Cations KrF^+, $XeOF_3^+$, XeF_3^+, and $XeOF_5^+$ and Oxidizing Properties of KrF^+

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Summary The $XeOF_5^+$ ion (prepared with KrF^+ as oxidizer) is related to $XeOF_3^+$; the latter is in turn related to XeF_3^+, the geometry of which has been established by *X*-ray crystallography.

In earlier communications[1] we showed that the adduct[2] $KrF_2,2SbF_5$ was the salt $KrF^+Sb_2F_{11}^-$. The stretching frequency $\nu(Kr\text{–}F^+) = 626\ cm^{-1}$ is in excellent agreement with Schaefer's theoretical prediction[3] of $620\ cm^{-1}$.

In accord with the expected[4] high value of the electron affinity of KrF^+, the cation has proved to be an extraordinary oxidizer. We have previously shown[1] that it oxidizes IF_5 to IF_6^+ and have now carried out the oxidation of $XeOF_4$ to $XeOF_5^+$ ($XeOF_4 + KrF^+ \rightarrow XeOF_5^+ + Kr$). Since the syntheses, which involve addition of $XeOF_4$ to $KrF^+Sb_2F_{11}^-$ (*ca.* $-10°$), were done in quartz apparatus, there was always contamination from O_2^+ salts, but the best preparations yielded no $XeOF_3^+$ salts. Raman data for $XeOF_5^+$ (compared with data for IOF_5 and its Xe relatives in Figure 1) show a pattern of lines consistent with an IOF_5-like species, but the Xe–F and Xe–O stretching frequencies are lower than for IOF_5. As is seen from

Figure 1, this resembles the situation in XeF_5^+ salts, where ν_{sym} (Xe–F) tends to be lower than ν_{sym} (I–F) in IF_5.

As part of our study [5] of the fluoride ion donor abilities of the xenon fluorides and oxyfluorides, we have also investigated the systems $XeOF_4$–SbF_5 and XeF_4–SbF_5. Unambiguous identification of the $XeOF_5^+$ ion demanded a full characterization of the former system. A combination of *X*-ray crystallographic and Raman spectroscopic data has established that XeF_3^+ is the only cation present in the XeF_4–SbF_5 system; Raman spectroscopic evidence indicates that the $XeOF_3^+$ cation is the only one present in the $XeOF_4$–SbF_5 system. Since we began our studies Gillespie and his co-workers have given vibrational and ^{19}F n.m.r. spectroscopic evidence for both XeF_3^+ [6] and $XeOF_3^+$.[7]

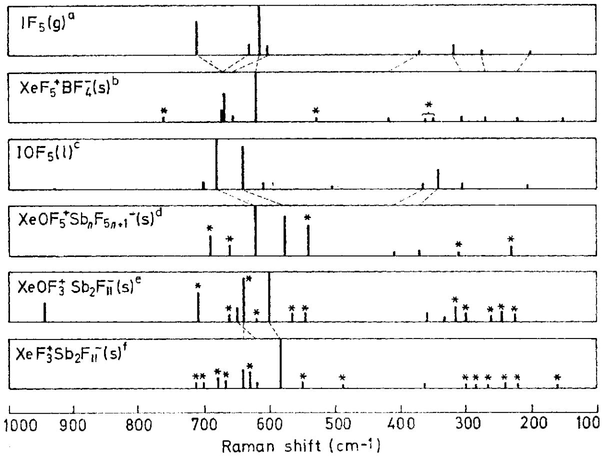

Figure 1. *Raman spectra of xenon cation species and related iodine species.*

* Raman line assigned to anion.

[a] Ref. 12. [b] C. J. Adams and N. Bartlett, to be published. The fundamental frequencies of XeF_5^+ are sensitive functions of the counterion and phase, although solid $XeF_5^+BF_4^-$ is a typical example. Common values for the stretching frequencies are: $\nu_1(a_1)$ 650—680; $\nu_2(a_1)$ 585—630; $\nu_4(b_1)$ 600—640; $\nu_7(e)$ 640—670 cm^{-1}. [c] Ref. 13. [d] This work. Lines attributable to dioxygenyl fluoroantimonates have been deleted. [e] This work. Assignments for $XeOF_3^+$: 944 cm^{-1}, ν(Xe–O); 649, ν_{asym} (*ax.* XeF_2); 638, ν(*eq.* Xe–F); 601 ν_{sym} (*ax.* XeF_2); 358, 333, δ(FXeF), δ(OXeF). Our assignments differ from those of Gillespie *et al.*[7] only in placing ν_{asym} (*ax.* XeF_2) higher than ν_{sym} (*ax.* XeF_2), as has been found for structurally related molecules, *e.g.* TeF_4.[14] [f] This work. Assignments for XeF_3^+: 640 cm^{-1}, ν(*eq.* Xe–F); 618 ν_{asym} (*ax.* XeF_2); 582 ν_{sym} (*ax.* XeF_2); 363 δ(FXeF).

Our studies have shown that in the XeF_4–SbF_5 system there are two compounds, $XeF_3^+SbF_6^-$ and $XeF_3^+Sb_2F_{11}^-$: efforts to make $Xe_2F_7^+SbF_6^-$ have failed. Both salts are pale yellow-green solids. $XeF_3^+SbF_6^-$ (m.p. 109—113°) is dimorphic, with a transition temperature of *ca.* 90°; the low temperature form is monoclinic with $a = 5{\cdot}50$ (1), $b = 15{\cdot}50$ (1), $c = 8{\cdot}95$ (1) Å, $\beta = 102{\cdot}9$ (3)°, $U = 743{\cdot}3\text{Å}^3$, $Z = 4$, $D_c = 3{\cdot}81$ g cm^{-3}. $XeF_3^+Sb_2F_{11}^-$ (m.p. 81—83°) is triclinic with $a = 8{\cdot}237(5)$, $b = 9{\cdot}984(20)$, $c = 8{\cdot}004(5)$ Å, $\alpha = 72{\cdot}54(5)$, $\beta = 112{\cdot}59(7)$, $\gamma = 117{\cdot}05(21)$°, $U = 534{\cdot}9\text{Å}^3$, $Z = 2$, $D_c = 3{\cdot}98$ g cm^{-3}. The structure of the latter has been refined in space group $P1$ using three-dimensional graphite-monochromatized Mo-K_α *X*-ray data. With anisotropic temperature factors for all atoms, a final conventional R factor of 0·035 for 1823 independent reflections for which $I \geqslant 3\sigma(I)$ has been obtained. The crystal structure is built up from the structural units, $XeF_3^+Sb_2F_{11}^-$, shown in Figure 2. The T shaped cation is planar and lies in the same plane as a fourth fluorine atom, which makes a close contact of 2·50 Å to the xenon atom. This interaction of the cation and the anion is consistent with a distorted trigonal bipyramidal configuration of two axial F ligands, one equatorial F ligand, and two sterically active, equatorial, non-bonding valence-electron pairs about the Xe atom. Such a cation should have a maximum polarizing effect normal to the triangular faces containing the two non-bonding pairs. As in the electronically related molecules ClF_3[8] and BrF_3[9] the axial bonds in XeF_3^+ (1·88 and 1·89 Å) are longer than the equatorial (1·83 Å). This is consistent with designation of the latter as an electron-pair bond and the former as three-centre four-electron bonds.[4,10]

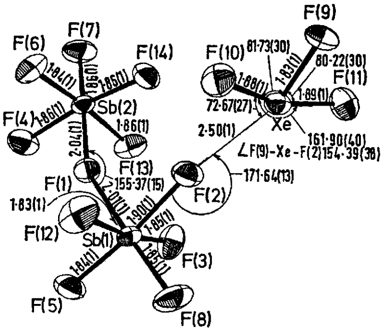

Figure 2. *The* $XeF_3^+Sb_2F_{11}^-$ *structural unit.*

In the $XeOF_4$–SbF_5 system, Selig had previously established[11] the compound $XeOF_4,2SbF_5$, but structural information was lacking until the recent report by Gillespie and his co-workers.[7] In our studies, two compounds have been isolated (1 : 1, m.p. 104—105° and 1 : 2, m.p. 61—66°). The $XeOF_4$, in the SbF_5 complexes, is certainly no longer molecular, as in the 1 : 1 $XeF_2,XeOF_4$ molecular adduct,[10] and the marked increase in the Xe–F stretching frequency indicates cation formation. Furthermore, comparisons of the Raman spectra of the SbF_5 complexes, given in Figure 1, indicate the salt formulations $XeOF_3^+SbF_6^-$ and $XeOF_3^+$-$Sb_2F_{11}^-$. The similarities of the $XeOF_3^+$ and XeF_3^+ spectra suggest a close structural relationship. It is therefore probable that the $XeOF_3^+$ geometry will resemble that of XeF_3^+ to which an oxygen atom has been added to a Xe electron-pair site (equatorial).

The similarity of the Xe–O stretching frequencies suggests that the Xe–O bonds in $XeOF_3^+$ and $XeOF_4$ must be nearly the same. Also, that the axial stretching frequencies of $XeOF_3^+$ lie higher than those of XeF_3^+ indicates that the Xe–F axial bonds will be slightly shorter in the former.

This work was supported by the U.S. Atomic Energy Commission and CJA is grateful to the Commonwealth Fund for a Harkness Fellowship.

(*Received*, *25th September* 1972; *Com.* 1639.)

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