

Vibrational Spectra and Force Constants for the Perfluorocyclopropenyl Cation

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Abstract: Full vibrational spectra of the perfluorocyclopropenyl cation, $C_3F_3^+$, are reported. These include infrared spectra of polycrystalline deposits of $C_3F_3^+BF_4^-$ and $C_3F_3^+Sb_2F_{11}^-$ and Raman spectra of sulfur dioxide solutions of $C_3F_3^+B_2F_7^-$ and $C_3F_3^+Sb_2F_{11}^-$. Vibrational fundamentals of $C_3F_3^+$ have been assigned as (a_1') 2014, 752; (a_2') [810]; (e') 1590, 999, 287; (a_2'') [240]; (e'') 642 cm^{-1} , where the values in brackets are estimates from calculations. Normal coordinate calculations in which valence field force constants for $C_3FH_2^+$, $C_3F_2H^+$, and $C_3F_3^+$ were simultaneously fitted in a selective overlay procedure gave the following values in $mdyn/\text{\AA}$ for CC stretching constants: $C_3FH_2^+$ 8.33 (two bonds), 7.13 (unique bond); $C_3F_2H^+$ 7.25 (two bonds), 8.57 (unique bond); $C_3F_3^+$ 7.71. These values compare with 7.87 for $C_3H_3^+$ and conform to a pattern of strengthening of CC bonds due to fluorine substitution on a contiguous carbon atom and of weakening of CC bonds due to cross-ring fluorine substitution. In $C_3F_3^+$ these effects cancel out.

Fluorine atom substituents exert a potent influence on the CC bonds in three-carbon ring systems. These substituent effects are seen qualitatively in the vibrational spectra and quantitatively in the empirical force constants fitted by normal coordinate calculations to the vibrational fundamentals. Studies of the vibrational spectra of monofluoro- and difluorocyclopropenyl cations have been published.^{1,2} Work on the vibrational spectroscopy of the cyclopropenyl cation itself and several deuterium isotopomers is nearing completion in our laboratory.^{3,4} In general, substitution of fluorine atoms on $C_3H_3^+$ rings increases the force constants of adjacent CC bonds and decreases the force constants of opposite CC bonds. The present paper reports on the vibrational spectroscopy of the perfluorocyclopropenyl cation.

The same pattern of influence of fluorine substitution on the strength of CC bonds in cyclopropenyl ring systems is found in cyclopropenes and cyclopropanes. 3,3-Difluoro-, 1,3,3-trifluoro-, and perfluorocyclopropene have been investigated in detail.⁵ For 1,1-difluoro-1,1,2,2-tetrafluoro-, and *cis*- and *trans*-1,2-difluorocyclopropanes complete vibrational assignments and fragmentary normal coordinate calculations are available.⁶ In the cyclopropenes and cyclopropanes changes in force constants due to fluorine substitution correlate with changes in bond length and electron density. Thus, in 3,3-difluorocyclopropene the double bond is longer (1.321 \AA vs. 1.296 \AA) and the CC single bonds are appreciably shorter (1.438 \AA vs. 1.509 \AA) than in cyclopropene.⁷ In 1,1-difluorocyclopropane the same pattern is found in the bond length changes: $r_{CC}(\text{opposite}) = 1.553 \text{\AA}$ and $r_{CC}(\text{adjacent}) = 1.464 \text{\AA}$ in comparison with 1.514 \AA in cyclopropane.⁸ In Professor C. W. Gillies' laboratory at Rensselaer microwave studies are nearing completion from which structures of tetrafluorocyclopropane and the *cis*- and *trans*-1,2-difluorocyclopropane will be available.⁹ Ab initio molecular orbital calculations show a decrease in electron density in the CC bond opposite the fluorine-substituted carbon atom in difluorocyclopropane and an increase in electron density in the adjacent CC

bonds in comparison with cyclopropane.¹⁰

At the present time nothing is known directly about bond length changes or bond strength changes due to fluorine substitution in the cyclopropenyl cation. However, it is reasonable to correlate increases in force constants for CC bonds with strengthening and shortening of these bonds and decreases in force constants with weakening and lengthening of these bonds.

Salts of the perfluorocyclopropenyl cation were first prepared by Sargeant and Krespan by reaction of perfluorocyclopropene and the Lewis acids, antimony pentafluoride and boron trifluoride,¹¹ e.g.,



Only the NMR spectrum in SO_2 was reported by these authors. We have used the same reagents and have observed the vibrational spectra of the perfluorocyclopropenyl cation for the first time. The Raman spectrum has been recorded for both the fluoroborate and fluoroantimonate salts in sulfur dioxide solution. Infrared spectra of polycrystalline films of this cation with both fluoroborate and fluoroantimonate counterions have also been obtained. Zero-order normal-coordinate calculations based on force constants transferred from the difluorocyclopropenyl cation have been used to guide some of the assignments of vibrational fundamentals of the $C_3F_3^+$ ion. A selective overlay calculation in which the force constants were simultaneously fitted to the monofluoro-, difluoro-, and perfluorocyclopropenyl cation has been used to obtain reasonably well-defined CC stretching force constants for the $C_3F_3^+$ ion as well as for the $C_3F_2H^+$ and $C_3FH_2^+$ ions. The empirical CC stretching force constants in these various substituted ions are compared with each other and with the empirical force constant for the unsubstituted cyclopropenyl cation.

Earlier West, Sadó, and Tobey prepared the perchlorocyclopropenyl and perbromocyclopropenyl cations and studied these ions by vibrational spectroscopy.¹² We consider the reported CC force constants for the $C_3Cl_3^+$ cation in relation to the ones found in the present study.

Experimental Section

Sample Preparation. Perfluorocyclopropene was prepared from pentafluorocyclopropane and purified as previously described.^{5,11}

Samples of the $C_3F_3^+B_2F_7^-$ salt dissolved in SO_2 for use in both NMR and Raman spectroscopies were prepared in standard 5-mm NMR tubes. On a good vacuum system perfluorocyclopropene was first condensed in the tube followed in order by SO_2 (distilled and P_2O_5 -dried, Matheson

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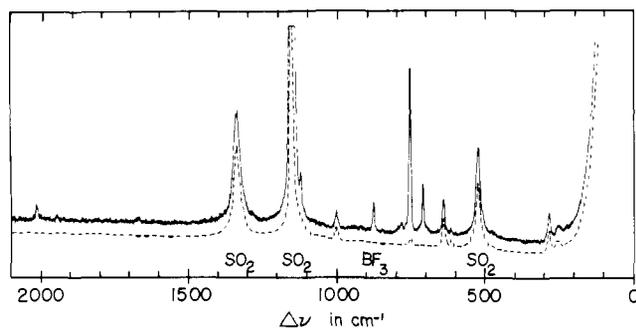


Figure 1. Raman spectrum of 8% $C_3F_3^+B_2F_7^-$ in SO_2 solution at $-30^\circ C$; 160-mW laser power. Solid line: polarization analyzer parallel. Dashed line: polarization analyzer perpendicular. Bands are apparent due to excess BF_3 (2:1) at 875 cm^{-1} and some unconverted C_3F_4 at 1944 , 708 , 614 , and 257 cm^{-1} .

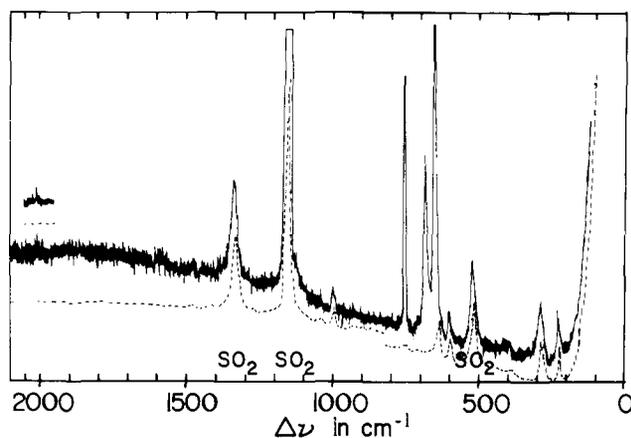


Figure 2. Raman spectrum of 8% $C_3F_3^+Sb_2F_{11}^-$ in SO_2 solution at $-30^\circ C$; 450-mW laser power. Solid line: parallel polarization. Dashed line: perpendicular polarization. Insert: accumulation of 9 scans with 9-point smooth.

anhydrous grade, 99.98%) and BF_3 (distilled Matheson C.P. grade, 99.5%). After the tube was flame sealed, it was allowed to warm slowly while swabbing the unfilled end with liquid-nitrogen-dampened glass wool. This procedure kept the BF_3 frozen while the SO_2 melted and dissolved the perfluorocyclopropene. Then, the BF_3 was allowed to vaporize and dissolve in the solution as the main portion of the sample was immersed in $-50^\circ C$ ether and shaken. The sample was kept below $-25^\circ C$ for spectroscopy or kept frozen in liquid nitrogen while not in use. With careful purification and sample handling nearly colorless samples, which were almost free of fluorescence, were prepared. Residual fluorescence diminished under exposure to the laser beam for many hours. Upon aging at $0^\circ C$ new bands developed in the Raman spectrum while the bands due to the perfluorocyclopropenyl cation decreased in intensity. Principal bands of the new species were the following (cm^{-1} , intensity, depolarization ratio): 1668 w, dp ; 1313 m, p ; 1075 m, p ; 952 w, dp ; 842 w, p ; 794 m, p ; 780 s, p ; 650 m, p ; 632 m, dp ; 395 w, dp ; 335 m, p ; 253 m, dp ; 225 m, p . Chemical shifts in the ^{19}F NMR spectrum were -88 and 80 ppm . It is likely that this new species is $C_3F_2SO_2F^+$ with the -88-ppm shift due to the ring fluorine nuclei and the 80-ppm shift due to the SO_2F fluorine nucleus. Analogous ions appeared to form in SO_2 solutions of $C_3H_3F^+$ and $C_3HF_2^+$.^{1,2}

One sample of $C_3F_3^+B_2F_7^-$ in SO_2 contained 0.7 mmol of C_3F_4 , 7 mmol of SO_2 , and 1.4 mmol of BF_3 . Despite the 2:1 ratio of BF_3 to C_3F_4 the Raman spectrum, Figure 1, showed incomplete conversion of C_3F_4 . A second sample, prepared with a 3:1 ratio of BF_3 to C_3F_4 , gave essentially complete conversion of C_3F_4 . The features of the ^{19}F NMR spectrum are given in the Results and Discussion section.

Samples of C_3F_4 and SbF_5 in SO_2 were prepared in NMR tubes by condensing in order SbF_5 (degassed, Peninsular Chem Research), SO_2 , and C_3F_4 . After being sealed, these samples were brought to room temperature to complete the reaction. With an SbF_5/C_3F_4 ratio of 1.3:1 the product mixture was not fully soluble in SO_2 . However, with a ratio of 2:1 complete solubility occurred, and the salt remained in solution to at least $-50^\circ C$. Raman spectra of both samples showed that conversion of C_3F_4 to $C_3F_3^+$ was complete. Figure 2 displays the spectrum of the 2:1 mixture. The features of the ^{19}F NMR spectrum are given in the Results and Discussion section.

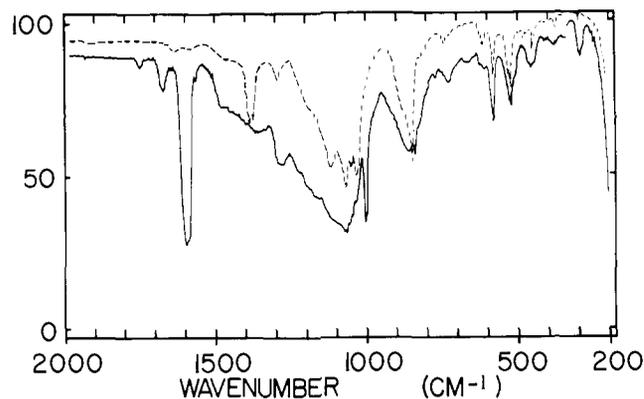


Figure 3. Infrared spectrum of polycrystalline $C_3F_3^+BF_4^-$ at 77 K , after warming the BF_3/C_3F_4 bilayer to $-70^\circ C$. Dashed line is the residual spectrum at 77 K after warming to room temperature in vacuo.

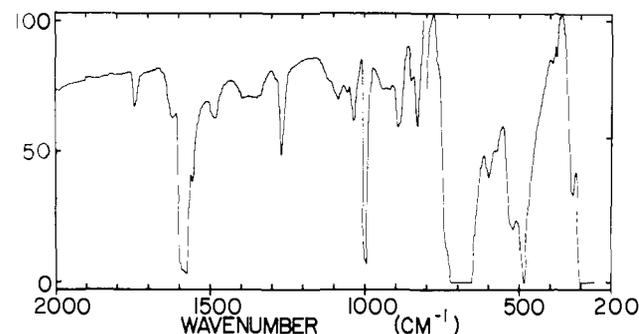


Figure 4. Infrared spectrum of polycrystalline $C_3F_3^+Sb_2F_{11}^-$ at 77 K , after warming the SbF_5/C_3F_4 bilayer to $-35^\circ C$.

Polycrystalline deposits of $C_3F_3^+BF_4^-$ and $C_3F_3^+Sb_2F_{11}^-$ for infrared spectroscopy were prepared in a Hornig-type cell on a cesium iodide window by the low-temperature, bilayer reaction technique that has been described before.^{1,2} At room temperature $C_3F_3^+BF_4^-$ underwent evaporative decomposition in vacuo, whereas the $C_3F_3^+Sb_2F_{11}^-$ salt was stable. The infrared spectra of the $C_3F_3^+BF_4^-$ and $C_3F_3^+Sb_2F_{11}^-$ salts are displayed in Figures 3 and 4, respectively.

Spectroscopy. Raman spectra were excited with filtered 514.5-nm light from a Coherent Radiation CR6 argon ion laser and were recorded at a spectral slit width of about 5 cm^{-1} on a Spex Ramalog 5 spectrometer/Nicolet 1180 computer system. A Harney-Miller-type low-temperature cell was used. Infrared spectra were run on Perkin-Elmer 621 and Perkin-Elmer 580B spectrometers with spectral slit widths less than 2 cm^{-1} . Frequencies in both spectroscopies are considered accurate to $\pm 1\text{ cm}^{-1}$.

^{19}F NMR spectra were obtained on a Perkin-Elmer R12B spectrometer. $CF_3CBrClH$ was used as an external fluorine reference, and then chemical shifts were expressed relative to $CFCl_3$ (76.1-ppm downfield from $CF_3CBrClH$).¹³

Results and Discussion

NMR Spectra.¹⁴ For $C_3F_3^+Sb_2F_{11}^-$ in SO_2 solution in the -39 to $-70^\circ C$ range Sargeant and Krespan reported an ^{19}F chemical shift of -63.1 ppm for the $C_3F_3^+$ ion.¹¹ We observed -63.5 ppm at $-50^\circ C$ in good agreement with their value. For the $B_2F_7^-$ system (vide infra) in SO_2 solution at $-30^\circ C$ repeated observations gave a somewhat larger shift of -65.3 ppm for the $C_3F_3^+$ ion. Unfortunately, for the previously studied $C_3FH_2^+$ and $C_3F_2H^+$ ions we do not have measurements of the ^{19}F shifts for both anion systems. For $C_3FH_2^+$ the shift was -65.8 ppm at $30^\circ C$ with $Sb_2F_{11}^-$ as the counterion; for $C_3F_2H^+$ the shift was -66.1 ppm at -20 to $-55^\circ C$ with $B_2F_7^-$ as the counterion.¹⁴ If we use the difference in shifts of 1.8 ppm between the $Sb_2F_{11}^-$ and $B_2F_7^-$

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(14) We are using the sign convention for ^{19}F chemical shifts recommended by Becker: Becker, E. D. "High Resolution NMR. Theory and Chemical Applications"; Academic Press: New York, 1980; p 57, 58, 64.

systems observed in the current $C_3F_3^+$ experiments as a correction for the $C_3FH_2^+$ ion, we obtain the following set of shifts for the fluorocyclopropenyl cations with the $B_2F_7^-$ counterion in SO_2 solution: $C_3FH_2^+$, -67.6 ppm; $C_3F_2H^+$, -66.1 ppm; $C_3F_3^+$, -65.3 ppm. These shifts show a very weak trend with increased fluorine substitution.

In the $C_3F_3^+Sb_2F_{11}^-$ solution in SO_2 the ^{19}F shift for the very broad $Sb_2F_{11}^-$ resonance was -113 ppm, in satisfactory agreement with the literature value of -112 ppm.¹¹ In the $3BF_3:1C_3F_4$ solution the $BF_3/B_2F_7^-$ resonance was at -133 ppm, and in the $2BF_3:1C_3F_4$ solution this resonance was at -142 ppm. This latter value reflects a greater contribution from the larger chemical shift of the BF_4^- and $B_2F_7^-$ ions relative to BF_3 .¹³

Structures of the Ions. All of the NMR and vibrational spectral evidence supports the conclusion that the $C_3F_3^+$ ion is a planar species with D_{3h} symmetry.

Qualitative evidence indicates that with BF_3 as the Lewis acid the $C_3F_3^+$ ion is less stable relative to its parent cyclopropene, C_3F_4 , than is $C_3F_2H^+$ relative to C_3F_3H and $C_3FH_2^+$ relative to $C_3F_2H_2$. Indeed, the sequence of stabilities in this sense is $C_3H_3^+ > C_3FH_2^+ > C_3F_2H^+ > C_3F_3^+$. As shown in Figure 1, conversion of C_3F_4 into the cation is incomplete in a $2BF_3:1C_3F_4$ mixture in SO_2 . The bands at 1944, 708, 614, and 257 cm^{-1} are due to C_3F_4 . However, in the spectrum of the $3BF_3:1C_3F_4$ mixture, which is not shown here, the conversion is essentially complete. In the spectrum of $C_3F_2D^+$ formed from a $1.4BF_3:1C_3F_3D$ mixture bands of some unconverted C_3F_3D were seen faintly.¹ In the spectrum of $C_3FH_2^+$ no unconverted $C_3F_2H_2$ was evident in the Raman spectrum of a $2BF_3:1C_3F_2H_2$ mixture.¹ 3-Fluorocyclopropene reacts so strongly with BF_3 to give $C_3H_3^+$ in SO_2 solution that the reaction could not be controlled to give colorless Raman samples.¹⁶ All four of the cations formed with BF_3 are less stable than the ones formed with SbF_5 . The BF_3 salts undergo decomposition in vacuo at room temperature, whereas the SbF_5 salts do not.^{1,2,17}

The principal anionic species in the SbF_5 reaction system is $Sb_2F_{11}^-$. The spectroscopic evidence for this characterization has been presented before.² Furthermore, in the current work we have found that the product of the reaction of a $1.3SbF_5:1C_3F_4$ mixture was not fully soluble in SO_2 even at room temperature, whereas the product of a $2SbF_5:1C_3F_4$ mixture was soluble. In our earlier experiments with the other two fluorocyclopropenyl cations the mixtures approximated 2:1 and were soluble.^{1,2} Moreover, Sargeant and Krespan prepared the solid salt of the $C_3F_3^+$ ion with an excess of SbF_5 and found that the $C_2Cl_3F_3$ -washed salt was soluble in SO_2 .¹¹ Thus, it seems that the SO_2 -soluble form of the salt is the one with the large $Sb_2F_{11}^-$ anion. Throughout this paper we formulate the fluoroantimonate salt with the $Sb_2F_{11}^-$ anion for both the polycrystalline solid and SO_2 solution.

The Raman spectrum of the BF_3/C_3F_4 mixture in SO_2 solution contains a broad, highly polarized band in the 710- cm^{-1} region, which we now interpret as evidence of an anionic species that we failed to recognize previously. In Figure 1 this band is dominated by the sharper feature due to residual C_3F_4 . However, in the spectrum of the 3:1 mixture, which is now shown here, the broad band was clearly apparent. The same broad, polarized band was observed in the Raman spectra of $C_3FH_2^+$, $C_3FD_2^+$, $C_3F_2H^+$, and $C_3F_2D^+$.^{1,2} In a previous discussion of this feature we ruled out several possible impurities as explanations and suggested that the band might be due to the BF_4^- symmetric stretch perturbed by ion pairing with the cations.

The presence of the same 710- cm^{-1} band in the Raman spectra of all the cyclopropenyl cation salts and a newly noted correlation of the intensity of this band with the intensities of the BF_3 band at 875 cm^{-1} and the BF_4^- band at 767 cm^{-1} led us to consider the $B_2F_7^-$ anion. When the intensity of the BF_3 band is high, as in the $3BF_3:1C_3F_4$ mixture, the intensity of the BF_4^- band is very low relative to the intensity of the 710- cm^{-1} band. Conversely,

when the intensity of the BF_3 band is low, as in the $1.4BF_3:1C_3F_3D$ mixture, the intensity of the BF_4^- band is high relative to the 710- cm^{-1} band.² Furthermore, Brownstein and co-workers have interpreted their studies of the lowering of BF_3 vapor pressure in CH_2Cl_2 solutions of $AgBF_4$ and Bu_4NBF_4 as due to the formation of $B_2F_7^-$ ions and possibly $B_3F_{10}^-$ ions.¹⁸ Hartman and Stilbs' ^{19}F NMR spectrum at -155 $^\circ C$ confirmed the formation of the $B_2F_7^-$ ion.¹⁹ Brownstein reports a large equilibrium constant for the reaction



in methylene chloride. Although our qualitative observations support the formation of $B_2F_7^-$ in SO_2 solutions, they do not imply such a favorable equilibrium in this medium.

No Raman spectrum of the $B_2F_7^-$ ion has been reported, and Brownstein and Paasivista's infrared spectrum of $Bu_4NB_2F_7$ is covered by solvent bands in the 710- cm^{-1} region.^{18a} Nonetheless, the 710- cm^{-1} frequency which is somewhat below the 767- cm^{-1} stretch of the BF_4^- ion is a reasonable frequency for a similar mode in $B_2F_7^-$. A weaker band which is a common feature in the 250- cm^{-1} region in fluoroborate systems but not in fluoroantimonate systems^{1,2} is likely also due to the $B_2F_7^-$ ion. The marked changes in the infrared spectra of the polycrystalline deposits of BF_3 /halocyclopropene reaction systems that were observed to occur in the -70 to -80 $^\circ C$ range are probably the consequence of loss of BF_3 from $B_2F_7^-$ ions in solid salts. This can be seen by comparing Brownstein and Paasivista's infrared spectrum of $Bu_4NB_2F_7$ in CH_2Cl_2 solution^{18a} with the infrared spectrum of the polycrystalline deposit of the product of BF_3 and $C_3F_2H_2$ before and after the transition temperature.¹ A similar change in the infrared spectrum was observed in the present study of $C_3F_3^+$ salts. Previously, we interpreted this change in the spectrum wrongly as due to a change in site symmetry for the BF_4^- ion.

For the purposes of the present work on the $C_3F_3^+$ ion it seems appropriate to formulate the $Bu_4NB_2F_7$ in SO_2 solution as largely $C_3F_3^+B_2F_7^-$ and the final, "high-temperature" polycrystalline deposit as $C_3F_3^+BF_4^-$.

Vibrational Assignment. The twelve vibrational fundamentals of the perfluorocyclopropenyl cation, which has D_{3h} symmetry, consist of eight distinct frequencies with the indicated activities in infrared (IR) and Raman (R) spectra: two a_1' (—; R, polarized); one a_2' (inactive); three e' (IR; R, depolarized); one a_2'' (IR; —); one e'' (—; R, depolarized). Each of the four modes of e symmetry is doubly degenerate.

Spectral evidence for the vibrational fundamentals of the perfluorocyclopropenyl cation is given in Figures 1-4 and in Table I. Figure 1 displays the Raman spectrum of $C_3F_3^+B_2F_7^-$ in SO_2 solution. Non- $C_3F_3^+$ features in this spectrum include obvious SO_2 solvent bands and weaker bands due to excess BF_3 and some unconverted perfluorocyclopropene. The bands due to C_3F_4 are at 1944, 708, 614, and 257 cm^{-1} . The bands due to unconverted C_3F_4 were absent from the spectrum of the $3BF_3:1C_3F_4$ mixture, which is not shown here. As discussed above, the broad band at about 710 cm^{-1} , which underlies the sharp 708- cm^{-1} band, is now understood to be due to $B_2F_7^-$. Figure 2 is the Raman spectrum of $C_3F_3^+Sb_2F_{11}^-$ in SO_2 solution. Figure 3 gives the infrared spectrum of polycrystalline $C_3F_3^+BF_4^-$, and Figure 4 gives the infrared spectrum of the $Sb_2F_{11}^-$ salt.

a_1' Modes. The two a_1' modes are assigned immediately to the strongly polarized Raman bands at 2014 and 752 cm^{-1} , which are seen on both Figures 1 and 2. The "ring mode" at 2014 cm^{-1} has a remarkably high frequency and a remarkably low intensity.

a_2' Mode. No spectral evidence was found for the single a_2' mode, which is not expected to be active in infrared or Raman spectra.

e' Modes. One of the three e' modes, $\nu_5 = 999$ cm^{-1} , was observed in both Raman spectra, Figures 1 and 2, and in both

(15) These values supersede those given in ref 1 and 2.

(16) Craig, N. C.; Sloan, K. L.; Sprague, J. R.; Stevens, P. S. *J. Org. Chem.* **1984**, *49*, 3847-8.

(17) For the $C_3H_3^+$ cation the reaction systems studied was $2SbF_5:1C_3ClH_3$. Thus, the anions contained some Cl^- .

(18) (a) Brownstein, S.; Paasivista, J. *Can. J. Chem.* **1965**, *43*, 1645. (b) Burchill, P. J.; Brownstein, S.; Eastham, A. M. *Can. J. Chem.* **1967**, *45*, 17.

(19) Hartman, J. S.; Stilbs, P. *J. Chem. Soc., Chem. Commun.* **1975**, 566.

Table I. Raman and Infrared Spectra (in cm^{-1}) and Assignments for the Perfluorocyclopropenyl Cation^d

	Raman, SO_2 soln ^a			infrared crystal		assignments		
	with $B_2F_{11}^-$		with $Sb_2F_{11}^-$	with BF_4^- ^b	with $Sb_2F_{11}^-$ ^c	freq	sym species	
2014	6	~0		2013 w, p			ν_1	fundamental
1944	8	p					C_3F_4	
1671	2	p					decomposition?	
				1590 vs	1588 vs	ν_4	fundamental	e'
1334	68	0.78	~1335 m, dp				SO_2	
1287	4	p					?	
1144	vs	p	~1145 vs, p				SO_2	
1120	15	p	~1120 w, p				$SO^{18}O$	
				1060 br			BF_4^-	
999	10	0.73	998 w, dp	999 s	1000 s	ν_5	fundamental	e'
875	17	~0					BF_3	
781	6	p					$C_3F_2SO_2F^+$?	
767	5	p					BF_4^-	
752	100	0.03	752 s, p			ν_2	fundamental	a_1'
708	30	~0					C_3F_4 and $B_2F_7^-$	
			683 m, p		700-		$Sb_2F_{11}^-$	
			650 s, p		665 vs			
642	20	0.78	642 m, dp			ν_8	fundamental	e''
614	4	dp	602 w, dp				C_3F_4	
				576 m			$Sb_2F_{11}^-$	
							BF_4^-	
524	55	0.72					SO_2	
479	2	~dp					BF_3	
				519 m			BF_4^-	
					520 m		$Sb_2F_{11}^-$	
					485 s		$Sb_2F_{11}^-$	
				455 w			?	
					330 m		$Sb_2F_{11}^-$	
			291 m, dp		300-		$Sb_2F_{11}^-$	
287	17	0.77		290 w		ν_6	fundamental	e''
257	5	dp					C_3F_4 and $B_2F_7^-$	
			230 m, dp		260 vs		$Sb_2F_{11}^-$	

^a $t = -30$ °C. ^b Recorded at -196 °C after temperature cycling to -70 °C. ^c Recorded at -196 °C after temperature cycling to -35 °C. ^d p = polarized; dp = depolarized; vs = very strong; s = strong; m = medium; w = weak; br = broad.

infrared spectra, Figures 3 and 4. The Raman bands are depolarized. A second e' mode, $\nu_6 = 287$ cm^{-1} , is readily found in both spectra of the fluoroborate salt, Figures 1 and 3. The Raman band is depolarized. Although this region in the infrared spectrum, Figure 4, of the fluoroantimonate salt is covered by an anion band, careful consideration of the Raman spectrum, Figure 2, reveals evidence of the 287- cm^{-1} band. In other spectra of fluoroantimonate salts of cyclopropenyl cations, a well-defined, depolarized doublet with maxima at about 295 cm^{-1} (strong) and 280 cm^{-1} (medium) was observed. Figure 2 has a single, broad, depolarized band at 291 cm^{-1} , which implies that the $C_3F_3^+$ band is filling in the gap of the doublet. The third e' mode, ν_4 , gives an intense band at about 1590 cm^{-1} in the infrared spectra of both salts, Figures 3 and 4. Despite computer accumulations of many scans, no trace of ν_4 could be found in this region in the Raman spectra. However, the absence of observable intensity in the Raman effect is consistent with this mode being largely anti-symmetric CF stretching.

a_2'' Mode. At first we took the infrared band at 455 cm^{-1} , Figure 3, which has no Raman counterpart, to be the one fundamental of a_2'' symmetry. However, zero-order normal-coordinate calculations (vide infra) showed this frequency, ν_7 , to be about 235 cm^{-1} . Careful searching of the infrared spectrum of the BF_4^- salt in the 200- cm^{-1} region, which was unfortunately at the limit of the range of the two instruments that were used, revealed no band. We also considered the possibility that the 455- cm^{-1} band is a combination tone of ν_7 . However, neither $2\nu_7$ nor $\nu_6 + \nu_7$ has the correct symmetry for an infrared-active mode. Thus, no spectral evidence for ν_7 exists. The 455- cm^{-1} band remains unassigned, although it may be due to the counterion.

e'' Mode. This infrared-inactive, Raman-active fundamental is seen clearly as a depolarized band in the Raman spectrum at 642 cm^{-1} in Figure 1. This band is also seen as a depolarized shoulder in the Raman spectrum of the $Sb_2F_{11}^-$ system, Figure 2. There is no corresponding band in the infrared spectrum of

Table II. Vibrational Fundamentals (cm^{-1}) and Corresponding Potential Energy Distributions for $C_3F_3^+$

		obsd	zero order	refined	PED ^a
a_1'	ν_1	2014	1987	2013	73 s CCC str, 27 s CF str
	ν_2	752	749	758	73 s CF str, 27 s CCC str
a_2'	ν_3		850	811	100 s CF bd
e'	ν_{4a}	1590 ^b	1628	1599	45 a CCC str(b), 35 a CF str(a), 15 a CF str(b)
	ν_{5a}	999	980	976	44 a CF str(b), 35 a CCC str(a), 13 a CF bd(a)
	ν_{6a}	287	281	285	50 a CF bd(b), 31 a CF bd(a), 15 a CCC str(b)
a_2''	ν_7		236	239	100 s CF flap
e''	ν_{8a}	642	638	641	97 a CF flap(b)
	av		error	7.0 cm^{-1}	

^a Potential energy distributions in percent. See Table III for distinction between (a) and (b) coordinate designations and for abbreviations. ^b From IR crystal spectrum; all others from liquid-phase Raman spectrum.

the fluoroborate salt, Figure 3. Unfortunately, this region is obscured by an anion band in the infrared spectrum of the $Sb_2F_{11}^-$ system, Figure 4.

Table II provides a summary of the overall assignment of fundamentals of the perfluorocyclopropenyl cation. Six of the eight fundamentals have been observed experimentally. The good agreement of the observed fundamentals with the zero-order normal-coordinate calculations suggests that the predicted values of $\nu_3(a_2')$ and $\nu_7(a_2'')$ are good estimates of these frequencies. Refined normal coordinate calculations, which are also given in Table II, support this interpretation. Thus, we conclude that a complete, though tentative assignment of vibrational fundamentals has been secured for the $C_3F_3^+$ ion.

Table III. Definitions of Symmetry Coordinates for $C_3F_3^+$

coordinate		description ^a	definition ^b
a_1'	S_1	s CCC str	$1/\sqrt{3}(R_1 + R_2 + R_3)$
	S_2	s CF str	$1/\sqrt{3}(r_1 + r_2 + r_3)$
a_2'	S_3	s CF bd	$1/\sqrt{3}(\alpha_1 + \alpha_2 + \alpha_3)$
e'	S_{4a}	a CCC str (a)	$1/2(2R_1 - R_2 - R_3)$
	S_{4b}	a CCC str (b)	$1/\sqrt{2}(R_2 - R_3)$
	S_{5a}	a CF str (a)	$1/2(2r_1 - r_2 - r_3)$
	S_{5b}	a CF str (b)	$1/\sqrt{2}(r_2 - r_3)$
	S_{6a}	a CF bd (a)	$1/2(2\alpha_1 - \alpha_2 - \alpha_3)$
	S_{6b}	a CF bd (b)	$1/\sqrt{2}(\alpha_2 - \alpha_3)$
a_2''	S_7	s CF flap	$1/\sqrt{3}(\beta_1 + \beta_2 + \beta_3)$
e''	S_{8a}	a CF flap (a)	$1/2(2\beta_1 - \beta_2 - \beta_3)$
	S_{8b}	a CF flap (b)	$1/\sqrt{2}(\beta_2 - \beta_3)$

^as = symmetric, a = antisymmetric, str = stretch, bd = bend. ^b R_1, R_2, R_3 are CC stretching coordinates; r_1, r_2, r_3 are CF stretching coordinates; $\alpha_1, \alpha_2, \alpha_3$ are CF in-plane bending coordinates; $\beta_1, \beta_2, \beta_3$ are CF out-of-plane flapping coordinates.

Table IV. Force Constants for $C_3F_3^+, C_3F_2H^+$, and $C_3FH_2^+$

force constant ^a	zero order	refined ^b		
		$C_3F_3^+$	$C_3F_2H(D)^+$	$C_3FH_2(D)^+$
CC str (F_3)	7.80	7.71 (22)		
CC str (unique, F_1)	7.16			7.13 (15)
CC str (F_1)	8.29			8.33 (12)
CC str (unique, F_2)	8.75		8.57 (25)	
CC str (F_2)	7.01		7.25 (16)	
CF str	7.92	7.86 (14)	7.86 (14)	7.86 (14)
CH str	5.32		5.32 (02)	5.32 (02)
CF bd	1.26	1.26 (04)	1.26 (04)	1.26 (04)
CH bd	0.55		0.54 (01)	0.54 (01)
CF flap	0.56	0.57 (01)	0.57 (01)	0.57 (01)
CH flap	0.43		0.43 (01)	0.43 (01)
CC str/CC str (F_3)	-0.14	0.14 (10)		
CC str/CC str (diff CC, F_1)	-0.63			-0.50 (19)
CC str/CC str (diff CC, F_2)	-0.14			
CC str/CF str (same C)	0.52	0.59 (05)	0.59 (05)	0.59 (05)
CC str/CH bd (same C)	-0.28		-0.28 (04)	-0.28 (04)
CF bd/CF bd	-0.08	-0.13 (05)	0.13 (05)	
CH bd/CH bd	0.05			0.05 (01)
CF flap/CF flap	-0.06	-0.06 (02)	-0.06 (02)	

^astr = stretch, bd = bend. ^bUnits are mdyne/Å for str and str/str; mdyne/Å/radian² for bd and bd/bd; mdyne/radian for str/bd.

Normal-Coordinate Calculations. The normal-coordinate calculations were done with computer programs expressed in the standard **G**, **F**, and **W** matrix formalisms.²⁰ Our programs are based on the ones developed in the Molecular Spectroscopy Laboratory at the University of Minnesota.

A non-redundant set of twelve internal coordinates was used: three CC bond stretches, three CF bond stretches, three in-plane CF bond bends, and three out-of-plane CF bond flaps. Bond lengths were estimated as $r_{CC} = 1.30$ Å and $r_{CF} = 1.35$ Å. Symmetry coordinates, which were used to help check internal coordinate coding and to express potential energy distribution, are defined in Table III.

For the zero-order calculations the force constants were those obtained previously in a selective overlay calculation for the monofluoro- and difluorocyclopropenyl cations.² For the $C_3F_3^+$ ion this set of force constants, Table IV, consisted of the four valence constants and four of the eight possible interaction constants. Table II gives the frequencies computed in the zero-order calculations. Average differences from the observed values are 16 cm^{-1} .

In the absence of experimental evidence for two fundamental frequencies of $C_3F_3^+$ and of frequencies for isotopomers of this ion, a refinement normal-coordinate calculation must be based on the overlay technique. We are particularly interested in the

Table V. Force Constants (mdyn/Å) for CC Bond Stretching in Cyclopropenyl Cations^a

	$C_3H_3^+$	$C_3FH_2^+$	$C_3F_2H^+$	$C_3F_3^+$
all CC bonds	7.87 (10) ^b			7.71 (22)
two CC bonds		8.33 (12)	7.25 (16)	
unique CC bond		7.13 (15)	8.57 (25)	

^aValues in parentheses are statistical dispersions in decimal units.

^bFrom ref 4.

effect of fluorine substitution on the CC bonds of the ring. Thus, we employ a *selective* overlay technique in which all the force constants for the CF and CH(D) bonds are taken to be the same in the series of ions $C_3FH_2^+, C_3FD_2^+, C_3F_2H^+, C_3F_2D^+$, and $C_3F_3^+$, but the force constants for CC stretching are refined separately for each ion type. It is reasonable to assume as a first approximation that the CF bonds, which are on the periphery of each ion, are little affected by successive fluorine substitution. Moreover, the very small changes in the NMR chemical shifts for fluorine atoms in the sequence of ions reinforces the validity of this approximation.

The selective overlay refinement started with the full set of force constants that had been obtained in the previous study of the monofluoro- and difluorocyclopropenyl cations.² These force constants are given in the first column of Table IV. They consist of eight constants, of which two are unique, for $C_3F_3^+$; thirteen constants, of which three are unique, for $C_3F_2H^+$; and twelve constants, of which four are unique, for $C_3FH_2^+$. The frequencies of $C_3F_2D^+$ and $C_3FD_2^+$ were also fitted in the refinement. Because it was poorly defined in the preliminary calculations one of the interaction constants for $C_3F_2H^+(D)$ was omitted in the final calculation. The final sets of force constants and their dispersions for each ion are given in Table IV. The frequencies for $C_3F_3^+$ from the refinement calculation are given in Table II. The average error in the fit of these frequencies is 7.0 cm^{-1} . As a measure of the fit of the frequencies for the other two ion species, which are omitted here, we note the average frequency differences: $C_3F_2H^+$, 6.6 cm^{-1} ; $C_3F_2D^+$, 9.3 cm^{-1} ; $C_3FH_2^+$, 9.5 cm^{-1} ; $C_3FD_2^+$, 11.6 cm^{-1} . That the frequency fits to the partly substituted ions are poorer is largely due to the use of less complete force fields for the F_1 and F_2 ions than for the $C_3F_3^+$ ion. We have used only 12 force constants out of the 29 constants of a general valence force field for each of them. Eight of twelve possible force constants were used for $C_3F_3^+$.

Table II contains the potential energy distributions (PED) in symmetry-coordinate space for the $C_3F_3^+$ ion. These PEDs are sums of the contributions from a given symmetry coordinate.²¹ Except for the modes that are unique to a symmetry species, the normal modes consist of substantial contributions of more than one symmetry coordinate. Such mixing causes the high frequency of 2014 cm^{-1} for the symmetric "ring stretch". Correspondingly, the symmetric "CF stretch" is low in frequency. Because of the good fit of the refined frequencies to the observed ones, the calculated values of the two missing fundamentals of $C_3F_3^+$, $\nu_3(a_2')$ and $\nu_7(a_2'')$, are considered to be good estimates.

Table V provides a comparison of the force constants for CC stretching in the series of cyclopropenyl cations from $C_3H_3^+$ to $C_3F_3^+$. Although the CC force constants are essentially the same for $C_3H_3^+$ and $C_3F_3^+$, substantial differences are found in the intermediate cases. For $C_3FH_2^+$ the CC bonds adjacent to the substituted carbon have increased force constants compared to $C_3H_3^+$ and the CC bond opposite to the substituted carbon has a decreased force constant. In the $C_3F_2H^+$ ion the force constant for the CC bond between the substituted carbons has been increased and the bonds to the unsubstituted carbon have been decreased. These effects can be rationalized if we understand that (1) the weakening effect of fluorine substitution on the opposite CC bond is greater than the strengthening effect on the adjacent

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CC bonds and (2) the strengthening effect on adjacent CC bonds is little affected by substitution of a second fluorine on the neighboring carbon atom. A similar pattern of the effect of fluorine substitution has been found for the CC force constants for the sequence of cyclopropenes, C_3H_4 , $\overline{CF_2-CH=CH}$, $\overline{CF_2-CF=CH}$, and $\overline{CF_2-CF=CF}$.⁵

West and co-workers assigned five of the six in-plane frequencies of $C_3Cl_3^+$ as observed in the infrared and Raman spectra of this ion.¹² They also studied the $C_3Br_3^+$ ion but were only able to obtain an infrared spectrum and to assign only two of this ion's fundamentals. A five-parameter Urey-Bradley potential function was fitted to the frequencies of the in-plane modes of the $C_3Cl_3^+$ ion. This potential function included a force constant for the nonbonded gem C...Cl interaction. When a small, but fixed value for a sixth constant, the nonbonded cis Cl...Cl interaction, was added, most of the other five force constants changed appreciably. Such high sensitivity of the calculation to a small modification implies a rather unstable numerical system and suggests being cautious in interpreting the results. Nonetheless, we shall compare West and co-workers' Urey-Bradley value of 6.31 mdy/Å with our valence force field values of 7.87 for $C_3H_3^+$ and 7.71 for $C_3F_3^+$. To do so we must take account of the contributions of the nonbonded F_{CCl} force constants.²² This raises the Urey-Bradley value of 6.31 to a valence field value of 7.77, which is close enough to the values for $C_3H_3^+$ and $C_3F_3^+$ to imply that no appreciable

change occurs in the CC bond strength when the cyclopropenyl cation is *fully* substituted with chlorine or fluorine atoms.

Conclusions

A complete assignment of the eight vibrational fundamentals of the perfluorocyclopropenyl cation has been proposed. Normal-coordinate calculations with a selective overlay procedure for the three ions, $C_3FH_2^+$, $C_3F_2H^+$, and $C_3F_3^+$, gives a set of CC stretching force constants that conforms to the pattern found for fluorine substitution in cyclopropane and cyclopropene ring systems. Substitution of fluorine on a contiguous carbon atom increases the CC force constant, whereas substitution of a fluorine atom on a cross-ring carbon atom decreases the CC force constant. These effects are substantial and are presumed to correlate with bond-strength changes. In $C_3F_3^+$ the effect of fluorine substitution cancels out; the CC force constant is essentially the same as that in $C_3H_3^+$.

Confirmation and interpretation of these effects of fluorine substitution must await ab initio electronic calculations. Geometric parameters and force constants would be of interest as well as changes in electron densities as a function of fluorine substitution.

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Measurement of the Dissociation Energies of Gas-Phase Neutral Dimers by a Photoionization Technique: Values for *trans*-2-Butene/Sulfur Dioxide, (*trans*-2-Butene)₂, and Benzene/Sulfur Dioxide

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Abstract: A method has been developed for the measurement of the dissociation energies of gas-phase neutral dimers using photoionization spectra of mass selected ions from molecular beams generated by jet expansion. This measurement involves the determination of the appearance potential for dissociative photoionization of the dimer using a difference technique. The 0 K dissociation energies obtained are 3.85 ± 0.23 , 2.9 ± 1.1 , and 4.40 ± 0.28 kcal/mol for *trans*-C₄H₈SO₂, (*trans*-C₄H₈)₂, and C₆H₆SO₂, respectively. The method is applicable for dimers in which the photoionization efficiency function of the partner of lower ionization potential begins with a distinct step at threshold, a condition that is satisfied for many molecules. The technique is best for heterodimers and less good for homodimers. At its best the experimental work can be accomplished within a day for a given dimer, and the data can be analyzed unambiguously in a model-independent fashion.

The universal long-range attraction of molecules for each other plays such a pivotal role in chemistry that chemists have made extraordinary efforts to understand the forces involved. Examples of such work are studies of virial coefficients,¹ infrared spectroscopy at elevated gas pressures,² and scattering in crossed molecular beams.³ Of special importance are the properties of weak complexes in the gas phase. With the advent of nozzle expansion techniques for their synthesis in molecular beams,⁴ and the introduction of laser fluorescence⁵ and dissociation,^{6,7} and microwave resonance methods⁸ for their investigation, the spectroscopic ex-

amination of weak complexes has achieved impressive elegance and power, and is now being enthusiastically pursued in several

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