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The Vibrational Spectrum and Structure of the Difluorochlorinium(III) Cation, ClF_2^+

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The Raman spectra of the compounds $ClF_2 \cdot SbF_6$, $ClF_2 \cdot AsF_6$, and $ClF_2 \cdot BF_4$ have been measured. The fundamental frequencies of the ClF_2^+ ion have been reassigned and force constants calculated. It is confirmed that ClF_2^+ is bent and it is concluded that there is fluorine bridging between the ClF_2^+ ion and the anions.

In a recent paper Christe and Sawodny[1] have reported the infrared spectra of $ClF_2 \cdot AsF_6$ and $ClF_2 \cdot BF_4$ and the Raman spectrum of $ClF_2 \cdot AsF_6$ and have given a reinterpretation of earlier infrared data on these compounds.[2] We report now the Raman spectra of $ClF_2 \cdot AsF_6$, $ClF_2 \cdot SbF_6$, and $ClF_2 \cdot BF_4$ and on the basis of these results we propose a reassignment of one of the fundamental frequencies of ClF_2^+ and new values for the force constants.

The Raman spectra of the three compounds are shown in Figure 1 and the frequencies of the bands are listed in Tables I–III together with our assignments.

TABLE I

RAMAN SPECTRUM OF $ClF_2^+SbF_6^-$

Rel intens[a]	Freq shift, cm^{-1}	Assignment
9	277	$\nu_5(SbF_6^-)$
13	291	
7	387	$\nu_2(ClF_2^+)$
25	532	$\nu_2(SbF_6^-)$
30	543	
5	596	
100	662	$\nu_1(SbF_6^-)$
91	805	$\nu_1(ClF_2^+)$
97	809	
63	830	$\nu_3(ClF_2^+)$

[a] Peak height.

TABLE II

INFRARED AND RAMAN SPECTRA OF $ClF_2^+AsF_6^-$

This work			Christe and Sawodny[1]		
Rel intens	Raman freq shift, $\Delta\nu$, cm^{-1}	Assignment	Raman freq shift, $\Delta\nu$, cm^{-1}	Ir freq, cm^{-1}	Assignment
14	373	$\nu_5(AsF_6^-)$	375 mw		$\nu_5(AsF_6^-)$
14	384	$\nu_2(ClF_2^+)$		406 m	$\nu_3(AsF_6^-)$
				520 w	$\nu_2(ClF_2^+)$
26	544	$\nu_2(AsF_6^-)$	544 m	558 m	
6	602		603	609 w	$\nu_2(AsF_6^-)$
77	693	$\nu_1(AsF_6^-)$	693 s		$\nu_1(AsF_6^-)$
				703 vs	$\nu_4(AsF_6^-)$
100	806	$\nu_1(ClF_2^+)$	811 vs	810 sh	$\nu_1(ClF_2^+)$
90	809				
51	821	$\nu_3(ClF_2^+)$		818 s	$\nu_3(ClF_2^+)$

TABLE III

INFRARED AND RAMAN SPECTRA OF $ClF_2^+BF_4^-$

Raman (this work), −110°			Ir (Christe and Sawodny[1])	
Rel intens	Freq, cm^{-1}	Assignment	Freq, cm^{-1}	Assignment
15	63			
10	91			
15	124			
15	134			
3	355	$\nu_2(BF_4^-)$		
6	373	$\nu_2(ClF_2^+)$		
12	396			
			519 m	$\nu_4(^{10}BF_4^-)$
4	526	$\nu_4(BF_4^-)$	529 sh	$\nu_4(^{11}BF_4^-)$
			537 ms	$\nu_2(ClF_2^+)$
54	762	$\nu_1(BF_4)$	766 m	$\nu_1(BF_4^-)$
76	788	$\nu_1(ClF_2^+)$	798 s	$\nu_1(ClF_2^+)$
100	798			
31	808	$\nu_3(ClF_2^+)$	813 sh	$\nu_3(ClF_2^+)$
4	930	$\nu_3(BF_4^-)$	978–1145 s	$\nu_3(BF_4^-)$

These assignments can be made very reasonably on the basis of ionic structures, *i.e.*, $ClF_2^+MF_6^-(MF_4^-)$, for these compounds using previously published assignments[3,4] for SbF_6^-, AsF_6^-, and BF_4^-. Our assignment for ClF_2^+ differs from that of Christe and Sawodny in that we assign ν_2 at 384 cm^{-1} rather than at 544 cm^{-1}. Bands are observed in the 520–540-cm^{-1} region for each of the compounds but in each case they are best assigned to the anion, and it is only a coincidence that all three compounds have a band in this region. A band is observed in all three compounds close to 380 cm^{-1} (actually split into a doublet at 373 and 396 cm^{-1} in $ClF_2 \cdot BF_4$) which cannot be reasonably attributed to the anion in any of the compounds and which we therefore assign as ν_2 of ClF_2^+. Further evidence against the former assignment for ν_2 is provided by the fact that on dissolving the compound $ClF_2 \cdot SbF_6$ in excess SbF_5 the doublet at 532–543 cm^{-1} disappears and is replaced by bands at 578 and 710 cm^{-1} as a consequence of the conversion of SbF_6^- to $Sb_2F_{11}^-$ or some higher polymer of the form $Sb_nF_{5n+1}^-$, while the bands attributed to ClF_2^+ remain unchanged. Finally, we note that ClO_2^-, which is isoelectronic with ClF_2^+, has frequencies of 786, 402, and 804 cm^{-1} for ν_1, ν_2, and ν_3, respectively,[3] which are very close to the frequencies of 808, 384, and 821 cm^{-1} that we now propose for ClF_2^+ in $ClF_2 \cdot AsF_6$. The slight increase in the stretching frequencies from ClO_2^- to ClF_2^+ may

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(1) K. O. Christe and W. Sawodny, *Inorg. Chem.*, **6**, 313 (1967).

(2) K. O. Christe and A. E. Pavlath, *Z. Anorg. Allgem. Chem.*, **335**, 210 (1965).

(3) H. Siebert, "Anwendungen der Schwingungsspektroskopie in der Anorganischen Chemie," Springer-Verlag, Berlin, 1966.

(4) G. M. Begun and A. C. Rutenburg, *Inorg. Chem.*, **6**, 2212 (1967).

indicate that the Cl–F bond strength in ClF_2^+ is greater than the Cl–O bond strength in ClO_2^-. This presumably results from the greater electronegativity of fluorine than oxygen and the increase in the electronegativity of chlorine resulting from its formal positive charge in ClF_2^+.

The splitting of the ν_2 (E_g) band of AsF_6^- and SbF_6^- and the observation of this band in the infrared spectrum of $ClF_2 \cdot AsF_6$ as well as in the Raman spectrum indicate that the MF_6^- ion is distorted from its ideal octahedral symmetry. A similar splitting of bands and departures from the mutual exclusion rule for molecules with a center of symmetry has been noticed in a number of other compounds of octahedral fluoroanions with fluorocations such as $SF_3^+SbF_6^-$, $SeF_3^+AsF_6^-$, and $XeF^+IrF_6^-$, and in these cases this has been attributed[5-7] to fluorine bridging between the anion and the cation which reduces the octahedral symmetry of the anion, and it seems reasonable to conclude that there is also fluorine bridging in $ClF_2 \cdot AsF_6$. Christe and Sawodny[1] noted the occurrence in the infrared spectrum of $ClF_2 \cdot BF_4$ of a relatively strong band at 766 cm^{-1} which they attributed to the forbidden ν_1 mode. They attributed this to the BF_4^- ion having a site symmetry in the crystal lower than T_d and this lowering of the site symmetry may be reasonably attributed to fluorine bridging between BF_4^- and ClF_2^+. We note that $\nu_4(BF_4^-)$ is also split in the infrared spectrum. This may be partly an isotopic splitting but it also presumably results from the lowering of the site symmetry of BF_4^-. The very small splitting of ν_1 of ClF_2^+ in $ClF_2 \cdot SbF_6$ and $ClF_2 \cdot AsF_6$ is presumably a crystal (*i.e.*, a factor group) splitting. On dissolving the $ClF_2 \cdot SbF_6$ compound in excess SbF_5, all the lines become rather broad due to solvent interactions and ν_1 and ν_3 of ClF_2^+ then appear as one broad band centered at 820 cm^{-1}.

In view of the very small difference between the symmetric and antisymmetric stretching frequencies for ClF_2^+ we concur with Christe and Sawodny's conclusion that the molecule must be bent. Using a simple valence force field, two frequencies and the bond angle are required to calculate the stretching force constant and the bending force constant d. The results of such calculations are shown in Table IV. We used the frequencies ν_2 and ν_3 and assumed values of the bond angle to calculate values for the force constants f and d and then used these values to calculate ν_1. These calculated frequencies are seen to be in good agreement with the observed values for all three compounds for values of the bond angle in the range 95–100°. In view of the lack of structural data for ClF_2^+ we do not consider that the more elaborate treatment of the spectroscopic data given by Christe and Sawodny in which they also calculate interaction constants between the bonds and between the bonds and the angle is justified.

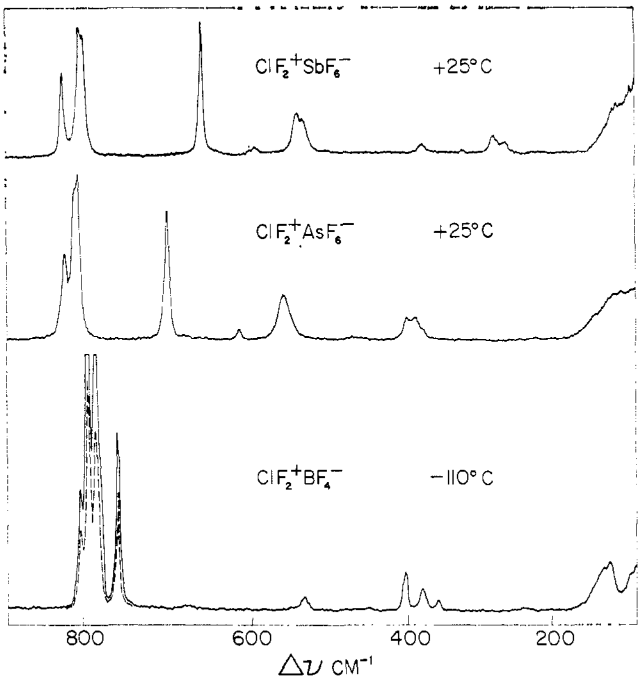

Figure 1.—Raman spectra of $ClF_2 \cdot SbF_6$, $ClF_2 \cdot AsF_6$, and $ClF_2 \cdot BF_4$.

For the angles that give the best value of the calculated frequency ν_1 we find values of the stretching force constants as follows: $ClF_2 \cdot SbF_6$, 4.8 mdyn Å^{-1}; $ClF_2 \cdot AsF_6$, 4.7 mdyn Å^{-1}; $ClF_2 \cdot BF_4$, 4.6 mdyn Å^{-1}. The bending force constants also show a slight decrease from 0.63 to 0.62 to 0.61 mdyn Å^{-1} in the same series. Although the small changes in the stretching force constant may not be significant, it is perhaps not unreasonable to assume that they reflect a slight decrease in the Cl–F bond strength in the series $ClF_2 \cdot SbF_6$, $ClF_2 \cdot AsF_6$, and $ClF_2 \cdot BF_4$ which may be a consequence of an increased extent of interaction between anion and cation by fluorine bridging. For comparison we note that the stretching force constant for the FCl molecule[3] is 4.34 mdyn Å^{-1} and for the isoelectronic ClO_2^- molecule[3] the values of the force constants are f = 4.26 and d = 0.52 mdyn Å^{-1}. Christe and Sawodny obtained

TABLE IV

FORCE CONSTANTS FOR THE ClF_2^+ CATION

$ClF_2^+SbF_6^-$ (ν_1 807, ν_2 387, ν_3 830 cm^{-1})				
Angle, deg	95	100	105	110
10^5f, dyn cm^{-1}	4.88	4.74	4.61	4.50
10^5d, dyn cm^{-1}	0.630	0.612	0.593	0.575
Calcd ν_1, cm^{-1}	822	799	776	753
$ClF_2^+AsF_6^-$ (ν_1 807, ν_2 384, ν_3 821 cm^{-1})				
Angle, deg	95	100	105	
10^5f, dyn cm^{-1}	4.77	4.63	4.51	
10^5d, dyn cm^{-1}	0.619	0.601	0.583	
Calcd ν_1, cm^{-1}	813	790	768	
$ClF_2^+BF_4^-$ (ν_1 793, ν_2 384, ν_3 808 cm^{-1})				
Angle, deg	95	100	105	
10^5f, dyn cm^{-1}	4.63	4.49	4.37	
10^5d, dyn cm^{-1}	0.620	0.602	0.585	
Calcd ν_1, cm^{-1}	802	778	756	

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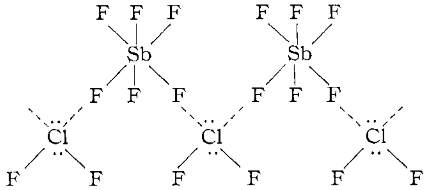
(5) M. Azeem, M. Brownstein, and R. J. Gillespie, *Can. J. Chem.*, **47**, 4159 (1969).

(6) R. J. Gillespie and A. Whitla, *ibid.*, in press.

(7) F. O. Sladky, P. A. Bulliner, and N. Bartlett, *J. Chem. Soc.*, *A*, 2179, (1969).

force constant values of $f = 4.705$ and $d = 1.256$ mdyn $Å^{-1}$ for a bond angle of 95° and $f = 4.714$ and $d = 1.216$ mdyn $Å^{-1}$ for a bond angle of 100° apparently using the frequencies they observed for $ClF_2 \cdot AsF_6$. Naturally the stretching force constant agrees well with our value but their bending force constant is twice our value which is a consequence of the much higher frequency that they assigned to the bending mode. We may note that their bending force constant is out of line with that for ClO_2^-. We note also that the force constants for PF_3 which might be expected to be fairly close to those of ClF_2^+ have been found to be $f = 5.21$ and $d = 0.62$ mdyn $Å^{-1}$.[3]

The most reasonable structure for these ClF_2^+ compounds would appear to be one that is closely similar to that of $BrF_2^+SbF_6^-$ in which bromine achieves a distorted square-planar coordination with an FBrF bond angle of 95° by forming fluorine bridges to the SbF_6^- ion.[8] As has been mentioned above there is some evidence from the vibrational spectra of this and related compounds that the symmetry of the octahedral anion is reduced and this can be reasonably accounted for in terms of fluorine bridging. The proposed structure for $ClF_2 \cdot SbF_6$ is shown diagrammatically as



The free ClF_2^+ ion has a chlorine valency shell of eight electrons which would be expected to give an angular molecule with a bond angle of somewhat less than the tetrahedral angle. In the fluorine-bridged structure the chlorine would have a valency shell of six electron pairs, and if the fluorine bridging was very strong, the six electron pairs would have an approximately octahedral arrangement leading to a bond angle of approximately 90°. However, as the fluorine bridge bonds are presumably appreciably weaker than the nonbridging Cl–F bonds, an FClF bond angle of rather greater than 90° is expected. The angle of 95–100° obtained by the simple valency force field calculation could be considerably in error but nevertheless it is satisfactory that it is at least consistent with the probable structure proposed above.

Experimental Section

Materials.—Materials were handled in a Monel vacuum line fitted with Whitey valves with Kel-F seats. Kel-F traps were attached with Swagelok fittings, and the line was well aged with ClF_3. Chlorine trifluoride and BF_3 (Matheson Co. Inc.) and AsF_5 (Ozark Mahoning Co.) were purified by low-temperature vacuum distillations. SbF_5 (Ozark Mahoning) was doubly distilled at atmospheric pressure in a glass still, followed by vacuum distillation.

The compounds were prepared by literature methods[2] in 4-mm thin-wall, clear, Kel-F tubes attached to the vacuum line. The excess ClF_3 was pumped off at 25° for the SbF_6^- and AsF_6^- salts and at −76° for the BF_4^- salt, and the Kel-F tube was heat-sealed under vacuum.

Raman Spectra.—Raman spectra were recorded using a Spex Industries Model 1400 spectrometer employing a double monochromator and a phototube detector with an electrometer amplifier and recorder. The exciting radiation was the green 5145-Å line of a Spectra-Physics Model 140 argon ion laser or the 6328-Å line of a Spectra-Physics Model 125 He–Ne laser. A spectral slit width of 3 cm^{-1} was used and the Raman shifts were estimated to be accurate to ±2 cm^{-1}.

The vertical laser beam was focused on the solids contained in the horizontally mounted Kel-F tube, and the light scattered at 90° was focused on the slits of the monochromator so that the image of the tube walls fell well outside the limits of the slit height. For low-temperature spectra the tube was mounted in a quartz tube with an evacuated jacket, silvered except at the center. Nitrogen was boiled off from a dewar and passed through the tube, and the temperature was recorded with a thermocouple.

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(8) A. J. Edwards and G. R. Jones, *J. Chem. Soc., A*, 1467 (1969).