Vibrational Spectra and a Potential Function for the Monofluorocyclopropenyl-d_0 and -d_2 Cations

Norman C. Craig,* Ronnie K.-Y. Lai, Lawrence G. Matus, J. Houston Miller, and Stephen L. Palfrey

Contribution from the Department of Chemistry, Oberlin College, Oberlin, Ohio 44074.

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Abstract: Monofluorocyclopropenyl-d_0 and -d_2 cations have been prepared by reaction of 3,3-difluorocyclopropene with BF_3 and SbF_5 in sulfur dioxide solution for Raman spectroscopy and in crystalline form for infrared spectroscopy. By ^1H and ^{19}F NMR spectroscopy the expected C_{2v} structure for the ion has been confirmed in SO_2 solutions of the fluoroantimonate salt at room temperature and of the fluoroborate salt at temperatures below −25 °C. Above −25 °C the fluoro cation undergoes fluoride exchange with BF_4^-. An assignment of the vibrational fundamentals has been obtained for all but the a_2 modes. For the d_0 cation these frequencies are (cm^{-1}) (a_1) 3153, 1835, 1339, 988, 830; (a_2) . . .; (b_1) 3119, 1372, 1014, 483; (b_2) 872, 477. The 22 observed frequencies for the two isotopic species have been fit to a 12-parameter, valence-type potential function. The two calculated CC force constants correlate with a weaker CC bond being opposite and stronger CC bonds being adjacent to the substituted carbon. Also, the high value of the CF stretching constant implies significant double-bond character in the CF bond.

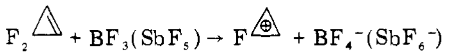
Introduction

i

The monofluorocyclopropenyl cation, i, is of interest as an example of a potent substituent effect on the simplest of Hückel-type aromatic systems. In other three-membered-ring systems fluorine substitution has a marked influence on the bonding in the ring. For the molecules $F_2\overline{CCH_2CH_2}$, $F_2\overline{CCH{=}CH}$, and $F_2\overline{CN{=}N}$, microwave and electron diffraction studies have shown that the bonds to the fluorine-substituted carbon atoms are appreciably shorter (0.05, 0.07, 0.06 Å) and the bonds opposite the fluorine-substituted carbon atoms are appreciably longer (0.04, 0.03, 0.06 Å) than those in the corresponding unsubstituted molecules.[1-6] The effect of fluorine substitution is also reflected in the potential constants for the ring bonds. In 3,3-difluorocyclopropene and difluorodiazirine force constants for the adjacent bonds are strengthened, and force constants for opposite bonds are weakened.[7] Preliminary normal coordinate analysis for difluorocyclopropane reveals a similar pattern.[8] Ab initio molecular orbital calculations have yielded electronic redistributions that correlate with these changes in bond lengths and potential constants.[9] For $C_3FH_2^+$, which cannot be investigated by microwave spectroscopy or electron diffraction, force constants are a principal experimental means for characterizing the CC bonds.

The present study of the vibrational spectra of $C_3FH_2^+$ and $C_3FD_2^+$ is the first detailed analysis of a partly substituted C_3 ion. Previous vibrational studies of simple cyclopropenyl cations have been confined to the parent ion, $C_3H_3^+$, and its deuterated modification, $C_3D_3^+$,[10] and to the fully substituted species, $C_3Cl_3^+$ and $C_3Br_3^+$.[11] The anionic species, $C_3O_3^{2-}$, has also been investigated.[12] In the absence of Raman spectra, the vibrational assignments for $C_3H_3^+$, $C_3D_3^+$, and $C_3Br_3^+$ are far from complete. From an infrared and Raman study of $C_3Cl_3^+$, only five of the eight fundamental frequencies have been assigned.[11] In the case of $C_3FH_2^+$ structural variety, as well as access to a deuterated modification, improves the prospects of observing all the fundamentals and of having a sufficient number of frequencies upon which to base normal coordinate calculations.

The monofluorocyclopropenyl cation, which is a new species, has been prepared by the reaction of the Lewis acids BF_3 and SbF_5 with 3,3-difluorocyclopropene.[13,14] The deuterated cation has been made from difluorocyclopropene-d_2. Samples for SbF_5 with 3,3-difluorocyclopropene.[13,14] The deuterated cation has been made from difluorocyclopropene-d_2. Samples for Raman spectroscopy have been prepared in liquid sulfur dioxide and sealed in NMR tubes in order that the cation's structure could be confirmed by ^1H and ^{19}F NMR. For infrared spectroscopy, polycrystalline deposits have been obtained by depositing separate layers of the two reactants on a window at −196 °C and then raising the temperature stepwise until reaction is complete.[15]



Experimental Section

Solutions for Raman and NMR Spectroscopy. To obtain colorless cation solutions that gave little fluorescence in Raman experiments, samples had to be prepared carefully on a good vacuum system. The glass system was lubricated with halocarbon grease, had an easily cleaned mercury manometer, and was heat gunned to hasten the evolution of adsorbed water.

3,3-Difluorocyclopropene and its d_2 modification were prepared and purified as described before.[7] In order to increase greatly the yield of fluorocyclopropene from dehydrohalogenation of 1,1-difluoro-2-bromocyclopropane,[16] the Ascarite was coated with a thin layer of bis[2-(2-methoxyethoxy)ethyl] ether. Boron trifluoride (Matheson Co., CP grade), sulfur dioxide (Matheson Co., anhydrous grade), and antimony pentafluoride (Peninsular ChemResearch Co.) were further purified by bulb-to-bulb distillation. The distilled SO_2 was also passed over phosphorus pentoxide.

For the preparation of the cation by reaction with BF_3, a typical mixture consisted of 0.7 mmol of the cyclopropene (bp 34 °C), 7 mmol of SO_2, and 1.5 mmol of BF_3. Each component was measured as a gas and frozen down separately in a standard-wall 5-mm NMR tube, which was then flame sealed under vacuum. The cyclopropene was the bottom layer, and the BF_3 the top layer. Then, when the sample was warmed, the cyclopropene was diluted by the SO_2 before reacting with BF_3. To reduce the pressure buildup by BF_3 while the SO_2 melted, the top of the NMR tube was swabbed with glass wool moistened with liquid N_2. Mixing was completed by alternating inversions of the sample tube with immersion in a −30 °C acetone bath. Samples were normally kept below −20 °C during experiments and stored in liquid nitrogen. At 0 °C the cation converted in several hours to another species (vide infra), and at room temperature coloration developed. Figures 1 and 2 show the Raman spectra of SO_2 solutions of $C_3FH_2^+BF_4^-$ and $C_3FD_2^+BF_4^-$, respectively.

Samples involving SbF_5 were prepared by first distilling SbF_5 (1.8 mmol) into the NMR tube and then condensing into the tube, in order, SO_2 (7 mmol) and the cyclopropene (1 mmol). Contact of SbF_5 with

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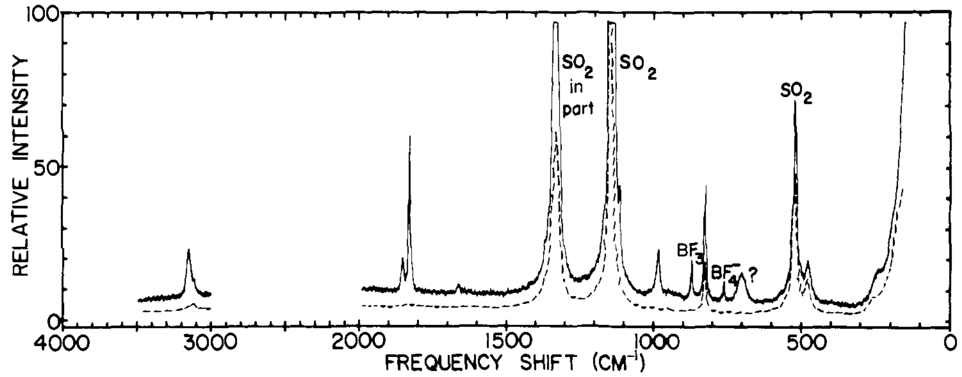

Figure 1. Raman spectrum of $C_3FH_2^+BF_4^-$ in solution in sulfur dioxide at −22 °C. Solid line, polarization analyzer parallel to the polarization of the laser beam: dashed line, polarization analyzer perpendicular.

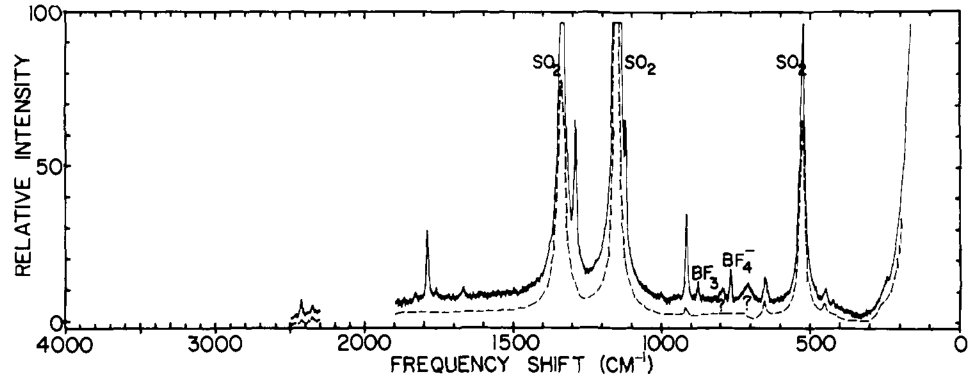

Figure 2. Raman spectrum of $C_3FD_2^+BF_4^-$ in solution in sulfur dioxide at −23 °C. Solid line, polarization analyzer parallel to the polarization of the laser beam; dashed line, polarization analyzer perpendicular.

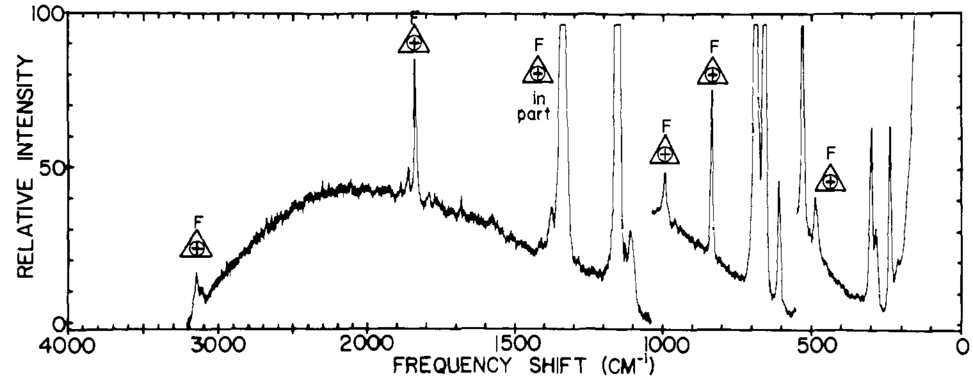

Figure 3. Raman spectrum of $C_3FH_2^+Sb_2F_{11}^-$ in solution in sulfur dioxide at −54 °C. Polarization analyzer removed.

mercury was avoided; the amount of SbF_5 was determined by weighing. The SbF_5 samples were the first ones prepared, and the less scrupulous techniques then in use gave spectra with marked fluorescence backgrounds. Figure 3 is the Raman spectrum of an SO_2 solution of $CFH_2^+Sb_2F_{11}^-$. The spectrum of the deuterated modification has been omitted for brevity. In contrast to the BF_3 system the cation in the SbF_5 system does not react further at temperatures as high as 35 °C.

Samples of BF_3 alone in SO_2 and SbF_5 alone in SO_2 were also prepared, and Raman spectra recorded. Frequencies of bands due to SO_2, BF_3, and the SO_2·SbF_5 complex were in satisfactory agreement with published spectra.[15,17,18]

The product of further reaction in the BF_3 system had a ^1H NMR peak δ 8.7 ppm which remained unsplit at −75 °C and had a ^{13}C doublet with J = 123 Hz, and a single fluorine resonance at −74 ppm (downfield). The Raman spectrum was (cm^{-1}) 3162 m, 3135 w, 1820 m, 1444 s, 1309 m, 1275 w, 1038 w, 901 w, 860 w, 794 m (714 m), 620 m, 389 m, and 313 w. All of these bands appeared to be polarized.[19]

Polycrystalline Material for Infrared Spectroscopy. Infrared experiments were conducted in a conventional low-temperature cell equipped with cesium iodide windows, a coolable cesium iodide disk, and a copper-constantan thermocouple. Silicone grease was used for this cell and the vacuum system because the slightly volatile fraction of halocarbon grease gave Fluorolube-like deposits on the cold disk, which contributed confusing bands to the spectra. For the BF_3 experiments an excess of the more volatile BF_3 was sprayed on the liquid N_2 cooled disk first, whereas for the SbF_5 experiments an excess of the more volatile cyclopropene was condensed first. Typical amounts of the two reagents were 125 and 25 μmol. The published vapor pressure of 4 Torr at room temperature was used in estimating the amount of SbF_5.[20]

Reaction between the BF_3 and cyclopropene layers was initiated by raising the temperature of the CsI disk to −150 °C with the infrared beam blocked off and then quickly cooling to −196 °C. In successive cycles of warming and cooling, the temperature was slowly raised in steps of about 2 °C until −110 °C, where the increments were increased to 10 °C. The progress of the reaction was followed by recording infrared spectra at −196 °C and noting the growth of the cation bands in the 1800-cm^{-1} region and the disappearance of bands

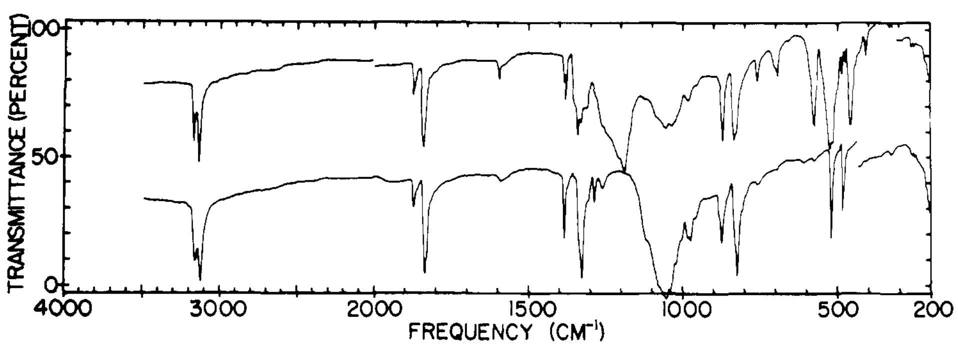

Figure 4. Infrared spectrum of polycrystalline $C_3FH_2^+BF_4^-$ at −196 °C. For the upper trace the temperature was raised only as high as −80 °C during reaction cycles. For the lower trace the temperature was raised to −70 °C.

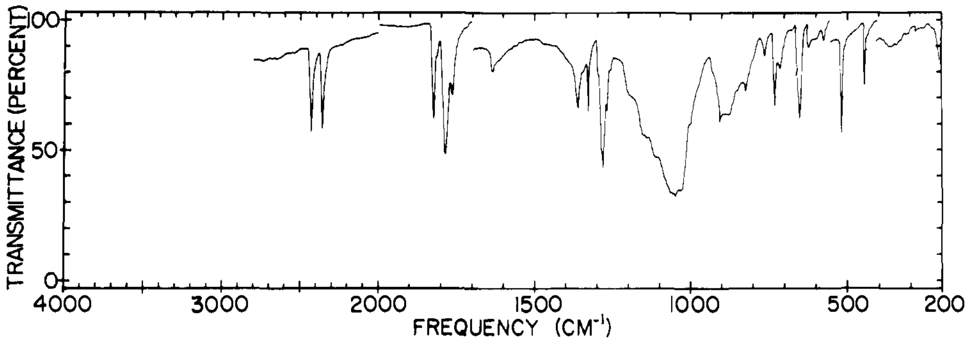

Figure 5. Infrared spectrum of polycrystalline $C_3FD_2^+BF_4^-$ at −196 °C. Temperature was raised to −50 °C during reaction cycles.

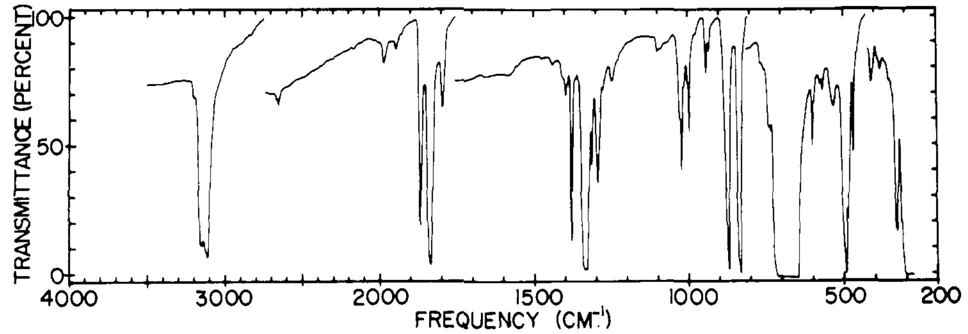

Figure 6. Infrared spectrum of polycrystalline $C_3FH_2^+Sb_2F_{11}^-$, SbF_6^- at −196 °C. Temperature was raised to −50 °C during reaction cycles.

due to polycrystalline BF_3[18] and polycrystalline difluorocyclopropene.[7] During the warmup process BF_3 sublimed back and forth between the CsI plate and the supporting copper block, thereby completing the conversion of the cyclopropene to the cation. When the temperature was raised above −80 °C, a marked change occurred in the spectrum of the product. Figure 4 gives the infrared spectra of both the lower temperature and higher temperature forms of $C_3FH_2^+BF_4^-$. Raising the temperature as high as −35 °C caused no further changes of significance. Pumping a good vacuum in the cold cell while it warmed to room temperature caused evaporative decomposition of most of the polycrystalline deposit. The residual deposit, which contained no bands due to the fluorocyclopropenyl cation, was removed by repolishing before each experiment. Figure 5 is the infrared spectrum of the higher temperature form of $C_3FD_2^+BF_4^-$.

For the SbF_5 experiments the temperature was raised to −100 °C to begin reaction and subsequently taken up to −15 °C in steps of 10 °C. Most of the reaction occurred in the first, −100 °C, step. In contrast to the BF_3 system, no significant changes were observed in the spectrum of the product as the temperature was raised, and the product did not undergo evaporative decomposition at room temperature. The residual deposit, which was reddish brown, had to be polished off the CsI crystal. Figures 6 and 7 are spectra of the $C_3FH_2^+$ and $C_3FD_2^+$ salts, respectively.

Spectroscopy. ^1H and ^{19}F NMR spectra were recorded on a Perkin-Elmer R12B spectrometer which was equipped with a variable-temperature probe. Proton chemical shifts are relative to external Me_4Si, and ^{19}F shifts are relative to external $CFCl_3$. Raman spectra were obtained with a Spex Ramalog 5 system and a Coherent Radiation CR5 argon-ion laser tuned to the 514.5-nm green line. A Harney-Miller type cold cell was used.[21] Infrared spectra were recorded on a Perkin-Elmer 621 spectrometer. Except for the Raman spectrum of the $C_3FH_2^+$ $Sb_2F_{11}^-$ system vibrational frequencies were read from expanded scale scans at 2.5-cm^{-1} resolution for Raman spectra and at better than 1-cm^{-1} resolution for infrared spectra. These frequencies are accurate to better than 2 cm^{-1}.

Results and Discussion

Structure of the Cation. The isolated fluorocyclopropenyl cation should be planar with C_{2v} symmetry in order to maximize the energy advantage of π-electron delocalization. The NMR spectra of the SbF_5 system at magnet temperature and of the BF_3 system below −25 °C are consistent with this model. The proton spectrum consists of a doublet with $J = 1.8$ Hz and δ 9.5 ppm; the ^{19}F spectrum is a triplet with $J = 1.9$ Hz and δ 67 ppm (upfield). Chemical shifts of 11.10 ppm for $C_3H_3^+$, 10.85 ppm for $C_3H_2Cl^+$, and 9.61 ppm for $C_3H_2OH^+$ have been reported.[22] That the fluoro cation has a shift close to that of the hydroxy cation is consistent with comparable electron

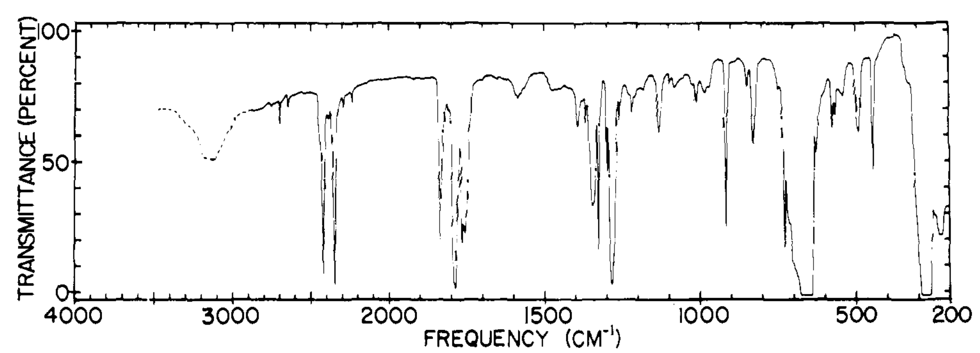

Figure 7. Infrared spectrum of polycrystalline $C_3FD_2^+SbF_6^-$, $Sb_2F_{11}^-$ at −196 °C. Temperature was raised to −30 °C during reaction cycles.

donation to the ring through partial CO and CF double bond character. A shift of 63.1 ppm was found in the fluorine spectrum of $C_3F_3^+$.[13] Above −20 °C the proton spectrum of the BF_3 system collapses into a singlet, and the ^{19}F spectrum consists of only a single broad peak at 143 ppm (upfield) due to all the ^{19}F in the system. This behavior implies donation of a fluoride ion from BF_4^- to the cation to re-form difluorocyclopropene at a significant rate at the higher temperature. The corresponding process must be much slower in the SbF_5 system. The difference between the NMR experiments with the BF_3 and SbF_5 systems is consistent with the observation that the BF_4^- salt undergoes evaporative decomposition whereas the fluorantimonate one does not. These observations correlate with SbF_5 being a stronger Lewis acid than BF_3.

Structure of the Anions. The marked changes that occur in the infrared spectrum of crystalline $C_3FH_2^+BF_4^-$ above −80 °C, as shown in Figure 4, are probably related to the fluoride ion exchange that occurs between BF_4^- and the cation in SO_2 solution. Above −80 °C the spectrum has the same BF_4^- bands, 1050 and 520 cm^{-1}, as are found in the crystalline alkali tetrafluoroborates.[23] Below this temperature the BF_4^- stretching mode is at 1190 cm^{-1} and the bending mode has satellites at 575 and 455 cm^{-1}. The infrared spectrum of crystalline $C_3FD_2^+BF_4^-$ undergoes the same changes, as do the spectra of the difluoro cation and its deuterated counterpart.[24] Since the vibration frequencies of the BF_4^- ion in the higher temperature crystal form are essentially the same as those of this ion in the alkali metal salts, the interaction between the fluoro cation and the BF_4^- ion must be nonspecific under these conditions. The different frequencies for the BF_4^- ion in the lower temperature crystal form imply a specific interaction between a nucleophilic fluorine atom of BF_4^- and the carbon atom which accepts a fluoride ion in the exchange reaction. In the spectra of the salts formed from SbF_5 no comparable change occurred in the spectra over the temperature range of −100 to −15 °C.

In the Raman spectra (Figures 1 and 2) of the solutions prepared with BF_3, the presence of the BF_4^- ion was confirmed by the polarized band at 766 cm^{-1}. The symmetric stretching frequency of BF_4^- occurs at 766 cm^{-1} in molten KBF_4.[23] A puzzling feature of the solution spectra is the broad, polarized band which appears at about 700 cm^{-1} in the spectra of the difluoro cation[24] as well as those reported here. Because of overlapping bands, it is not possible to tell if the 700-cm^{-1} band also occurs in the solutions prepared with SbF_5. Rejected explanations for this band because they do not fit the frequency are (1) contamination from halocarbon grease; (2) SO_2F^-;[25] (3) SiF_4.[26] Further, the spectrum of BF_3 in SO_2 shows no bands other than ones due to SO_2 or BF_3 alone. An explanation of the 700-cm^{-1} band which would correlate with our interpretation of the temperature dependence of the NMR spectra and of the infrared spectra of the crystal is that this band is due to a perturbation of the symmetric stretch of BF_4^- engaged in site-specific interaction with the cation. In addition to the puzzling 700-cm^{-1} band unexplained bands appear at about 245 and 260 cm^{-1} in the various spectra.

The principal anion in the SO_2 solutions of the SbF_5 system appears to be the $Sb_2F_{11}^-$ ion. Gillespie and co-workers have shown with NMR studies that SbF_5 and SbF_6^- form a stable complex in a solution of $CsF{\cdot}2SbF_5$ in SO_2.[27] Although the Raman spectrum shown in Figure 3 was of a sample with an 80 mol % excess of SbF_5, the weakness of the band at 1120 cm^{-1} shows that only a small amount of the SbF_5 solvate, $SbF_5{\cdot}SO_2$, was present.[15] In the Raman spectrum of the deuterated cation, which is not shown, the bands attributable to the fluoroantimonate species were essentially the same and no intensity was at 1120 cm^{-1}. The Raman spectrum of crystalline $CsSb_2F_{11}$ has bands which agree well in frequency and intensity with those observed at 684, 652, 605, 296, 282, and 230 cm^{-1} in the present solution spectrum.[28] Some SbF_6^- is also presumably present, but the principal Raman bands for this species are nearly coincident with those of $Sb_2F_{11}^-$.

Even though the crystalline material for infrared spectroscopy was made with a substantial excess of the cyclopropene, the spectral evidence suggests that $Sb_2F_{11}^-$ may also be present in these preparations. Polycrystalline $KSbF_6$ is reported to have the following infrared bands above 250 cm^{-1} (cm^{-1}): 661 vs, 575 s, 294 m, and 278 m. The $Sb_2F_{11}^-$ ion has the following principal bands (cm^{-1}): 695 vs, 681 m, and 280 m, b.[29] In the infrared spectra of the d_0 cation, Figure 6, the strength of the intensity near 700 cm^{-1} and the absence of significant intensity near 575 cm^{-1} suggest that the $Sb_2F_{11}^-$ ion is the dominant species. In the spectrum of the d_2 cation, Figure 7, relatively more SbF_6^- appears to be present since the intensity in the 700-cm^{-1} region is weaker and the intensity in the 575-cm^{-1} region is stronger. The band just below 500 cm^{-1}, which is much stronger in Figure 6, and which is also in the spectra of the difluoro cation salts made with SbF_5,[24] must be related to the $Sb_2F_{11}^-$ anion or to its interaction with the fluoro cations. Fortunately, the concurrence of many features in the spectra of the salts formed from BF_3 (Figures 4 and 5) and of the salts formed from SbF_5 (Figures 6 and 7) shows that knowledge of the exact nature of the anion species is not critical to the analysis of the vibrational spectra of the fluorocyclopropenyl cations.

Vibrational Assignments for $C_3FH_2^+$ and $C_3FD_2^+$. A site-specific interaction between BF_4^- and the fluoro cation would cause the cation to distort from a planar shape. However, with the exception of the low-temperature form of the crystal, evidence is lacking for a large effect of this sort. Normal coordinate calculations have shown that a 0.2-Å distortion of the equilibrium position of the fluorine atom from the plane of the ring causes frequency shifts of 20 cm^{-1} or less. Thus, we have chosen to analyze the vibrational spectra of the fluorocyclopropenyl cation in terms of a planar ion with C_{2v} symmetry. In this representation, the cation has $5a_1 + 1a_2 + 4b_1 + 2b_2$ normal modes, where the b_1 modes are symmetric in the plane of the ion. The totally symmetric a_1 modes are polarized in the

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

Raman, SO_2 soln[a]				infrared, crystal[b]		assignment		
with BF_4^-[c]	$I_\parallel$[e]	$I_\parallel/I_\perp$[e]	with $Sb_2F_{11}^-$[d]	with BF_4^-	with SbF_6^-, $Sb_2F_{11}^-$	freq		sym species
3153	30	0.11	3155 m, p	3164 m	3157 s	ν_1	fund.	a_1
					3144 s			
3119	5	0.75	3125 w, dp	3127 s	3119 s	ν_7	fund.	b_1
					3108 s			
1860	21	p	1861 w, p	1878 w	1868 s	$\nu_8 + \nu_{10} = 1855$		A_1
1835	100	<0.02	1836 s, p	1840 s	1839 vs	ν_2	fund.	a_1
				1833 sh				
					1798 w	$\nu_4 + \nu_5 = 1818$		A_1
~1670	6	p					SO_2	
1372	~5	dp?	1375 w, ?	1388 m	1379 s	ν_8	fund.	b_1
1339	sh	p	1341 sh, p	1339 sh	~1330 vs	ν_3	fund.	a_1
				1330 s				
1332	152	dp?	1332 s, dp?				SO_2	
					1314 m	ν_3	^{13}C?	
				1290 w	1294 m	$\nu_{11} + \nu_{12} = 1349$		A_1
						Fermi resonance with ν_3		
1149	>200	p	1149 vs, p				SO_2	
1121	35	p	1125 m, p				$SO^{18}O$	
			1104 m, p				$SbF_5 \cdot SO_2$	
				1055 br, vs			BF_4^-	
					1022 m	ν_9	fund.	b_1
988	31	p	991 m, p	987 m	997 m	ν_4	fund.	a_1
				977 m				
					~940 w	$2\nu_{12} = 954$		A_1
874	24	p					BF_3	
				876 m	869 s	ν_{11}	fund.	b_2
830	73	0.36	832 s, p	835 sh, m	832 s	ν_5	fund.	a_1
				827 s				
766	13	p					BF_4^-	
707	17	p						
			684 vs, p		680 vs		$Sb_2F_{11}^-$	
			652 vs, p		~660 vs		$Sb_2F_{11}^-$, SbF_6^-	
			605 m, dp		601 m		$Sb_2F_{11}^-$	
524	130	0.62	526 s, dp?				SO_2	
				520 s			BF_4^-	
					498 s		$Sb_2F_{11}^-$?	
483	21	0.75	483 m, dp	489 m	470 m	ν_{10}	fund.	b_1
			~475 sh?			ν_{12}	fund.	b_2
					413 w			
					330 m			
			296 s, dp		~300 vs		$Sb_2F_{11}^-$, SbF_6^-	
			282 m, dp					
361	~3	0.78						
246	6	p						
			230 s, dp				$Sb_2F_{11}^-$	

[a] p = polarized, dp = depolarized, w = weak, m = medium, s = strong, vs = very strong, sh = shoulder, br = broad. $T = -22$ °C for BF_4^- solution; $T = -54$ °C for $Sb_2F_{11}^-$ solution. [b] $T = -196$ °C after warming BF_4^- crystal to -70 °C and SbF_6^- (?) crystal to -15 °C. [c] For frozen SO_2 solution, frequencies were 3153, 3120, 1860, 1835, 1373, ~1342 sh, 1332, 1146, 1121, 1014, 988, 872, 830, 766, 704 br, 526, 483, 477, ~405, 263, 251 cm^{-1}. [d] These frequencies are from survey scans, which tends to make them high. [e] Intensity (I) with analyzing polarizer parallel ($\parallel$) and perpendicular ($\perp$) to the polarization of the laser beam.

Raman spectrum, and the a_2 modes are not infrared active in the isolated ion.

The five modes of a_1 symmetry are assigned without difficulty for both the d_0 and d_2 modifications. In the Raman spectrum of the BF_4^- salt in Figure 1 obvious polarized bands at 3153, 1835, 988, and 830 cm^{-1} reveal four of the a_1 modes of the d_0 ion. The fifth band is almost coincident with the SO_2 solvent band[30] at 1334 cm^{-1} as is indicated by the appearance of this band as a shoulder at 1342 cm^{-1} in the spectrum of the frozen solution (Table I, footnote *c*) and as is shown by the intense bands at 1330 cm^{-1} in the infrared spectra of the fluoroborate and fluoroantimonate salts (Figures 4 and 5). The same four, clear bands due to a_1 modes are seen in the Raman spectrum, Figure 3, of the fluoroantimonate salt and in the infrared spectra of the two salts. Details of these assignments are in Table I.

For the d_2 ion the Raman spectrum, shown in Figure 2, has four obviously polarized bands at 2426, 1790, 1289, and 914 cm^{-1}. The band at 1289 cm^{-1} confirms ν_3 of the d_0 ion which, as we have seen, is obscured by the solvent band.

The Raman spectrum of the cation formed with SbF_5 (Table II) and the infrared spectra of the two salts (Figures 6 and 7) assure these four assignments. The fifth a_1 mode must be represented by the marginally polarized band at 650 cm^{-1} in the Raman spectrum of the BF_4^- salt. Bands due to the anionic species obscure the 650-cm^{-1} region in the two SbF_5 systems, but a corresponding absorption band is in the infrared spectrum of crystalline $C_3FD_2^+BF_4^-$. The overall assignment of the a_1 modes for the two isotopic species is supported by the good agreement between the theoretical and observed product rule ratios: 0.509 and 0.523, respectively.

For the four b_1 modes, we find strong evidence for three of

Table II. Raman and Infrared Spectra (cm^{-1}) and Assignments for the Monofluorocyclopropenyl-d_2 Cation

Raman, SO_2 soln[a]				infrared crystal[b]		assignment		
	with BF_4^- I	$I/I_\perp$	with $Sb_2F_{11}^-$	with BF_4^-	with SbF_6^-, Sb_2F_{11}	freq		sym species
2426	13	0.1	2426 w, p	2433 m	2421 s	ν_1	fund.	a_1
2353	5	dp	2355 w, dp	2362? m	2349 s	ν_7	fund.	b_1
1830	4	p	1830 vw, p	1829 m	1840 m	$2\nu_4 = 1828$		a_1
1790	58	0.05	1790 m, p	1792 s	1793 s	ν_2	fund.	a_1
1760	6	p	1760 vw, p	1768 m	1761 m	$\nu_8 + \nu_{10} = 1777$		a_1
				1360 m	1350 m	$\nu_4 + \nu_{10} = 1360$		B_1
					1343 m			
1333	>230	dp?	1332 vs, dp?				SO_2	
				1333 m	1329 m	ν_8	fund.	b_1
					1302 w			
1289	100	0.02	1289 s, p	1285 s	1289 vs	ν_3	fund.	a_1
					1280 sh			
~1150	vs	p	1147 vs, p				SO_2	
~1125	w	p	1122 w, p				$SO^{18}O$	
					1133 w			
				~1055 vs			BF_4^-	
914	73	0.1	913 s, p	911–	919 m	ν_4	fund.	a_1
				875 m				
~870	14	p					BF_3	
				~825 m	~830 w	ν_9	fund.	b_1
~788	8	p?					?	
766	26	p		767 w			BF_4^-	
			740 w	735 m	730 m	ν_{11}	fund.	b_2
~713	13	p					?	
			684 s, p		~675-		$Sb_2F_{11}^-$	
			652 s, p		640 vs		$Sb_2F_{11}^-$, SbF_6^-	
650	20	0.61	~650 m?	656 m		ν_5	fund.	a_1
				653 sh				
			603 m, ?				$Sb_2F_{11}^-$	
					579 w		SbF_6	
					568 w		SbF_6^-	
524	240	0.68	525 s, p?				SO_2	
				524 m			BF_4^-	
					~495 w			
446	13	0.77	466 w, dp?	450 m	448 m	ν_{10}	fund.	b_1
424	6	0.8	424 w, dp?			ν_{12}	fund.	b_2
			294 m, dp?		~290-		$Sb_2F_{11}^-$, SbF_6^-	
			279 m, dp?		265 vs		$Sb_2F_{11}^-$, SbF_6^-	
~270	dp							
~250	p							
			229 m, dp?		230 m		$Sb_2F_{11}^-$	

[a] See footnotes to Table I. $T = -23$ °C for BF_4^- solution; $T = -54$ °C for $Sb_2F_{11}^-$ solution. [b] $T = -196$ °C, but after warming BF_4^- crystal to -60 °C and SbF_6^- (?) crystal to -30 °C.

them in the spectra of each of the isotopic species. For the d_0 ion, depolarized bands occur at 3119 and 483 cm^{-1} in the Raman spectra. A third band is an indistinct shoulder at 1372 cm^{-1} in the liquid-phase Raman spectrum of the BF_4^- salt and an obvious feature in the Raman spectrum of the $Sb_2F_{11}^-$ salt, which was recorded at a lower temperature. The Raman spectrum of the frozen SO_2 solution of the BF_4^- salt also shows this band as a distinct feature at 1373 cm^{-1}. All three of these b_1 modes are seen in the two infrared spectra. For the d_2 ion depolarized bands are found at 2353 and 446 cm^{-1} in the Raman spectra, and corresponding bands are in the infrared spectra. Although ν_8 is now completely overshadowed by the SO_2 solvent band in the Raman spectra, it is readily seen at about 1333 cm^{-1} in the infrared spectra. The assignments for ν_9, the remaining b_1 modes of the two isotopic species, are based on more tenuous evidence. No trace of this mode is found in the Raman spectrum of either the d_0 or the d_2 species. However, for the d_2 ion bands of reasonable frequency are found in the 825-cm^{-1} region in the infrared spectra of both salts. For the d_0 ion, a band of moderate intensity occurs at 1022 cm^{-1} in the infrared spectrum of cation with SbF_5 and the Raman spectrum of the frozen solution has a band at 1014 cm^{-1}. Unfortunately, in the infrared spectrum of the BF_4^- salt this spectral region is obscured by the broad band of the anion. Low Raman intensity and moderate infrared intensity are also the pattern for the equivalent, largely CH(D) bending modes in 3,3-difluorocyclopropene.[7] With the incorporation of these two assignments for ν_9 the b_1 frequencies are in satisfactory agreement with the isotope product rule ratio: 0.538 for the theoretical ratio, 0.552 for the observed one.

Evidence for the two b_2 modes in both the d_0 and d_2 modifications is fragmentary. For the ν_{11} mode of the d_2 ion, appropriate bands are near 730 cm^{-1} in the infrared spectra of both salts. Weak features are also found in this region in both of the liquid-phase Raman spectra. For ν_{12} we have no choice but to use the weak Raman bands of uncertain polarization at 424 cm^{-1}. No support for this assignment is found in the infrared spectra. Turning to the d_0 species, we find good candidates for ν_{11} at about 870 cm^{-1} in the infrared spectra of both salts but no counterparts in the Raman spectra. We presume that ν_{12} is nearly degenerate with ν_{10} and assign it to the shoulder at 477 cm^{-1} in the Raman spectrum of the frozen SO_2 solution. These assignments for the d_0 species are supported by the use of the $\nu_{11} + \nu_{12}$ combination tone to explain the band

Table III. Vibrational Fundamentals and Potential Energy Distributions for the Monofluorocyclopropenyl-d_0 and -d_2 Cations

		$C_3FH_2^+$			$C_3FD_2^+$		
		freq, cm^{-1}			freq, cm^{-1}		
		obsd[a]	calcd	PED[b]	obsd[a]	calcd	PED[b]
a_1							
	ν_1	3153	3158	sym CH str 97	2426	2418	sym CD str 82, sym CCC str 10
	ν_2	1835	1842	sym CCC str 72, CF str 33[c]	1790	1783	sym CCC str 63, CF str 39, CD str 11[c]
	ν_3	1339	1341	CC(opp) str 75, CF str 24	1289	1287	CC(opp) str 75, CF str 18
	ν_4	988	989	sym CCH bd 77, CF str 16	914	912	CF str 40, sym CCC str 26, sym CD bd 20, CC(opp) str 13
	ν_5	830	833	CF str 27, sym CH bd 21, sym CCC str 20, CC(opp) str 14	650	648	sym CD bd 80
a_2							
	ν_6		944	HCCH torsion 100		765	DCCD torsion 100
b_1							
	ν_7	3119	3134	asym CH str 99	2353	2333	asym CD str 95
	ν_8	1372	1372	asym CCC str 90, CF bd 10	1331[d]	1332	asym CCC str 86, CF bd 10
	ν_9	*1014*[d]	1007	asym CH bd 95	*828*[d]	838	asym CD bd 83, CF bd 17
	ν_{10}	483	487	CF bd 84	446	436	CF bd 73, asym CD bd 18
b_2							
	ν_{11}	872[d]	883	asym CH flap 94	732[d]	713	asym CD flap 80, CF flap 20
	ν_{12}	*477*[d]	472	CF flap 94	*424*	436	CF flap 80, asym CD flap 20
av errors			5.6			8.5	

[a] Values in italics are uncertain assignments. [b] Contributions greater than 9 to the potential energy distribution expressed in symmetry coordinate space. sym = symmetric, asym = antisymmetric, str = stretch, bd = bend (wag), opp = opposite to CF carbon. [c] Interaction between symmetric CCC stretch and CF stretch, −13 for both isotopic species. [d] From spectra of frozen solution and crystals; all others from spectra of SO_2 solution.

near 1292 cm^{-1} that appears to be in Fermi resonance with the a_1 fundamental at 1339 cm^{-1}. The assignments for the b_2 modes also gain support from the product rule ratios of 0.742 (theory) and 0.746 (observed).

No evidence was found for the single a_2 mode in the Raman spectrum of either isotopic species. This disappointment recalls the silence of the corresponding HCCH torsional mode in cyclopropenone[31] and its uncertain detection in 3,3-difluorocyclopropene.[7] Frequencies of 945 and 766 cm^{-1} obtained from normal coordinate calculations are given for the two a_2 modes in the summary of vibrational fundamentals in Table III. If the force constant for interaction between the two CH flapping modes is transferred from difluorocyclopropene, then these a_2 frequencies are computed as 1064 and 863 cm^{-1}. The frequency ranges suggested by these two sets of values include possibilities for masking due to overlaps with observed bands.

In summary, given the cumulative evidence from the several spectra of the two isotopic species, we believe that the assignment of the fundamentals for the two fluorocyclopropenyl cations is nearly complete. The five a_1 modes for each ion are secure, and the b_1 modes are almost as certain. Owing to the fragmentary experimental evidence, some doubt attends the b_2 assignments. This uncertainty is propagated through the normal coordinate analysis into the calculated frequencies of the a_2 frequencies, which must be viewed as rough approximations.

Normal Coordinate Analysis. A normal coordinate analysis has been carried out on the vibrational fundamentals of the fluorocyclopropenyl-d_0 and -d_2 cations. As part of a forthcoming paper on the spectroscopy of the difluorocyclopropenyl cation, we will include a full presentation of the normal coordinate calculations for the two fluoro cation systems. For the present we give an abbreviated account of the results for the monofluoro cation.

Vibrations of the monofluoro cation were expressed in terms of the changes in a nonredundant set of 12 internal coordinates: the six bond lengths, the three pairwise angle differences for in-plane wagging of the CH and CF bonds, and the three angles which the CH and CF bonds make with the plane of the ring during out-of-plane motion. For construction of the G matrices geometric parameters were derived from several sources.[3,4,32–34]

The combined set of 22 observed fundamentals for the two isotopic modifications has proved sufficient to define a 12-parameter, modified valence potential function. Table IV gives several sets of potential constants: (1) the zero-order set from which the standard least-squares perturbation procedure started in each case,[7] (2) the refined set which was fit to a fluoro cation model having differentiated CC bond lengths, (3) a second refined set which was fit to a fluoro cation model having equal CC bond lengths, and (4) a third refined set which was obtained in an overlay calculation with the difluorocyclopropenyl-d_0 and -d_1 cations. In the overlay calculation different pairs of CC stretching constants were defined for the two ions, but the other diagonal constants were a single set. Three of the seven interaction constants were also common to the two ions. The good agreement between the results of the first refinement (column 2) and the overlay calculation (column 4) gives us confidence in the set of potential constants. The overlay calculation provides added constraint on the motions of the heavy atoms, which deuterium substitution does little to exercise. In the calculations for the monofluoro cation alone the interaction constant between the two different types of CC bonds was refined even though its statistical dispersion was somewhat larger than its magnitude for the case of unequal CC bond lengths. When the larger value from the overlay calculation was used, the other 11 constants refined to values close to those in Table IV.

Table III gives the frequencies that were calculated in the single ion refinement in comparison with the observed values. Average frequency errors were 5.6 and 8.5 cm^{-1}, respectively, for the two isotopic species. The well-behaved normal coordinate calculations support the present assignment of fundamentals. Table III also gives the principal contributions to the potential energy distributions (PED), expressed in symmetry coordinate space. The PEDs show that most of the normal modes are dominated by a single symmetry coordinate and thus may be viewed as group frequencies. However, as in related fluorocarbons,[7] CF stretching is extensively mixed into several normal modes. The highest frequency ring mode, which is at 1835 cm^{-1} in the d_0 species, is principally the stretching of the

Table IV. Potential Constants for the Fluorocyclopropenyl Cation (mdyn Å^{-1} to mdyn Å rad^{-2})

		refinement for monofluoro cation^c		overlay with
description^a	zero order^b	unequal r_{CC}	equal r_{CC}	difluoro cation^c
$f_{CC}{}^{str}$ (unique)	6.18	6.835(209)	6.99(18)	7.16(17)
$f_{CC}{}^{str}$	6.18	8.276(140)	8.75(16)	8.29(14)
$f_{CH}{}^{str}$	5.35	5.331(29)	5.33(3)	5.32(3)
$f_{CF}{}^{str}$	6.16	8.354(517)	7.32(34)	7.92(20)
$f_{CH}{}^{wag}$	0.51	0.540(12)	0.54(1)	0.55(1)
$f_{CF}{}^{wag}$	1.03	1.227(64)	1.21(7)	1.26(5)
$f_{CH}{}^{flap}$	0.32	0.423(11)	0.43(1)	0.43(1)
$f_{CF}{}^{flap}$	0.40	0.520(24)	0.55(3)	0.56(2)
$f_{CC,CC}{}^{str}$ (different)	0.0	−0.241(321)	−0.38(29)	−0.63(25)
$f_{CC,CF}{}^{str}$ (local)	0.0	0.780(208)	0.84(15)	0.52(8)
$f_{CC,CH}{}^{str,wag}$ (both)	0.0	−0.210(38)	−0.18(5)	−0.29(4)
$f_{CH,CH}{}^{wag}$	0.0	0.045(11)	0.04(1)	0.05(1)

[a] str = stretch; wag occurs in the plane of the ion; flap is out of plane. [b] Adapted from ref 7. [c] Statistical dispersions in parentheses with last number corresponding to last decimal place.

two, stronger CC bonds. As is characteristic of species with high-frequency ring modes, noteworthy mixing occurs between the symmetric CH (and CD) stretching modes and the highest frequency ring mode. As a consequence, the symmetric CH and CD stretching frequencies are appreciably higher than the antisymmetric ones. This difference is greater for the deuterated species, owing to the smaller difference between the frequencies of the natural CD stretching mode and the ring mode. For the monofluorocyclopropenyl cation, the symmetric CH stretching frequency is 34 cm^{-1} higher than the antisymmetric one, and the symmetric CD one is 73 cm^{-1} higher than the antisymmetric one.

In keeping with the marked influence of fluorine substitution on the bonds in other three-membered rings, we find that the force constant for the CC bond opposite the point of fluorine substitution, $f_{CC}{}^{str}$ (unique), is substantially weaker than the force constant for the CC bonds involving the fluorine-bearing carbon. The weaker CC force constant is larger than that estimated for a 1.33 bond strength (6.18 mdyn Å^{-1}) from the force constants of 3,3-difluorocyclopropene.[7] However, the principal effect has been to strengthen the force constant for the CC bonds adjacent to the fluorine-substituted carbon. To check on the possibility that the assumption of differentiated CC bond lengths contributed significantly to the difference in the CC force constants, we did a calculation in which all three CC bond lengths were 1.37 Å. The potential function obtained in this calculation, which is given in column 3 in Table IV, is not greatly different from the preferred one. In particular, this strong-weak difference is preserved in the CC stretching constants.

The substantial interaction of the fluorine atom with the cyclopropenyl ring is also apparent in a marked increase in the CF stretching force constant in comparison with the one in 3,3-difluorocyclopropene (column 1, Table IV). This change, which reflects considerably greater double-bond character in the CF bond in the cation than in the cyclopropene, implies significant overlap of the p_y orbital of fluorine with the π-bond system of the cyclopropenyl ring. However, describing this interaction as electron donation into the lowest unfilled molecular orbital of the correct symmetry[35] predicts weakening of the adjacent CC bonds and strengthening of the opposite CC bond, a prediction that is in conflict with the magnitudes of the two CC force constants. Thus, is seems that a frontier-orbital analysis of the interaction of a fluorine atom with the cyclopropenyl ring fails as does a corresponding analysis for fluorocyclopropanes.[2] A full molecular orbital treatment was needed to rationalize the bond-length changes due to fluorine substitution on the cyclopropane and cyclopropene rings.[9]

The force constant for CH stretching in fluorocyclopropenyl cations reveals a bond to a carbon atom with considerable s character. CH stretching constants are about 4.9 for sp^3 hybridization, 5.1 for sp^2, and 5.9 for sp.[36] Thus, for the fluorocyclopropenyl cation the value of 5.33 mdyn Å^{-1} indicates a bond with considerable sp character, as would be expected for a description in terms of the simple Walsh molecular orbital model for C_3 rings.[37] A similar MO description would apply to the CH carbon atoms in 3,3-difluorocyclopropene, for which the CH stretching force constant has essentially the same value.[7]

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A UV Photoelectron Spectroscopic Investigation of the Bonding in Some Tri-, Tetra-, and Pentacoordinated Dialkylamino Compounds of Chromium, Molybdenum, Niobium, and Tantalum

M. H. Chisholm,*[1a] A. H. Cowley,*[1b] and M. Lattman[1b]

Contribution from the Departments of Chemistry, Indiana University, Bloomington, Indiana 47401, and the University of Texas at Austin, Austin, Texas 78712. *Received June 25, 1979*

Abstract: Helium(I) ultraviolet photoelectron spectra (UV PES) are reported for the compounds $Cr(N\text{-}i\text{-}Pr_2)_3$, $Cr(NEt_2)_4$, $Mo(NMe_2)_4$, $Mo(NEt_2)_4$, $Nb(NMe_2)_5$, and $Ta(NMe_2)_5$. The interpretation of the UV PES of the paramagnetic dialkylamide, $Cr(N\text{-}i\text{-}Pr_2)_3$, was aided by a SCF-X$\alpha$ scattered wave (Xα-SW) calculation on the model compound $Cr(NH_2)_3$. In contrast to previous UV PES work on $Cr[N(SiMe_3)_2]_3$, ionizations are detectable from the metal MOs of $Cr(N\text{-}i\text{-}Pr_2)_3$. The UV PES of the tetracoordinate molybdenum compounds, $Mo(NR_2)_4$, R = Me, Et, are in excellent agreement with X-ray crystallographic data on $Mo(NMe_2)_4$ and exhibit a low-energy ionization (~5.3 eV) which is attributable to electron ejection from the essentially pure Mo $4d_{x^2-y^2}$ MO of b_1 symmetry. The pentacoordinate compounds, $M(NMe_2)_5$, M = Nb, Ta, exhibit very similar UV PES and therefore appear to be isostructural in the vapor phase.

Introduction

The use of dialkylamido and disilylamido ligands has permitted the isolation of mono- and dinuclear transition metal derivatives with widely varying coordination numbers.[2] Compounds of this type are well suited to investigation by ultraviolet photoelectron spectroscopy (UV PES) because, as shown in previous studies,[3–5] the peaks at lower binding energies corresponding to electron ejection from metal-centered MOs, nitrogen lone pair MOs, and metal-nitrogen σ-bonding MOs fall into distinct regions. The UV PES data can be used, therefore, not only for the delineation of bonding schemes but also for gaining insights into the stereochemistry of metal amides.

The present paper is concerned with the measurement and interpretation of the UV PES of $Cr(N\text{-}i\text{-}Pr_2)_3$, $Cr(NEt_2)_4$, $Mo(NMe_2)_4$, $Mo(NEt_2)_4$, $Nb(NMe_2)_5$, and $Ta(NMe_2)_5$. Our interest in the tricoordinate species, $Cr(N\text{-}i\text{-}Pr_2)_3$, was generated by the fact that in the corresponding silylamide, $Cr[N(SiMe_3)_2]_3$, it was impossible to detect UV PES peaks corresponding to the ionization of metal-localized MOs.[5] The tetracoordinate dialkylamides, $Cr(NEt_2)_4$ and $Mo(NR_2)_4$, R = Me, Et, are the first group 6B amides to be studied by UV PES; particular interest is associated with these compounds because the molybdenum amides are diamagnetic yet $Cr(NEt_2)_4$ is paramagnetic. Finally, the pentacoordinate amides, $M(NMe_2)_5$, M = Nb, Ta, were investigated because of the apparently close energies of the trigonal-bipyramidal and square-pyramidal MN_5 geometries and the possibility of detecting conformational effects in the vapor phase.

A SCF-Xα scattered-wave calculation[6] (hereafter referred to as Xα-SW) has been performed on the model amide $Cr(NH_2)_3$ to facilitate the interpretation of the UV PES data. As is well known, this theoretical approach has the advantage of avoiding the use of Koopmans' theorem[7] by means of the transition-state method.[8]

Experimental Section

Materials. The compounds $Cr(N\text{-}i\text{-}Pr_2)_3$,[9] $Cr(NEt_2)_4$,[10] $Mo(NMe_2)_4$,[11] $Mo(NEt_2)_4$,[11] $Nb(NMe_2)_5$,[12] and $Ta(NMe_2)_5$[13] were prepared and purified as described in the literature.

Spectroscopic Measurements. All UV PES data were recorded on a Perkin-Elmer Model PS-18 photoelectron spectrometer using a He(I) photon source (21.22 eV). The heated inlet probe was used for all samples and temperatures in the range 35-100 °C were necessary to obtain suitable spectra. Each spectrum was calibrated with xenon (12.130 eV) and argon (15.759 eV) used as internal standards. Spectral resolution was maintained between 25 and 50 meV for the argon line. All ionization energies are read as the band maxima, unless otherwise noted, and are the average of at least three different runs.

Computational Procedures. The Xα-SW calculation on $Cr(NH_2)_3$ was made by employing the spin-restricted procedure of Johnson and Slater,[6] setting the occupation numbers of the 6e and $4a_1$ levels at two and one, respectively, in accord with the observed ground-state electronic configuration.[9] The bond distances and angles for $Cr(NH_2)_3$ were based on those observed by X-ray crystallography for $Cr(N\text{-}i\text{-}Pr_2)_3$,[14] except that the N-H bond distance was taken to be 1.01 Å. The atomic sphere radii were chosen on the basis of optimizing the virial ratio, and the outer sphere was set tangential to the hydrogen spheres.[15] Schwartz's exchange parameters, α_{HF}, were used for

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