated using MP2/3-21//3-21G or MP2/6-31G*//6-31G* calculations (see text).

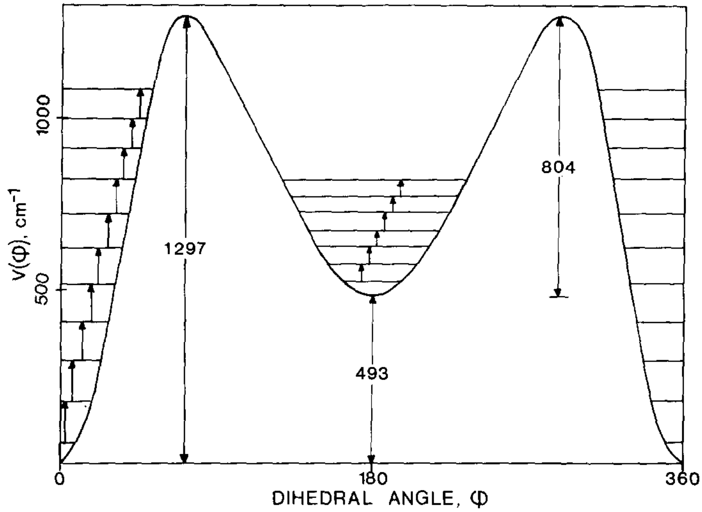

Fig. 5. Asymmetric torsional potential function for fluoroacetyl fluoride as determined from far infrared spectral data. The dihedral angle of 0° corresponds to the *trans* conformer.

shown in Fig. 5 with the *trans* to *cis* barrier having a value of 1297 ± 26 cm^{-1} (3.71 ± 0.07 kcal mol^{-1}) and the *cis* to *trans* barrier a value of 803 ± 26 cm^{-1} (2.30 ± 0.07 kcal mol^{-1}).

VIBRATIONAL ASSIGNMENT

Although the presently reported vibrational assignment (Table 4) is in reasonable agreement with those previously reported [3,4] a number of differences are present in the regions where the CH_2 deformations, C–C stretch, and low-frequency skeletal bending fundamentals are expected to be observed. The assignments in these regions of the spectrum were facilitated by the Raman spectrum of the gas, which has not been previously reported.

A sharp *Q* branch observed in the Raman spectrum of the gas at 1445 cm^{-1} has been assigned, consistent with the previous studies [3,4], to the CH_2 deformation of both conformers. Also present in the Raman spectrum of the gas, in this frequency region, is a relatively weak line at 1400 cm^{-1}. This frequency coincides with an *A*-type band in the infrared spectrum of the gas and is assigned to the CH_2 wagging motion of the *trans* conformer. The corresponding fundamental for the *cis* rotamer is assigned to the *A*-type band observed at 1376 cm^{-1}. We have assigned the A'' CH_2 twisting motion to the only apparent *C*-type band observed between 1400 and 1200 cm^{-1}, at 1257 cm^{-1}, which corresponds to the depolarized Raman line observed at 1253 cm^{-1}.

The A'' CH_2 rocking mode of the *trans* conformer was previously [4] assigned to an infrared band observed at 872 cm^{-1} in the spectrum of the gas.

TABLE 4

Observed[a] infrared and Raman frequencies (cm^{-1}) and vibrational assignment for fluoroacetyl fluoride

Infrared				Raman						Assignment	
Gas	Rel. int.	Solid	Rel. int.	Gas	Rel. int.	Liquid	Rel. int. & depol.	Solid	Rel. int.	ν_i[b]	Approximate description
2981 *Q*,*C*	m	3010	s	2986	vw	3000	sh,dp	3007	s	ν_{11}	CH_2 antisymm. stretch
		2980	m	2969	w			2978	w		
2965 *R*											
2955 *Q*,*A*	m	2964	s	2955	vs	2961	vs,p	2960	vs	ν_1	CH_2 symm. stretch
2948 *P*											
				2936	w						
2883 *R*											
2875 min,*B*				2876	w	2860	w,p	2856	w		$2\nu_3$
								1889	w		$\nu_{13}+\nu_7$
1904 *R*											
1898 min,*B*	vs	1870	vs	1899	s	1870	s,p	1865	s	ν_2	CO stretch
								1854	sh		
1872 *R*											
1865 *Q*,*A*	vs			1865	m	1854	sh,p			ν_2'	CO stretch
1858 *P*											
		1825	w					1826	vw		
1453 *R*											
1445 *Q*,*A*/*B*	m	1435	s	1445	m	1438	s,p	1432	s	ν_3	CH_2 def.
1408 *R*											
1401 *Q*,*A*	m	1402	s	1400	vw	1400	vw,p	1400	w	ν_4	CH_2 wag
1390 *P*		1392	s								
		1388	s								
1376 *Q*,*A*	m									ν_4'	CH_2 wag
1370 *P*											
1300 *R*											
1295 min,*B*	w										
1786 *P*											
1257 *Q*,*C*	s	1257	s	1261	bd,vw	1253	m,dp	1257	m	ν_{12}	CH_2 twist
1238 *R*											
1232 min,*B*	s			1240	vw					ν_5'	C(O)F stretch
1224 *P*											
1157 *R*											
1148 *Q*,*A*	s			1146	vw					ν_6'	H_2C-F stretch
1130 *R*								1129	sh		
1123 *Q*,*A*	s	1133	vs	1136	vw	1138	m,dp,(?)	1125	m	ν_5	C(O)F stretch
1102 *R*											
1096 *Q*,*A*	vs	1070	vs	1098	vw	1073	m,p	1075	w	ν_6	H_2C-F stretch
1093 *Q*											
1085 *P*											
		1044	sh					1049	w		$\nu_7+\nu_{15}$
1030 *Q*,*C*	w	1022	s			1022	vw,dp	1023	w	ν_{13}	CH_2 rock
		1016	s								
		1010	s								
		912	w			910	w,p	912	vw		$2\nu_9$
880 *R*											

TABLE 4 (continued)

Infrared				Raman						Assignment	
Gas	Rel. int.	Solid	Rel. int.	Gas	Rel. int.	Liquid	Rel. int. & depol.	Solid	Rel. int.	ν_i[b]	Approximate description
875 Q,A	s	878	s	872	s	874	s,p	876	s	ν_7	C–C stretch
864 P											
840 *R*											
832 min,*B*	s			833	m	828	m,p			ν'_7	C–C stretch
827 *P*											
				802	vw			807	vw		impurity
		798	vw								$\nu_{14}+\nu_{10}$
768 *Q*	vvw							817	vw		$\nu_8+\nu_{15}$
				682	vw						
663 *R*								649	m		
655 *Q,A/B*	s	642	vs	654	w	643	m,p	638	m	ν_8	C(O)F def.
650 *P*											
638 *R*											
630 *Q,A*	s			633	vw					ν'_8	C(O)F def.
620 *P*											
624 *Q*	sh			624	vw						hot band
						575	vw,p				$\nu_{10}+\nu_{14}$
541 *Q,C*	m									ν'_{14}	C(O)F wag
536 *Q*											
528 *Q,C*	m	536	s			534	vw,dp	532	w	ν_{14}	C(O)F wag
510 *Q*	sh					520	vw,p				$2\nu_{10}$
499 *Q,A*	sh			500	vw					ν'_9	C(O)F rock
460 *R*											
452 *Q,A*	w	454	s	454	s	457	s,p	458	s	ν_9	C(O)F rock
446 *P*											
370 *Q*	vw					423	vw				$\nu_{10}+\nu_{15}$
305 *Q*	vw										$\nu'_{10}+\nu'_{15}$
260 *R*											
252 min,*B*	s	265	s	252	vw	264	w	263	w	ν_{10}, ν'_{10}	$(CH_2)F$–C–C bend
245 *P*											
200 *Q*											$\nu'_{10}-\nu'_{15}$
118 *Q,C*	s	175	bd,vs					174	bd,vw	ν_{15}	asymm. torsion
65 *R*											
52 *Q,C*	s									ν'_{15}	asymm. torsion
30 *P*											

[a] Abbreviations used: s, strong; m, moderate; w, weak; v, very; sh, shoulder; bd, broad; p, polarized, dp, depolarized; min, minimum; *P*, *Q*, and *R* refer to vibrational-rotational branches; *A*, *B* and *C* refer to infrared band contours.

[b] ν'_i refers to the assignments made for the *cis* conformer.

This band, however, is coincident with a sharp *Q* branch occurring at 875 cm^{-1} in the Raman spectrum of the gas and therefore must arise from a fundamental of *A'* symmetry and is presently assigned to the C–C stretch. We believe that a more reasonable assignment for the CH_2 rocking mode is to the C–type band at 1030 cm^{-1} in the infrared spectrum of the gas. This band coincides with a depolarized line observed at 1022 cm^{-1} in the Raman spectrum of the liquid

TABLE 5

Sum and difference bands (cm^{-1}) arising from the asymmetric torsion of the *cis* conformer of fluoroacetyl fluoride with the skeletal bend observed at 252.65 cm^{-1}

ν_{sum}	ν_{diff}	$\nu_{sum}-\nu_{ref}$	$\nu_{ref}-\nu_{diff}$	$\Delta\nu^{a}$	$\nu_{obs}{}^{b}$	$\Delta\nu^{c}$
304.75	200.55	52.10	52.10	0.00	52.06	−0.04
304.40	201.65	51.75	51.00	−0.75	51.04	0.04
304.06	-[d]	51.41	-	-	50.09	-
303.75	203.45	51.10	49.20	−1.90	48.59	−0.61
302.55	205.75	49.90	46.90	−3.00	46.35	−0.55

[a] Defined as $(\nu_{ref}-\nu_{diff})-(\nu_{sum}+\nu_{ref})$.
[b] Frequencies observed from far infrared spectrum, see Table 1.
[c] Defined as $\nu_{obs}-(\nu_{ref}-\nu_{diff})$.
[d] This band was obscured by the water band occurring at 202.7 cm^{-1}.

which supports the assignment of this band to an A'' mode. The assignments of the remaining skeletal stretching modes are consistent with both of the previously reported studies [3,4], although the observed frequencies somewhat differ.

Finally, for each conformer, we expect to observe four skeletal bending motions in the region between 700 and 200 cm^{-1}. The three A' fundamentals arising from the more stable *trans* can be assigned from the Raman spectrum of the gas to the Q branches occurring at 654, 454, and 252 cm^{-1} which correspond to the C(O)F deformation, C(O)F rock and the $(CH_2)FCC$ bend, respectively. For the *cis* rotamer the C(O)F deformation and C(O)F rock are observed as A-type shoulders at 630 and 499 cm^{-1}, respectively, in the infrared spectrum of the vapor. The $(CH_2)FCC$ bend for the *cis* conformer is degenerate, or very nearly so, with the corresponding fundamental of the *trans* form. This degeneracy can easily be verified via the sum and/or difference bands observed between this fundamental and the asymmetric torsion of each conformer. For the *cis* conformer a complete analysis of the sum and difference bands of ν'_{10} with ν'_{15} is summarized in Table 5. For the *trans* rotamer only the sum bands were clearly observable and are readily apparent at ~370 cm^{-1} in Fig. 1A. The C(O)F wag for the *trans* and *cis* conformers has been observed in the mid-infrared spectrum of the gas as C-type Q branches occurring at 528 and 541 cm^{-1}, respectively.

Although the assignment of the fundamental asymmetric torsional modes to the strong C-type Q branches occurring at 118.90 and 52.06 cm^{-1} in the far infrared spectrum of the vapor for the *trans* and *cis* conformers, respectively, has been addressed (Table 2) the corresponding assignments for the liquid and solid phases require some comment. A band occurring at 171 cm^{-1} in the infrared spectrum of the liquid was previously assigned [4] to the FCC bend of the less stable *cis* rotamer. This band apparently corresponds to the frequency of 175 cm^{-1} which we have observed in the far infrared spectrum of the annealed solid (Fig. 1B). Based on its persistence in the spectrum of the annealed solid we believe a more reasonable assignment to this feature would be to the asymmetric torsional mode of the more stable *trans* conformer.

AB INITIO CALCULATIONS

The LCAO-MO-SCF restricted Hartree–Fock calculations were performed with the programs [13] GAUSSIAN-82 using Gaussian-type basis functions. The energy minima with respect to the nuclear coordinates were obtained by the simultaneous relaxation of all geometric parameters using the gradient method of Pulay [14]. The use of the previously determined [2] mixed r_0/r_s structures for both the *trans* and *cis* conformations in the initial calculations was found to significantly reduce the computer time which was required to reach geometry optimization. For comparative purposes both 3-21G and 6-31G* basis sets were employed.

Structural parameters

Except for the methylene C–F and C–C distances, trends in the structural parameters between the two conformers established from the microwave investigation [2] compare remarkably well with the ab initio results (Table 6). For example, in the *trans* conformer the proximity of the methylene fluorine atom to the oxygen atom gives rise to a repulsion between these atoms. The result of this repulsion is an opening of the CCO angle for the *trans* rotamer as opposed to the *cis* form where this repulsive force is minimized. Similarly, both of the FCC angles and the C–C bond distance have been determined to be larger in the *cis* conformer than in the *trans* conformer in order to minimize the repulsive energy arising from eclipsing of the two fluorine atoms in the high energy *cis* conformation. However, it is clear from these ab initio data that there is a problem with the value of the C–C bond distance for the *trans* conformer obtained from the microwave data [2]. Although the absolute values for the C–C bond distances obtained from the ab initio calculations may be in error by a significant amount (~0.01 Å) the relative values for this parameter between the two conformers should be quite accurate. At the 6-31G* level the C–C bond distance is calculated to be 0.006 Å longer for the *cis* conformer whereas this difference is 0.024 Å from the values obtained from the microwave data [2]. Therefore the C–C distance of 1.483 Å reported from the microwave study for the *trans* conformer is undoubtedly too short.

Conformational stability

In order to calculate the energy difference between the two rotamers of fluoroacetyl fluoride, structural parameters were initially optimized at the *trans*

TABLE 6

Comparison of structures (bond lengths in Å, bond angles in degrees), rotational constants (MHz) and dipole moments (D) obtained for the *trans* and *cis* conformers of fluoroacetyl fluoride by microwave spectroscopy and ab initio calculations

Parameter	Microwave				Ab initio			
	trans (r_2)[a]	*trans* (r_s)	*cis* (r_s)[a]	*cis* (r_0)	3-21G		6-31G*	
					trans	*cis*	*trans*	*cis*
r(C=O)	1.194 ± 0.013	1.183 ± 0.005	1.195 ± 0.005	1.188 ± 0.008	1.177	1.183	1.163	1.168
r(C-F)	1.351 ± 0.014	1.350 ± 0.008	1.322 ± 0.016	1.333 ± 0.008	1.358	1.342	1.324	1.309
r(C-C)	1.483 ± 0.007	1.508 ± 0.007	1.507 ± 0.007	1.513 ± 0.008	1.495	1.503	1.504	1.510
r(H_2C-F)	1.366 ± 0.007	1.367 ± 0.007	1.362 ± 0.010	1.369 ± 0.008	1.388	1.388	1.348	1.352
r(C-H)	1.096 ± 0.003	1.092 ± 0.001	1.097 ± 0.007	1.108 ± 0.004	1.079	1.079	1.082	1.081
∠ (C-C=O)	129.9 ± 0.7	129.5 ± 0.5	123.8 ± 0.9	124.1 ± 0.8	131.0	125.2	129.0	124.1
∠ (C-C-F)	110.3 ± 0.5	108.6 ± 0.3	112.3 ± 0.5	113.4 ± 0.9	109.0	110.3	109.8	111.6
∠ (H_2C-C-F)	109.6 ± 1.0	110.1 ± 0.2	113.8 ± 0.5	112.6 ± 0.7	107.4	113.0	108.8	113.4
∠ (C-C-H)	109.2 ± 0.4	109.5 ± 0.3	108.5 ± 1.1	107.1 ± 0.7	108.9	108.7	109.0	108.4
∠ (H-C-H)	109.0 ± 0.4	108.2 ± 0.2	109.1 ± 1.3	112.3 ± 0.4	108.7	108.6	108.9	109.0
A	10508.906		10223.84		10482	10253	10826	10528
B	3855.06		4110.53		3882	4184	3944	4212
C	2870.71		2991.99		2883	3027	2944	3066
μ_a	0.456 ± 0.01		1.18 ± 0.03		0.45	1.26	0.35	1.46
μ_b	2.63 ± 0.05		1.68 ± 0.04		3.14	2.32	3.09	1.56
μ_c	0.0		0.0		0.0	0.0	0.0	0.0
μ_t	2.67 ± 0.05		2.05 ± 0.06		3.17	2.64	3.11	2.14
$-E$ (hartree)					348.7077136	348.7055425	350.6355218	350.6346990

[a] Values of bond lengths, bond angles and rotational constants are taken from ref. 2 and dipole moments are from ref. 1.

and the *cis* positions. Although both basis sets predict the *trans* conformation to be of lower energy the values of the energy difference between the two conformations are quite different. The 6-31G* basis set predicts the *trans* conformer to be more stable than the *cis* form by 182 cm^{-1} (520 cal mol^{-1}) while an even greater stability of 476 cm^{-1} (1361 cal mol^{-1}) is calculated using the 3-21G basis set. Thus, the smaller basis set gives an energy difference in better agreement with the experimental value of 456 ± 32 cm^{-1} than does the larger basis set. These theoretical results are compared with the experimental values in Table 3.

These two basis sets were also used to predict the potential surfaces for internal rotation. The dihedral angle of internal rotation for the CFO moiety was allowed to vary while the structural parameters were held fixed at the optimized values for the more stable, *trans*, conformer. The potential surfaces subsequently obtained predicted the dihedral angle of internal rotation for the only other stable form to be approximately 30° away from that of the *cis* position, i.e. a *gauche* conformation. The potential function obtained from the use of the 6-31G* basis set is shown in Fig. 6 (dashed line). It is not uncommon to find theoretical studies in which the geometries are optimized only at those points on a determined potential surface which occur as minima. If the presently obtained results are handled in this manner a *trans/gauche* potential surface is obtained with a significant *gauche* to *gauche* barrier of 305 cm^{-1} (872 cal mol^{-1}), and a *trans* to *gauche* energy difference of 263 cm^{-1}. On the other hand, if geometry optimization is carried out at the *cis* position it can be shown

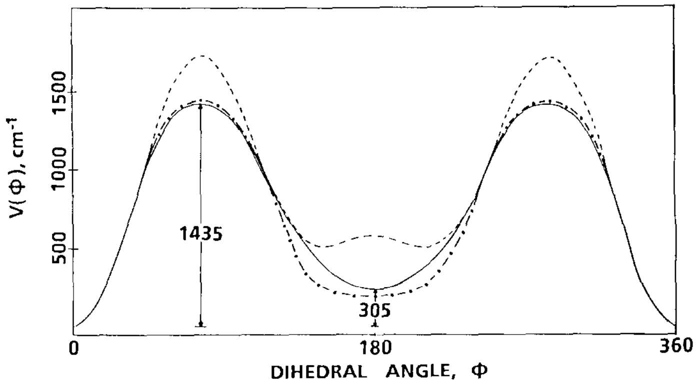

Fig. 6. Potential function governing internal rotation of fluoroacetyl fluoride as determined by ab initio calculations with the 6-31G* basis set. The potential surface given by the dashed line was obtained by allowing the torsional dihedral angle to vary by ten degree increments while all other structural parameters were held fixed at the optimized values obtained for the *trans* conformer. The potential surface given by the dashed-point line was obtained by optimization at the *gauche* minimum and at the transition states by relaxation of all of the geometric parameters. The potential surface given by the bold line was calculated using second order perturbation configuration interaction at all minima and maxima on the surface.

that the energy of this structure optimizes well below that of the *gauche* geometry. Furthermore, as suggested by van Eijck and co-workers [2], we have calculated that the energy involved in geometry relaxation of 386 cm^{-1} (1104 cal mol^{-1}), is greater than the calculated *trans* to *cis* energy difference of 182 cm^{-1}. However, the calculated energy of 386 cm^{-1} involved in geometry relaxation is smaller than the presently determined experimental enthalpy difference of 456 cm^{-1}. Therefore, in agreement with experimental results, the minimum predicted close to the *cis* position has been shown to be false minimum on the potential surface and the *cis* conformer has been established as the only other stable form.

The geometry at the transition state of the *trans* to *cis* barrier was also optimized with the 6-31G* basis set by maximizing the energy with respect to the angle of internal rotation and minimizing the energy with respect to the remaining parameters. Under these conditions, the *trans* to *cis* barrier height is calculated by the 6-31G* set to be 1446 cm^{-1}. The 3-21G basis set gives a barrier height of 1533 cm^{-1} compared to an experimentally obtained *trans* to *cis* barrier of 1297 cm^{-1}.

In an attempt to obtain better agreement between the calculated and experimentally determined values of the energy differences, additional ab initio calculations using perturbation CI calculations of the second order at the MP2 level were also carried out. Using MP2/6-31G*//6-31G* calculations, the energy difference increases to 305 cm^{-1} (872 cal mol^{-1}), while with MP2/3-21G//3-21G this quantity also increases, from 496 to 616 cm^{-1} (1762 cal mol^{-1}). In order to determine the barriers, these additional calculations were also included for the "transition state". The resulting values of 1435 and 1130 cm^{-1} are obtained for the *trans* to *cis* and *cis* to *trans* barriers, respectively, with MP2/6-31G*//6-31G* and the corresponding values with MP2/3-21G//3-21G calculations are 1502 and 886 cm^{-1}, respectively. Although the calcu-

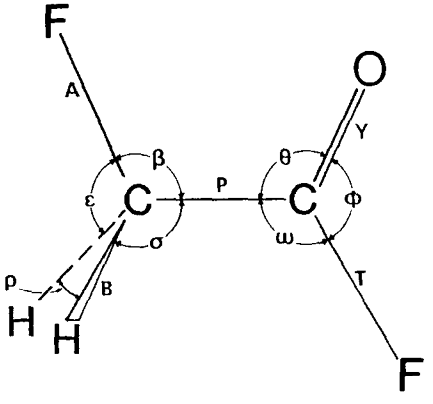

Fig. 7. Internal coordinates for fluoroacetyl fluoride.

TABLE 7

Force constants (mdyn Å^{-1}) for *trans* fluroacetyl fluoride

	A	P	B_1	B_2	Y	T	β	σ_1	σ_2	ϵ_1	ϵ_2	ρ	θ	ω	ϕ	η	τ
A	7.076	0.250	0.157	0.157	0.077	0.059	0.355	−0.295	−0.295	0.244	0.244	−0.270	−0.122	0.134	−0.012	0.000	0.000
P		4.744	0.098	0.098	0.298	0.344	0.210	0.142	0.142	−0.137	−0.137	−0.213	0.103	0.118	−0.221	0.000	0.000
B_1			5.950	0.071	−0.015	0.025	−0.064	0.088	−0.085	0.000	−0.033	0.095	0.023	−0.024	0.001	−0.004	0.038
B_2				5.950	−0.015	0.025	−0.064	−0.085	0.088	−0.033	0.000	0.095	0.023	−0.024	0.001	0.004	−0.038
Y					17.049	1.167	−0.143	0.069	0.069	0.002	0.002	0.004	0.097	−0.369	0.272	0.000	0.000
T						7.050	0.142	−0.016	−0.016	−0.038	−0.038	−0.034	−0.528	0.344	0.194	0.000	0.000
β							0.942	−0.160	−0.160	−0.222	−0.222	−0.184	−0.123	0.149	−0.026	0.000	0.000
σ_1								0.712	−0.116	−0.069	−0.234	−0.119	0.068	−0.066	−0.003	0.096	−0.040
σ_2									0.712	−0.234	−0.069	−0.119	0.068	−0.066	−0.003	−0.096	0.040
ϵ_1										0.927	0.317	−0.097	−0.001	−0.009	0.010	0.017	−0.124
ϵ_2											0.927	−0.097	−0.001	−0.009	0.010	−0.017	0.124
ρ												0.616	−0.009	−0.003	0.012	0.000	0.000
θ													0.597	−0.198	−0.399	0.000	0.000
ω														0.704	−0.506	0.000	0.000
ϕ															0.905	0.000	0.000
η																0.562	0.004
τ																	0.104

TABLE 8

Force constants (mdyn Å^{-1}) for *cis* fluoroacetyl fluoride

	A	P	B_1	B_2	Y	T	β	σ_1	σ_2	ϵ_1	ϵ_2	ρ	θ	ω	ϕ	η	τ
A	7.039	0.249	0.156	0.156	0.082	0.100	0.312	−0.290	−0.290	0.252	0.252	−0.260	0.139	−0.128	−0.011	0.000	0.000
P		4.701	0.097	0.097	0.426	0.192	0.311	0.127	0.127	−0.166	−0.166	−0.234	0.039	0.226	−0.265	0.000	0.000
B_1			5.951	0.073	0.006	0.005	−0.063	0.060	−0.062	0.025	−0.054	0.097	−0.019	0.022	−0.003	−0.032	0.035
B_2				5.951	0.006	0.005	−0.063	−0.062	0.060	−0.054	0.025	0.097	−0.019	0.022	−0.003	0.032	−0.035
Y					16.638	1.149	0.142	−0.024	−0.024	−0.033	−0.033	−0.031	0.167	−0.384	0.217	0.000	0.000
T						7.504	−0.126	0.068	0.068	0.002	0.002	−0.011	−0.467	0.187	0.280	0.000	0.000
β							1.010	−0.177	−0.177	−0.238	−0.238	−0.196	0.080	−0.019	−0.061	0.000	0.000
σ_1								0.712	−0.112	−0.073	−0.222	−0.115	−0.045	0.040	0.004	−0.009	−0.008
σ_2									0.712	−0.222	−0.073	−0.115	−0.045	0.040	0.004	0.009	0.008
ϵ_1										0.816	−0.200	−0.093	−0.001	−0.016	0.017	0.036	−0.380
ϵ_2											0.816	−0.93	−0.001	−0.016	0.017	−0.036	0.380
ρ												0.623	0.009	−0.029	0.020	0.000	0.000
θ													0.642	−0.225	−0.417	0.000	0.000
ω														0.738	−0.503	0.000	0.000
ϕ															0.920	0.000	0.000
η																0.650	−0.074
τ																	0.017

TABLE 9

Symmetry coordinates for fluoroacetyl fluoride

A′ Species	
CH_2 symmetric stretch	$S_1 = B_1 + B_2$
C=O stretch	$S_2 = Y$
CH_2 deformation	$S_3 = (\sqrt{6}+2)\rho - (\sqrt{6}-2)\beta - \sigma_1 - \sigma_2 - \epsilon_1 - \epsilon_2$
CH_2 wag	$S_4 = \sigma_1 + \sigma_2 - \epsilon_1 - \epsilon_2$
C-F_7 stretch	$S_5 = T$
C-F_1 stretch	$S_6 = A$
C-C stretch	$S_7 = P$
FCO deformation	$S_8 = \theta + \omega - 2\phi$
F_7CO rock	$S_9 = \theta - \omega$
CCF_1 bend	$S_{10} = (\sqrt{6}-2)\rho - (\sqrt{6}+2)\beta + \sigma_1 + \sigma_2 + \epsilon_1 + \epsilon_2$
redundancy	$S_{1R} = \theta + \omega + \phi$
redundancy	$S_{2R} = \beta + \sigma_1 + \epsilon_1 + \sigma_2\epsilon_2 + \rho$
A″ Species	
CH_2 antisymmetric stretch	$S_{11} = B_1 - B_2$
CH_2 twist	$S_{12} = \sigma_1 - \sigma_2 - \epsilon_1 + \epsilon_2$
CH_2 rock	$S_{13} = \sigma_1 - \sigma_2 + \epsilon_1 - \epsilon_2$
FCO wag	$S_{14} = \eta$
torsion	$S_{15} = \tau$

lated energy difference between the two conformers is much improved, the calculated barrier values are not significantly different from those calculated without correlation interaction.

Normal coordinate analysis

In order to obtain a more complete description of the molecular motions involved in the normal modes of fluoroacetyl fluoride we have carried out a normal coordinate analysis. This analysis was performed utilizing ab initio calculations and the Wilson matrix method [15] with the computer program written by Schachtschneider [16]. The force field in Cartesian coordinates was calculated by the GAUSSIAN-82 program [13] with the 3-21G basis set. Seventeen internal coordinates (Fig. 7) were used to calculate the **G** matrix using the structural parameters obtained with the 3-21G basis set (Table 6). The force field in Cartesian coordinates was then converted to a force field in the internal coordinates (Tables 7 and 8). Initially, all scaling factors were kept fixed at a value of 1.0 to reproduce the pure ab initio calculated vibrational frequencies. Subsequently, scaling factors of 0.9 for stretching coordinates, 0.8 for bending coordinates, and 1.0 for C(O)F wagging and torsional coordinates, and the geometric average of scaling factors [17] for interaction force con-

TABLE 10

Comparison of observed and calculated frequencies (cm^{-1}) for the *trans* conformer of fluoroacetyl fluoride

	Fundamental	Ab initio[a]	Fixed scale[b]	Observed[c]	PED
A'					
ν_1	CH_2 symmetric stretch	3263	3096	2955	$100S_1$
ν_2	C=O stretch	2081	1972	1898	$86S_2$
ν_3	CH_2 deformation	1663	1488	1445	$97S_3$
ν_4	CH_2 wagging	1555	1399	1401	$81S_4$
ν_5	(O)C-F stretch	1280	1198	1123	$57S_5$,$17S_8$,$15S_7$
ν_6	(H_2)C-F stretch	1215	1148	1096	$91S_6$
ν_7	C-C stretch	938	880	875	$53S_7$,$17S_5$,$14S_{10}$
ν_8	C(O)F deformation	693	626	655	$57S_8$,$19S_{10}$,$12S_5$
ν_9	C(O)F rock	478	434	452	$30S_9$,$29S_8$,$19S_7$,$15S_{10}$
ν_{10}	CCF bend	244	218	252	$44S_{10}$,$50S_9$
A''					
ν_{11}	CH_2 antisymmetric stretch	3307	3137	2981	$99S_{11}$
ν_{12}	CH_2 twist	1370	1228	1257	$94S_{12}$
ν_{13}	CH_2 rock	1165	1073	1030	$70S_{13}$,$20S_{15}$
ν_{14}	C(O)F wag	599	580	528	$66S_{14}$,$27S_{13}$
ν_{15}	asymmetric torsion	128	128	118	$97S_{15}$

[a] Calculated using the 3-21G basis set.

[b] Calculated using scaling factors at 0.9 for stretches, 0.8 for bends, and 1.0 for C(O)F wag and torsion.

[c] Frequencies are from the spectrum of the gas.

stants were used to obtain the "fixed scale" force field and resultant frequencies. Seventeen symmetry coordinates were used (Table 9) to determine the corresponding potential energy distributions (PED) which are given in Tables 10 and 11.

For the unscaled force fields the frequencies calculated for the in-plane modes were found to be 3 to 15% higher than the experimental frequencies for both conformers, except for the CCF bend of the *trans* conformer which was predicted to be 3% lower. The out-of-plane frequencies were calculated to be 9 to 13% higher than the observed frequencies with the exception of the torsional fundamental for the *cis* conformer which was predicted to be 34% lower. After scaling the "average" overall frequency fit was improved to 5% for the *trans* and 6% for the *cis* conformers. The major use of such calculations is to establish a limited range for specific normal modes and to give a reasonable estimate for the potential energy distribution for the normal modes.

TABLE 11

Comparison of observed and calculated frequencies (cm^{-1}) for the *cis* conformer of fluoroacetyl fluoride

	Fundamental	Ab initio[a]	Fixed scale[b]	Observed[c]	PED
A'					
ν_1	CH_2 symm. stretch	3264	3097	2955	$100S_1$
ν_2	C=O stretch	2043	1935	1865	$86S_2$
ν_3	CH_2 def.	1660	1485	1445	$98S_3$
ν_4	CH_2 wagging	1538	1379	1376	$89S_4$
ν_4	(O)C-F stretch	1378	1296	1232	$50S_5,26S_7,15S_8$
ν_5	(H_2)C-F stretch	1205	1137	1148	$83S_6$
ν_6	C-C stretch	899	847	832	$47S_7,36S_5$
ν_7	C(O)F def.	665	598	630	$62S_8,26S_{10}$
ν_8	C(O)F rock	522	475	499	$41S_9,19S_7,17S_{10},15S_8$
ν_9	CCF bend	260	233	252	$46S_{10},50S_9$
ν_{10}					
A''					
ν_{11}	CH_2 antisymm. stretch	3307	3137	2981	$100S_{11}$
ν_{12}	CH_2 twist	1378	1243	1257	$98S_{12}$
ν_{13}	CH_2 rock	1151	1056	1030	$83S_{13},15S_{14}$
ν_{14}	C(O)F wag	614	592	541	$72S_{14},21S_{13}$
ν_{15}	asymm. torsion	34	34	52	$66S_{15},26S_{14}$

[a] Calculated using the 3-21G basis set.

[b] Calculated using scaling factors of 0.9 for stretches, 0.8 for bends, and 1.0 for C(O)F wag and torsion.

[c] Frequencies are from the spectrum of the gas.

DISCUSSION

Fluoroacetyl fluoride exists as two rotameric forms in the vapor and liquid states and this conclusion is consistent with the previously reported studies of the rotational [1,2] and vibrational [3,4] spectra. The *cis* conformer is in about 20% abundance at ambient temperature and although this percentage appears to be high in consideration of the experimental enthalpy difference (456 cm^{-1} for the gas) the entropy change between the conformers is presently determined to be rather large (1.64 e.u. for the gas). Using statistical thermodynamics, it can be shown that this entropy change is almost entirely due to the difference in the frequency values of the asymmetric torsional fundamentals.

As pointed out earlier, the C–C bond distance determined by microwave spectroscopy [2] for the *trans* form is extremely short (1.483 Å) whereas a reasonable value (1.507 Å) was obtained for the *cis* form. Additionally, the methylene C–F distance does not follow the trend given by the ab initio calculations between the two conformers. The determination of an unreasonably short C–C bond distance for the *trans* conformer and a rather short (O)C–F bond distance in the *cis* conformer can, at least in part, be attributed to the very small substitution coordinates of the sp^2 carbon atoms in both conformations. We have, therefore, determined an r_0 structure compatible with the previously reported rotational constants for each conformation using a newly developed program [18]. It consists of direct iterative adjustments of structural parameters to the observed rotational constants.

The calculations of the r_0 structure for the *trans* form presented no difficulties. As input to the program, we utilized the previously reported r_s values except for the C–C bond distance which was taken as the value from the ab initio calculations. The presently determined values agree fairly well with the previously published r_s values, with the exception of the C=O and C–C bond distances (Table 12). Our value of 1.183 Å for the C=O distance is slightly smaller than the r_s value of 1.194 Å; however, it is still within the reported uncertainty. The presently determined value of 1.508 Å for the C–C bond distance is a more reasonable value. However, it should be noted that there is a very high correlation between the (O)C–F bond and the C–C bond distances, as expected.

For the *cis* rotamer, on the other hand, there were difficulties in the determination of the r_0 structure using the published rotational constants. We subsequently noticed the discrepancies between the substitution coordinates for the hydrogen atoms derived from "single" and "double" substitution. Therefore, a decision was made to incorporate the rotational constants obtained for the d_1 and d_2 derivatives with very low weighings in the determination of the structural parameters. Additionally, we fixed the C=O bond distance at 1.185 Å, which is only slightly larger than the value obtained for this parameter for the *trans* conformer. This action seemed prudent since there is a very high level of correlation of the C–C, (O)C–F, and C=O bond distances. The determined values were not significantly different from the r_s values previously reported [2] except the carbonyl bond was 0.010 Å shorter and the (O)C–F bond was found to be 0.025 Å longer than the r_s value. Also it appeared that the ∠CCH of 105.0° is entirely too small, which in turn leads to an angle of 116.1° for the ∠HCH parameter which is certainly too large. The fit to the rotational constants was quite good except for A and C of the d_1 and d_2 species. By gradually increasing the weight for these rotational constants we obtained a satisfactory fit (2 MHz) but the fit for the other rotational constants were significantly degraded (0.6 MHz) and the C–H distance appeared to be too long, i.e., 1.106 Å. Additionally, the C–C bond distance was 1.501 Å which is too short compared to the ab initio calculations. We concluded that the parameters determined holding the C=O distance constant were unsatisfactory.

At this point we then let all parameters vary but placed fairly large uncertainties on the reported rotational constants for each successive isotopic spe-

TABLE 12

Diagnostic least-squares adjustment of the structural parameters of *trans* and *cis*-fluoroacetyl fluoride

Parameter	*trans*		*cis*	
	Initial value	Adjusted value	Initial value	Adjusted value
r(C–C) (Å)	1.504 ± 0.010	1.508 ± 0.007	1.513 ± 0.010	1.508 ± 0.006
r(C–F) methylene (Å)	1.366 ± 0.010	1.367 ± 0.007	1.368 ± 0.010	1.366 ± 0.004
r(C–H Å)	1.096 ± 0.010	1.092 ± 0.001	1.092 ± 0.010	1.093 ± 0.009
r(C=O Å)	1.194 ± 0.010	1.183 ± 0.005	1.185 (fixed)	1.185
r(C–F) carbonyl (Å)	1.351 ± 0.010	1.350 ± 0.008	1.357 ± 0.010	1.347 ± 0.005
∠ (CCF) methylene (deg.)	110.30 ± 3.00	110.09 ± 0.22	109.97 ± 3.00	112.96 ± 0.20
∠ (CCH) (deg.)	109.20 ± 3.00	109.52 ± 0.34	109.66 ± 3.00	105.04 ± 2.06
∠ (CCO) (deg.)	129.90 ± 3.00	129.52 ± 0.52	126.12 ± 3.00	124.71 ± 0.36
∠ (CCF) carbonyl (deg.)	109.60 ± 3.00	108.56 ± 0.34	115.29 ± 3.00	113.28 ± 0.21
∠ (dih. HCCF) methylene (deg.)	120.45 ± 3.00	120.73 ± 0.23	120.63 ± 3.00	118.52 ± 0.98

Molecule	Rotational constant	*trans*			*cis*		
		Obs.	Cal.	Δ	Obs.	Calc.	Δ
$^{12}CH_2F^{12}CF^{16}O$	A	10508.90	10509.52	−0.62	10223.84	10224.66	−0.82
	B	3855.06	3855.26	−0.20	4110.53	4111.17	−0.64
	C	2870.71	2871.11	−0.40	2992.00	2991.24	0.76
$^{12}CH_2F^{12}CF^{18}O$	A	9817.68	9817.37	0.32	10054.38	10054.50	−0.12
	B	3834.78	3834.54	0.24	3936.10	3936.53	−0.43
	C	2805.59	2805.78	−0.19	2884.72	2883.87	0.85
$^{13}CH_2F^{12}CF^{16}O$	A	10397.78	10397.68	0.10	10094.64	10094.75	−0.11
	B	3839.62	3839.51	0.11	4092.93	4093.60	−0.67
	C	2853.86	2854.01	−0.15	2971.71	2970.78	0.93
$^{12}CH_2F^{13}CF^{16}O$	A	10505.37	10505.10	0.28	10222.16	10222.23	−0.07
	B	3848.17	3848.01	0.16	4098.17	4098.57	−0.40
	C	2866.63	2866.76	−0.13	2985.30	2984.36	0.94
$^{12}CD_2F^{12}CF^{16}O$	A	9486.89	9486.92	−0.04	9188.80	9187.05	1.75
	B	3778.04	3778.35	−0.32	4015.42	4015.10	0.32
	C	2796.99	2796.41	0.58	2901.97	2903.15	−1.18
$^{12}CHDF^{12}CF^{16}O$	A	9967.70	9967.88	−0.18	9672.06	9673.33	−1.27
	B	3817.73	3817.74	−0.01	4065.36	4064.35	1.01
	C	2832.29	2832.26	0.03	2944.53	2945.32	−0.79

cies. There was no indication that any one particular set of rotational constants was in error. At this point, we utilized the reported [2] experimental uncertainties of all of the rotational constants and the r_0 parameters reported in Table 12 were obtained. All of the heavy atom parameters appear to be very reasonable and they follow the trends relative to the corresponding values for the *trans* conformer as predicted from the ab initio calculations. However, the C–H distance seems too long and the ∠HCH is probably too large.

One is then left with r_0 structural parameters for the *cis* conformer which are not totally satisfactory. It is possible that the reported [2] rotational constants for two of the species are for excited states or, alternatively, that the very low frequency for the asymmetric torsion has led to an unusually large anharmonicity. It would be interesting to carry out an electron diffraction study of this molecule to see if better structural parameters could be obtained by this technique.

The interatomic distance between the fluorine atom on the methylene moiety and the oxygen atom is slightly larger than the sum of the atomic radii of the two atoms for the *trans* conformer. For the *cis* form, however, the interatomic distance between the two fluorine atoms is considerably less than the sum of the radii of the two fluorine atoms. To partially relieve this steric strain the bond distances are elongated and the appropriate angles are opened.

The ab initio calculations at the 3-21G and the 6-31G* basis set are consistent with spectroscopic data in the determination of the conformational equilibrium. The barriers calculated at the 3-21G level are consistently higher than those determined from far infrared spectral data. However, the resulting energy difference obtained is in excellent agreement with the experimentally measured value. With the 6-31G* basis set, the same is true for the *trans* to *cis* barrier; however, the *cis* to *trans* barrier is calculated to be considerably higher than the corresponding quantity from the experimentally determined potential function. This results from the value of the energy difference between the two isomeric forms which was calculated to be considerably lower than that determined experimentally (182 cm^{-1} compared to 456 cm^{-1}). In fact, for many small molecules for which we are currently carrying out ab initio calculations, the energy differences between the predicted stable conformations have been calculated to differ by as much as 50% from the experimentally determined values. However, since the energy differences between the conformers are reasonably small, one cannot expect to obtain results which agree any better with the experimental values. Therefore, the present use of the larger basis set (6-31G*), as opposed to the smaller one (3-21G), does not give better agreement between the calculated and the experimentally obtained energy difference.

The calculated frequencies of the normal modes from the ab initio force fields are consistently and systematically higher than those observed experimentally. Scaling the force fields in an effort to improve the fit between the predicted and experimental frequencies results in the percentage error in frequencies being reduced to 5% and 6% for the *trans* and *cis* conformers, respectively. A better fit could have been obtained by giving each coordinate a different scaling factor [19,20], but the transferability of the theoretically predicted values to other molecules would then be lost. For each conformer of fluoroacetyl fluoride, the corresponding potential energy distribution among the symmetry coordinates appears to be surprisingly pure, particularly for the normal modes in the A'' symmetry block. For the low frequency modes for the A' symmetry block, some mixing was calculated. This is also true for the C–C and C–F stretches which show about 50% mixing, as expected. Finally, it should be noted that the mixing is somewhat dependent on the chosen symmetry coordinates.

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REFERENCES

1 E. Sagebarth and E.B. Wilson, J. Chem. Phys., 46 (1967) 3088.
2 B.P. van Eijck, P. Brandts and J.P. Maas, J. Mol. Struct., 44 (1978) 1.
3 K.R. Loos, Ph.D. diss., Massachusetts Institute of Technology, Cambridge (1964).
4 A.Y. Khan and N. Jonathan, J. Chem. Phys., 52 (1970) 148.
5 F.A. Miller and B.M. Harney, Appl. Spectrosc., 24 (1970) 291.
6 J.R. Durig, M. Zhen, H.L. Heusel, P.J. Joseph, P. Groner and T.S. Little, J. Phys. Chem., 89 (1985) 2877.
7 J.R. Durig, H.D. Bist and T.S. Little, J. Chem. Phys., 77 (1982) 4884.
8 J.R. Durig, H.D. Bist, S.V. Saari, J.A. Smith and T.S. Little, J. Mol. Struct., 99 (1983) 217.
9 I.M. Watanabe, S. Mizushima and Y. Masiko, Sci. Pap. Inst. Phys. Chem. Res. Jpn., 40 (1943) 425.
10 A. Wada, J. Chem. Phys., 22 (1954) 198.
11 M.V. Vol'kenschtein and V.I. Brevdo, Zh. Fiz. Khim., 28 (1954) 1313.
12 P. Groner, R.D. Johnson and J.R. Durig, J. Mol. Struct., 142 (1986) 363.
13 J.S. Binkley, M.J. Frisch, D.J. DeFrees, K. Raghavachari, R.A. Whiteside, H.B. Schlegel, E.M. Fleuder and J.A. Pople, Gaussian 82, Carnegie Mellon University, Pittsburgh, PA (1984).
14 P. Pulay, Mol. Phys., 17 (1969) 197.
15 E.B. Wilson, Jr., J.C. Decius and P.C. Cross, Molecular Vibrations, McGraw-Hill, New York, NY, 1955.
16 J.H. Schachtschneider, Vibrational Analysis of Polyatomic Molecules, V and VI, Technical Reports No. 231-64 and 57-65, respectively, Shell Development Co., Houston, TX.
17 G. Fogarasi and P. Pulay, in J.R. Durig (Ed.), Vibrational Spectra and Structure, Vol. 14, Elsevier, Amsterdam, 1981, p. 125.
18 P. Groner, J.S. Church, Y.S. Li and J.R. Durig, J. Chem. Phys., 82 (1985) 3894.
19 G. Fogarasi and P. Pulay, J. Mol. Struct., 39 (1977) 275, and references therein.
20 F. Torok, A. Hegedus, K. Kosa and P. Pulay, J. Mol. Struct., 32 (1976) 93.