to I_4^{2+} at low temperatures.[12] The bromine cations Br_2^+ and Br_3^+ are evidently considerably less stable than the corresponding iodine cations although Br_2^+ has been obtained as a stable solid with the very weakly basic anion $Sb_3F_{16}^-$, and Br_3^+ has been obtained as the hexafluoroarsenate. It may be predicted that the corresponding chlorine cations Cl_2^+ and Cl_3^+ will be still less stable in solution than the bromine cations and this is discussed in a following paper.[14] The vibrational frequencies of the halogens and their cations are summarized in Table VII. No vibrational frequencies have yet been reported for I_3^+.

TABLE VII

VIBRATIONAL FREQUENCIES OF THE HALOGENS AND THEIR CATIONS

	Cl_2	Cl_2^+	Cl_3^+	Br_2	Br_2^+	Br_3^+	I_2	I_2^+
ν_1	555	640	514	320	360	290	215	238
ν_2	...	...	208	...	...	?	...	...
ν_3	...	...	535	...	...	290	...	...

Experimental Section

The methods used for magnetic susceptibility, uv and visible, and conductometric measurements and the calculation of γ values have been described previously.[1,4,6,12,15] Solutions were handled in a drybox using smooth glass syringes fitted with Teflon plungers and platinum needles (Hamilton Syringe Co.) as weight droppers. Materials were prepared and purified as described previously.[1,3,6,12,15]

Raman spectra were recorded using a Spex Industries Model 1400 double monochromator with dc amplification and with a spectral slit width of 3 cm^{-1}. Raman shifts were accurate to ± 2 cm^{-1}. The beam of exciting radiation from a Spectra Physics Model 125 helium–neon laser or a Spectra Physics Model 140 argon ion laser entered the sample compartment in a vertical direction and was focused on the sample sealed in a horizontally mounted 2-mm o.d. glass melting point tube. The light scattered at right angles to the incident beam and the tube axis was focused on the entrance slit of the monochromator. For resonance Raman studies in which the Raman intensities were compared using different excitation frequencies, the laser output at the sample was attenuated to 10 mW to minimize heating. The areas of the Raman peaks on the recording chart were measured using a Du Pont 310 curve analyzer and at each exciting wavelength the areas of the Br_2^+ resonance Raman peaks were compared to the areas of the solvent peaks.

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Chlorine Cations in Highly Acidic Media

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The reaction of ClF and of ClF–Cl_2 with the superacid medium HSO_3F–SbF_5–$3SO_3$ has been investigated in order to obtain further evidence on the possible formation of ClF^+ and Cl_2^+ which have been claimed to be products from the reaction of ClF with SbF_5 and HSO_3F–SbF_5. This reaction was however found to produce $ClOSO_2F$ and no evidence was obtained for Cl_2^+ or ClF^+. An esr spectrum that is obtained from many of these solutions and which was assigned previously to ClF^+ appears to be due to an oxygen-containing species which is proposed to be either $OClF^+$ or O_2ClF^+.

Iodine in the 1+ oxidation state is completely disproportionated in solution in fluorosulfuric acid to the I_2^+ ion and $I(SO_3F)_3$.[1] Recently we have shown[2] that bromine(I) fluorosulfate is disproportionated to an appreciable extent to the Br_2^+ ion and $Br(SO_3F)_3$ in solution in the superacid SbF_5–$3SO_3$–HSO_3F. It was interesting therefore to explore the possibility that chlorine in the 1+ oxidation state might disproportionate in a similar manner in a sufficiently acidic medium at least to an extent which would enable the Cl_2^+ cation to be detected by a sensitive technique, *e.g.*, the resonance Raman spectrum which has proved particularly useful for the detection of the I_2^+ and Br_2^+ cations at low concentrations.[2,3]

By oxidizing iodine or bromine with a suitable oxidizing agent, *e.g.*, $S_2O_6F_2$, the cations I_3^+ and Br_3^+ have been obtained in highly acidic solutions,[1,2] a rather lower acidity being sufficient to stabilize these ions than is necessary for the corresponding I_2^+ and Br_2^+ cations. Consequently it also seemed reasonable to search for the formation of the Cl_3^+ cation in acidic media, particularly as we have recently been able to prepare the solid compound $Cl_3^+AsF_6^-$ at low temperature and to establish its identity by means of its Raman spectrum.[4] There has been an as yet unpublished claim (cited in ref 5) that Cl_2^+ can be obtained as the salt $Cl_2^+IrF_6^-$ and Olah and Comisarow have attributed a seven-line esr spectrum which they obtained on dissolving ClF in SbF_5, HSO_3F–SbF_5, or HF–SbF_5 to the Cl_2^+ cation.[6] These authors also attributed a second more complex esr spectrum that they observed in solutions of ClF_3 or ClF_5 in these solvents to the ClF^+ radical ion[7] and they suggested that

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a Raman line observed in these solutions at 819 cm⁻¹ is due to this radical ion. The assignment of the esr spectra to the Cl_2^+ and ClF^+ cations has however been recently criticized by Symons, *et al.*, who suggested that they are due, respectively, to the Cl_2O^+ and $ClOF^+$ radical ions,[8] and by Christe and Muirhead,[9] who claimed that radicals are *not* produced in the reaction of highly purified SbF_5 and ClF_3 or ClF_5 and that the radicals observed by Olah and Comisarow must have been due to impurities.

The purpose of the work described in this paper was to attempt to obtain more substantial evidence for the Cl_2^+ cation particularly by studies of solutions in the superacid medium HSO_3F–SbF_5–$3SO_3$,[10] to study the possible formation of the Cl_3^+ cation in such media, and to investigate the nature of the species giving rise to the esr spectra observed by Olah and Comisarow.[6]

Results and Discussion

Chlorine monofluoride reacts with the superacid mixture SbF_5–$3SO_3$–HSO_3F to produce a pale yellow solution which has a negligible vapor pressure at room temperature. The Raman spectrum of the solution contained seven new lines in addition to those of the solvent (Table I). No line was observed near 640 cm⁻¹ which is the vibrational frequency of the Cl_2^+ ion previously observed in the gas phase.[11] Clearly the seven lines must arise from some new species other than Cl_2^+ or ClF which has a single stretching frequency[11] of 774 cm⁻¹. Comparison with the infrared spectrum of $ClOSO_2F$[12] shows that the new species is $ClOSO_2F$ produced by the reaction $ClF + SO_3 \rightarrow ClOSO_2F$. Not all the Raman lines expected for $ClOSO_2F$ are observed as some are obscured by solvent lines. A peak at 214 cm⁻¹ which has not been observed in the infrared spectrum is assigned to the Cl–O–S deformation (Table I). As frequencies of 490, 508, and 225 cm⁻¹ have been assigned previously[4] for the Cl_3^+ cation, this species could be at least partially responsible for the weak bands at 214 and 487 cm⁻¹ and it might therefore be present in rather small amounts. We conclude that $ClOSO_2F$ is rather stable toward disproportionation in the superacid medium and that no Cl_2^+ is formed although there could be a small amount of Cl_3^+. An attempt was made to increase the amount of Cl_3^+ by saturating the $ClOSO_2F$ solution with chlorine in the hope that the following equilibrium would be displaced to the right

TABLE I

VIBRATIONAL SPECTRUM OF $ClOSO_2F$

Raman[a] (soln in SbF_5–$3SO_3$–HSO_3F)	Infrared[b] (solid)	Assignment[b]
214 w		COS bend[a]
368 m	364 mw	SF wag
	390 w	SO_2 torsion
487 w	487 mw	SO wag
	532 m	SO_2 rock
	545 vw	SO_2 bend
	573 ms	
707 s	709 ms	OC str
	837 ms	SO str
1055 w	876 s	SF str
1242 m	1238 vs	SO_2 sym str
1477 w	1458 vs	SO_2 asym str

[a] This work. [b] Reference 12.

$$ClOSO_2F + Cl_2 + H_2SO_3F^+ \rightleftharpoons Cl_3^+ + 2HSO_3F \quad (1)$$

Although the pressure of chlorine above the solution was increased to 3 atm, no changes were observed in the Raman spectrum except for an increase in the intensity of the peak at 560 cm⁻¹ which is due to the solvent but must also contain a contribution from the Cl–Cl stretch of the dissolved chlorine (558 cm⁻¹ in the gas phase[11]). In particular there was no increase in the intensity of the peaks at 214 and 487 cm⁻¹ which could have contained contributions from the Cl_3^+ cation. Consequently it must be concluded that it is unlikely that any appreciable amount of Cl_3^+ is formed by disproportionation of $ClOSO_2F$ in solution in superacid. Since I_2^+ and Br_2^+ are only stable at higher acidities than the I_3^+ and Br_3^+ cations, it is most unlikely that Cl_2^+ can be obtained in this medium in view of the apparent instability of the Cl_3^+ cation.

The conductivities of solutions of ClF and ClF–Cl_2 in the superacid medium were measured at 25°. In both cases there was a small decrease in the conductivity which corresponded almost exactly to the decrease expected from the removal of SO_3 to form $ClOSO_2F$ (Table II). Formation of the Cl_3^+ or Cl_2^+ cations by disproportionation of $ClOSO_2F$ or, in the case of ClF–Cl_2 solutions, by reaction with chlorine as in eq 2 and 3 would have led to a much larger decrease in conductance because of the titration of $H_2SO_3F^+$ by SO_3F^-.

$$ClOSO_2F + Cl_2 \rightleftharpoons Cl_3^+ + SO_3F^- \quad (2)$$

$$2ClOSO_2F + Cl_2 \rightleftharpoons 2Cl_2^+ + 2SO_3F^- \quad (3)$$

TABLE II

CONDUCTIVITIES OF SOLUTIONS OF ClF AND ClF–Cl_2 IN 0.184 *m* SbF_5–2.94 *m* SO_3 IN HSO_3F

ClF		ClF–Cl_2[a]	
10^3[ClF], *m*	$10^2\kappa$, ohm⁻¹ cm⁻¹	10^3[ClF], *m*	$10^2\kappa$, ohm⁻¹ cm⁻¹
...	3.671	...	3.672
2.775	3.586	3.374	3.552
5.275	3.491	6.010	3.451
7.365	3.427	8.630	3.338
9.610	3.325	11.370	3.206

[a] Mole ratio 1:0.66.

We conclude that there is therefore no evidence that either Cl_3^+ or Cl_2^+ is a stable species in the superacid medium that we have used. Since the other media in which the existence of these ions has been claimed by Olah and Comisarow are less acidic than our medium, it seems very probable that their claims are incorrect.

Olah and Comisarow obtained a seven-line esr spectrum from solutions of ClF in SbF_5, HSO_3F–SbF_5, and HF–SbF_5, $g = 1.998$, which they attributed to the Cl_2^+ cation with hyperfine coupling constants of 2.59 G for ^{35}Cl ($I = {}^3/_2$) and 2.15 G for ^{37}Cl ($I = {}^3/_2$). From a solution of ClF_3 in SbF_5 they obtained a second spectrum

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[8] R. S. Eachus, T. P. Sleight, and M. C. R. Symons, *Nature (London)*, **222**, 769 (1969).

[9] K. O. Christe and J. S. Muirhead, *J. Amer. Chem. Soc.*, **91**, 7777 (1969).

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[12] K. O. Christe, C. J. Schack, and E. C. Curtis, private communication, 1970.

in addition to the first. This spectrum could also be obtained by warming the ClF solution. This was a more complex six-line spectrum with $g = 2.006$ which they attributed to the ClF^+ cation with hyperfine coupling constants of 14.75 G for ^{35}Cl, 12.25 G for ^{37}Cl, and 24.0 G for fluorine. If ClF_5 was dissolved in these solvents instead of ClF_3, only this second six-line spectrum was obtained. These authors did not provide any explanation as to why it was necessary to use ClF_5 to obtain a species containing chlorine in the 2+ oxidation state and they attempted to explain the complete quenching of the spin–orbit coupling required for the observation of such well-resolved spectra by postulating very strong interaction with the solvent. Recently Symons, *et al.*,[8] have criticized these conclusions and have suggested that the postulated strong solvation is very improbable. Instead these authors conclude that the spectrum previously attributed to ClF^+ is due to the $ClOF^+$ cation as the spin densities on chlorine and fluorine add up to only 0.62 and the esr parameters fit in well with those of the isostructural FOO, ClOO, ClO_2, and NF_2 radicals. It has also been pointed out by Christe and Muirhead[9] that the 819-cm^{-1} Raman line attributed by Olah and Comisarow to the ClF^+ cation is in fact the strong Cl–F stretch of the ClF_2^+ cation[13,14] which is known to be formed from ClF_3 and SbF_5.

We have found that solutions of the $ClF_2^+SbF_6^-$ salt in SbF_5 give the same seven-line spectrum as that reported by Olah and Comisarow and assigned by them to Cl_2^+ and also a broad six-line spectrum which is very similar to the spectrum assigned by these authors to ClF^+, although the additional fine structure that they observed was not resolved due to the viscosity of the medium we were using. On adding a small amount of water to a sample of the $ClF_2^+SbF_6^-$ salt in SbF_5 contained in a 4-mm Kel-F tube, the intensity of the six-line esr signal increased by a factor of several hundred to give a very strong signal, with a signal-to-noise ratio of 1000:1. Meanwhile, the color of the initially colorless solution turned *via* a transient bright green to purple and finally to black. This experiment was repeated with 10% ^{17}O-enriched water, but no ^{17}O satellites were observed, and hence the presence of oxygen in the radical was not proven. Nevertheless, the dependence of the esr signal intensity on the presence of water indicates that the six-line spectrum is probably an oxy radical, and the analysis of the fine structure of the splitting in terms of ^{35}Cl and ^{37}Cl by Olah, *et al.*, shows that the spin is coupled to one chlorine atom and one nucleus of spin $^1/_2$, *e.g.*, fluorine. However the proposal of Symons, *et al.*, that the radical responsible for the six-line spectrum is $ClOF^+$ (or $OClF^+$) is not the only possibility and another equally plausible possibility is ClO_2F^+ which, we may note, is isoelectronic with the stable radical ClO_3, just as $OClF^+$ is isoelectronic with ClO_2.

By analogy with bromine and iodine,[2,3] the Cl_2^+ cation is expected to have a strong visible absorption band at around 400 nm which might give rise to a resonance Raman effect, with a strong fundamental close to 640 cm^{-1}. At the closest argon ion exciting wavelength of 457.9 nm, it is expected that if Cl_2^+ does indeed give a resonance Raman spectrum, this would enable concentrations as low as 10^{-4} *m* to be detected. Raman studies of solutions of chlorine fluorides in the superacid medium gave no evidence for the Cl_2^+ cation. Similar studies of the products of the reactions between ClF, Cl_2, and SbF_5 or AsF_5 resulted in the identification of the Cl_2F^+ and Cl_3^+ cations[4] but again no evidence for Cl_2^+ was obtained. In view of these results, the previous claim, cited in ref 5, that the reaction of chlorine and iridium hexafluoride gives the salt $Cl_2^+IrF_6^-$ may be incorrect. The material that was obtained could have been a mixture of the Cl_2F^+ and Cl_3^+ salts.

It is concluded that there is no evidence for the existence of the Cl_2^+ or ClF^+ cations in solution in strong acids. Furthermore, for the reasons given above, the existence of the Cl_2^+ cation as a stable species in any of the systems described is considered most unlikely. When ClF is dissolved in superacid, the only product appears to be $ClOSO_2F$.

Experimental Section

Electrical Conductivity Measurements.—The apparatus and techniques used for electrical conductivity measurements in the superacid solvent have been described previously.[9] Additions of concentrated solutions were made in a drybox using smooth glass syringes fitted with Teflon plungers and platinum needles (Hamilton Syringe Co.). The ends of the needles could be capped withKel-F tubing and the syrings were weighed before and after additions.

Raman Spectra.—Raman spectra were recorded using a Spex Industries Model 1400 double monochromator with a phototube detector and dc amplification. A spectral slit width of 3 cm^{-1} was used, and Raman shifts were accurate to ±2 cm^{-1}. The exciting radiation was provided by a Spectra Physics Model 125 He–Ne laser or a Spectra Physics Model 140 argon ion laser.

Samples were made up in quartz or thin-wall Kel-F tubes which could be attached to the Monel vacuum line. The samples were mounted horizontally, and light scattered at right angles to the incident laser beam and to the axis of the tube was focused on the entrance slit of the monochromator. The plane of potensation of the incident beam was at right angles to the direction of observed Raman scattering.

Esr Spectra.—Samples were run in Kel-F or quartz tubes of up to 5-mm outer diameter. These were obtained with a JEOLCO Model JES 3BS-X spectrometer and the *g* values were obtained by comparison with manganous ion.

Materials.—Fluorosulfuric acid, sulfur trioxide, chlorine trifluoride, and chlorine monofluoride were prepared and purified as described previously.[2,4,14] The antimony pentafluoride (Ozark Mahoning Inc.), after double distillation in an atmosphere of dry air, was distilled under vacuum on a grease-free Pyrex and Teflon vacuum line.

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