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AND OXIDIZING PROPERTIES OF KrF$^+$

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The Cations KrF$^+$, XeF$_3$ $^+$, XeOF$_3$ $^+$ and XeOF$_5$ $^+$ and Oxidizing Properties of KrF$^+$

By D. E. McKee, C. J. Adams, A. Zalkin, and Neil Bartlett

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Summary - The XeOF$_5$ $^+$ ion (prepared by exploiting KrF$^+$ as an oxidizer) is related to, but distinguishable from 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$_2$F$_{11}^-$·. The stretching frequency $\nu$(Kr-F$^+$) = 626 cm$^{-1}$ is in excellent agreement with Schaefer's theoretical prediction$^3$ of 620 cm$^{-1}$.

In accord with the anticipated$^4$ 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$^+$ → XeOF$_5$ $^+$ + Kr). Since the syntheses, which involve addition of XeOF$_4$ to KrF$^+$Sb$_2$F$_{11}^-$ (~10), have been executed in quartz apparatus, there has always been some contamination from O$_2$ $^+$ salts, but the best preparations have 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 may be seen from Figure 1, this is akin to the situation in XeF$_5$ $^+$ salts, where $\nu_{\text{symm}}$(Xe-F) tends to be somewhat lower than $\nu_{\text{symm}}$(I-F) in IF$_5$. 
As part of our study\(^5,6,7\) 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\(_5\): moreover, 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 the onset of our studies Gillespie and his coworkers have given vibrational and \(^{19}\text{F}\) nmr spectroscopic evidence for both XeF\(_3^+\) (Ref. 8) and XeOF\(_3^+\) (Ref. 9).

Our studies have shown that in the XeF\(_4\)/SbF\(_5\) system there are two compounds, XeF\(_3^+\)SbF\(_6^-\) and XeF\(_3^+\)Sb\(_2\)F\(_{11}^-\): efforts to make XeF\(_7^+\)SbF\(_6^-\) have failed. Both salts are pale yellow-green solids. XeF\(_3^+\)SbF\(_6^-\) (m.p. 109-113\(^\circ\)) is dimorphic, with a transition temperature of -90\(^\circ\); the low temperature form is monoclinic with \(a = 5.50\), \(b = 15.50\), \(c = 8.95\) (all \(\pm 0.01\) \(\text{Å}\)), \(\beta = 102.9 \pm 0.3^\circ\), \(V = 743.3\) \(\text{Å}^3\), \(z = 4\), \(D_c = 3.81\) g \(\text{cm}^{-3}\). XeF\(_3^+\)Sb\(_2\)F\(_{11}^-\) (m.p. 81-83\(^\circ\)) is triclinic with \(a = 8.237(5)\), \(b = 9.984(20)\), \(c = 8.004(5)\), \(\alpha = 72.54(5)\), \(\beta = 112.59(7)\), \(\gamma = 117.05(21)^\circ\), \(V = 534.9\) \(\text{Å}^3\), \(z = 2\), \(D_c = 3.98\) g \(\text{cm}^{-3}\). The structure of the latter has been successfully refined in space group \(\text{PT}\) using three-dimensional graphite-monochromatized MoK\(_\alpha\) X-ray data. With anisotropic temperature factors for all atoms, a final conventional \(R\) factor of 0.035 for 1823 independent reflections for which \(I > 3\sigma(I)\) has been obtained. The crystal structure is built up from the structural units, XeF\(_3^+\)Sb\(_2\)F\(_{11}^-\), shown in Figure 2. The \(I\) shaped cation is planar and lies in the same plane as a fourth fluorine atom, which makes a close contact of 2.50 \(\text{Å}\)
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$_3$ (Ref. 10) and BrF$_3$ (Ref. 11) 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-center four-electron bonds$^{4,12}$.

In the XeOF$_4$/SbF$_5$ system, Selig had previously established$^{13}$ the compound XeOF$_4$·2SbF$_5$, but structural information was lacking until the recent report by Gillespie and his coworkers$^9$. 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$^{12}$, and the marked increase in the Xe-F stretching frequency clearly evinces 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$_2$F$_{11}^-$.

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 be very like that of XeF$_3^+$ to which an oxygen atom has been added at 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 somewhat higher than
those of XeF$_3^+$ indicates that the Xe-F axial bonds will be slightly shorter in the former than in the latter.

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References


Figure 1: Raman Spectra of Xenon-Cation Species and Iodine Relatives

$\text{XeF}_3^+ \text{BF}_4^-$ (s) (b)

$\text{XeOF}_3^+ \text{Sb}_n \text{F}_{5n+1}^-$ (s) (a)

$\text{XeOF}_3^+ \text{Sb}_2 \text{F}_{11}^-$ (s) (a)

$\text{XeF}_2^+ \text{Sb}_2 \text{F}_{11}^-$ (s) (a)
Footnotes for Figure 1.

* Raman line assigned to anion.

(a) Ref. 14.

(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 cm$^{-1}$; $\nu_2(a_1)$ 585-630 cm$^{-1}$; $\nu_4(b_1)$ 600-640 cm$^{-1}$; $\nu_7(e)$ 640-670 cm$^{-1}$.

(c) Ref. 15.

(d) This work. Lines attributable to dioxygenyl fluoroantimonates have been deleted.

(e) This work. Assignments for XeOF$_3^+$: 944 cm$^{-1}$, $\nu$(Xe-O); 649, $\nu_{\text{asym}}$ (ax. XeF$_2$); 638, $\nu$(eq. Xe-F); 601 $\nu_{\text{symm}}$ (ax. XeF$_2$); 358, 333, $\delta$(FXeF), $\delta'(OXeF).$ Our assignments differ from those of Gillespie et al. (Ref. 9) only in placing $\nu_{\text{asym}}$ (ax. XeF$_2$) higher than $\nu_{\text{symm}}$ (ax. XeF$_2$), as has been found for structurally related molecules, e.g. TeF$_4$ (Ref. 16).

(f) This work. Assignments for XeF$_3^+$: 640 cm$^{-1}$, $\nu$(eq. Xe-F); 618 $\nu_{\text{asym}}$ (ax. XeF$_2$); 582 $\nu_{\text{symm}}$ (ax. XeF$_2$); 363 $\delta$(FXeF).
NOTE TO PRINTER: Figure 2 comprises the drawing (page 9) and the table (page 10).
Figure 2: The $\text{XeF}_3^+\text{Sb}_2\text{F}_{11}^-$ structure unit.
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**Figure 2:** The XeF$_3^+$Sb$_2$F$_{11}^-$ Structure unit.
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