Contribution from the Inorganic Materials Research Division, Lawrence Berkeley Laboratory, and the Department of Chemistry, University of California, Berkeley, California 94720

Preparation and Raman Spectra of the Salts $[XeF_3^+][SbF_6^-]$, $[XeF_3^+][Sb_2F_{11}^-]$, $[XeOF_3^+][SbF_6^-]$, and $[XeOF_3^+][Sb_2F_{11}^-]$

D. E. McKEE, C. J. ADAMS, and NEIL BARTLETT*

Received December 18, 1972

Raman spectroscopic and crystallographic investigations for the systems XeF_4-SbF_5 and $XeOF_4$-SbF_5 have revealed the following salts: $[XeF_3^+][SbF_6^-]$ (pale yellow-green, mp 109-113°), $[XeF_3^+][Sb_2F_{11}^-]$ (pale yellow-green, mp 81-83°), $[XeOF_3^+][SbF_6^-]$ (colorless, mp 104-105°), $[XeOF_3^+][Sb_2F_{11}^-]$ (colorless, mp 61-66°). $[XeF_3^+][SbF_6^-]$ is dimorphic with a transition temperature of ~95°; the low-temperature form is monoclinic with $a = 5.50$, $b = 15.50$, $c = 8.95$ Å (all ±0.01 Å), $\beta = 102.9 \pm 0.3°$, $V = 743.3$ Å^3, $Z = 4$, $d_c = 3.81$ g cm^{-3}. A crystal structure determination[1] of the $[XeF_3^+]$-$[Sb_2F_{11}^-]$ salt has given the geometry of the XeF_3^+ ion. The Raman data suggest that $XeOF_3^+$ is like XeF_3^+ to which an oxygen atom has been attached at an equatorial valence-electron-pair site.

Introduction

Bartlett and Sladky[2] have presented evidence for a decrease in fluoride ion donor ability of the xenon fluorides in the sequence $XeF_6 > XeF_2 > XeF_4$. Indeed, since XeF_2 and XeF_6 form complexes with RuF_5 and AsF_5, whereas XeF_4 does not, this provides for the chemical purification of the tetrafluoride. The X-ray crystal structures of these complexes (which have been carried out recently in these laboratories) indicate the salt formulations $[Xe_2F_3^+][AsF_6^-]$,[3] $[XeF_5^+]$-$[AsF_6^-]$,[4] $[XeF^+][RuF_6^-]$,[5] and $[XeF_5^+][RuF_6^-]$.[5] It remained to establish, however, that XeF_4 could behave as a fluoride ion donor. It was known form early work[6] that XeF_4 was capable of complexing with the best fluoride ion acceptor, SbF_5. More recently Martin[7] claimed 2:1 and 1:4 complexes but adequate characterization was lacking. It seemed to us that a similar variety of complexes might occur in the XeF_4-SbF_5 system as had been established for the XeF_2-MF_5[8] and XeF_6-MF_5[9] systems. Furthermore, since the XeF_4 molecule has a simple relationship to $XeOF_4$, we decided upon a parallel study with that compound. Selig had established[10] a complex $XeOF_4 \cdot 2SbF_5$, but structural information was not given.

Since the onset of our study, Gillespie, *et al.*,[11] have provided ^{19}F nmr structural information and vibrational spectroscopic evidence for the salt $[XeF_3^+][Sb_2F_{11}^-]$. Our vibrational spectroscopic findings are in substantial agreement with theirs and our crystallographic findings, reported in an accompanying paper,[1] establish the salt formulation. We have also established the salt $[XeF_3^+][SbF_6^-]$. Two complexes have been identified in the $XeOF_4$-SbF_5 system and are formulated as $[XeOF_3^+][SbF_6^-]$ and $[XeOF_3^+][Sb_2F_{11}^-]$. The latter has been described in a recent note[12] by Gillespie and his coworkers.

Experimental Section

Reagents. Xenon tetrafluoride was prepared by the method of Claassen, Selig, and Malm.[13] It was purified by melting in a Kel-F tube with ruthenium pentafluoride or arsenic pentafluoride, after the procedure given by Bartlett and Sladky.[2] The high purity of each batch was established by Raman spectroscopy and melting point (117°).

Xenon oxide tetrafluoride (*caution!*) was prepared by the interaction of XeF_6 with quartz at 50°.[14] (*It was essential, for safety and effectiveness, to immerse the entire bulb up to the enclosing valve in the water bath.*) Before the characteristic yellow color of XeF_6 had completely disappeared, the contents of the quartz bulb were transferred under vacuum to a Kel-F trap containing sodium fluoride. (*Caution!* If all of the XeF_6 is consumed, XeO_3 may form and detonate.) SiF_4 was removed under vacuum at −78°. The mixture in the trap was heated to 50° to convert remaining XeF_6 to the NaF-XeF_6 complex.[15] Finally, $XeOF_4$ was separated by vacuum distillation at room temperature to traps at −196°. Infrared spectroscopy showed only those bands characteristic of $XeOF_4$.[16]

Antimony pentafluoride was prepared from the oxide by fluorination[17] in an inclined Pyrex tube and purified by trap-to-trap distillation in a dynamic vacuum.

Complexes. The complexes of $XeOF_4$ and of XeF_4 with SbF_5 were prepared from their components as detailed below. The components were mixed in a variety of known molar ratios and each composition was characterized by Raman, X-ray powder, and (occasionally) single-crystal data. These studies indicated that compounds exist with the compositions $XeF_4 \cdot SbF_5$, $XeF_4 \cdot 2SbF_5$, $XeOF_4 \cdot SbF_5$, and $XeOF_4 \cdot 2SbF_5$.[18]

$XeOF_4 \cdot 2SbF_5$ (mp 61-65°) was prepared by distilling a known weight of $XeOF_4$ into a quartz trap, followed by an excess of SbF_5. The trap was heated until solution was complete and then cooled to room temperature, at which point the excess SbF_5 was removed by vacuum distillation. A colorless solid remained. A 1.60-g sample of $XeOF_4$ (7.18 mmol) yielded 4.81 g of adduct (*i.e.*, 7.32 mmol of $XeOF_4 \cdot 2SbF_5$).

$XeOF_4 \cdot SbF_5$ (mp 104-105°) was prepared by distilling excess $XeOF_4$ onto a known weight of $XeOF_4 \cdot 2SbF_5$ in a quartz trap, which was gently heated to complete solution. Excess $XeOF_4$ was removed

---

(1) D. E. McKee, A. Zalkin, and N. Bartlett, *Inorg. Chem.*, 12, 1713 (1973).

(2) N. Bartlett and F. O. Sladky, *J. Amer. Chem. Soc.*, 90, 5316 (1968).

(3) F. O. Sladky, P. A. Bulliner, N. Bartlett, B. G. DeBoer, and A. Zalkin, *Chem. Commun.*, 1048 (1968).

(4) F. Hollander, Ph.D. Thesis, University of California, Berkeley, Calif., 1971.

(5) N. Bartlett, M. Gennis, D. D. Gibler, B. K. Morrell, and A. Zalkin, *Inorg. Chem.*, 12, 1717 (1973).

(6) N. Bartlett and N. K. Jha, unpublished observation, 1964.

(7) D. Martin, *C. R. Acad. Sci., Ser. C*, 1145 (1969).

(8) F. O. Sladky, P. A. Bulliner, and N. Bartlett, *J. Chem. Soc. A*, 2179 (1964).

(9) G. L. Gard and G. H. Cady, *Inorg. Chem.*, 3, 1745 (1964).

(10) H. Selig, *Inorg. Chem.*, 5, 183 (1966).

(11) R. J. Gillespie, B. Landa, and G. J. Schrobilgen, *Chem. Commun.*, 1543 (1971).

(12) R. J. Gillespie, B. Landa, and G. J. Schrobilgen, *J. Chem. Soc., Chem. Commun.*, 607 (1972).

(13) H. H. Claassen, H. Selig, and J. G. Malm, *J. Amer. Chem. Soc.*, 84, 3593 (1962).

(14) C. L. Chernick, H. H. Claassen, J. G. Malm, and P. L. Plurien, "Noble-Gas Compounds," H. H. Hyman, Ed., University of Chicago Press, Chicago, Ill., and London, 1963.

(15) I. Sheft, T. M. Spittler, and F. H. Martin, *Science*, 145, 701 (1964).

(16) G. M. Begun, W. H. Fletcher, and D. F. Smith, *J. Chem. Phys.*, 42, 2236 (1963).

(17) A. A. Woolf and N. N. Greenwood, *J. Chem. Soc.*, 2200 (1950).

(18) As an illustration of our technique consider the 1:1 XeF_4-SbF_5 compound. Raman and X-ray powder photography established one phase to be present when the XeF_4 and SbF_5 were in 1:1 molar ratio by gravimetry. Addition of excess XeF_4 resulted in this compound revealing itself in the Raman and X-ray data. Similarly addition of excess SbF_5 gave evidence of the 1:2 compound. Of course the gravimetry merely established the composition $XeSbF_9$. The Raman and X-ray data showed that the "phase" was not an equimolar mixture of $[XeF^+][SbF_6^-]$ and $[XeF_5^+][SbF_6^-]$ both of which were available to us.

by vacuum distillation and yielded a colorless solid. A 0.64-g sample of SbF_5 (2.95 mmol) yielded 1.32 g of adduct (*i.e.*, 3.00 mmol of $XeOF_4 \cdot SbF_5$).

$XeF_4 \cdot 2SbF_5$ (mp 81–83°) was prepared similarly to $XeOF_4 \cdot 2SbF_5$. The solid was pale yellow-green. A 1.17-g sample of XeF_4 (5.64 mmol) yielded 3.50 g of adduct (*i.e.*, 5.45 mmol of $XeF_4 \cdot 2SbF_5$).

$XeF_4 \cdot SbF_5$ (mp 109–113°) was derived from the 1:2 compound by combining equimolar quantities of XeF_4 and $XeF_4 \cdot 2SbF_5$. The compounds were placed in a Pyrex tube closed with a Kel-F tipped Whitey valve, 1KS4. The mixture was heated under dry nitrogen until a homogeneous melt was obtained. The melt was allowed to cool slowly to room temperature. A 0.17-g sample of XeF_4 (0.82 mmol) and 0.50 g of $XeF_4 \cdot 2SbF_5$ (0.78 mmol) yielded a solid which gave no evidence of either XeF_4 or $XeF_4 \cdot 2SbF_5$ impurity. $XeF_4 \cdot SbF_5$ was also prepared by directly combining and melting together equimolar quantities of XeF_4 and SbF_5 [2.83 g of SbF_5 (1.31 mmol) and 2.71 g of XeF_4 (1.31 mmol) yielded 5.54 g of $XeF_4 \cdot SbF_5$ (1.31 mmol)]. The solid was pale yellow-green. It proved to be dimorphic, with a transition temperature of 95°. Each form provides a distinctive Raman spectrum (see Table I). At room temperature the transition to the low-temperature form required 2–3 days.

Crystal Data. Single crystals of $XeF_4 \cdot SbF_5$ (low-temperature form) were obtained by slow removal of the solvent, at –10°, from a solution in anhydrous HF. Crystal data obtained were as follows: monoclinic, $a = 5.50$, $b = 15.50$, $c = 8.945$ Å (all ±0.01 Å), $\beta = 102.9 \pm 0.3°$, $V = 743.3$ Å^3, $Z = 4$, $d_c = 3.81$ g cm^{-3}. Excess XeF_4 in fused admixture with $XeF_4 \cdot SbF_5$ failed to produce compounds richer in XeF_4.

Raman Spectra. Powdered solid samples in thin-walled quartz capillaries of ~1-mm diameter were prepared in a Vacuum Atmospheres Dri-Lab. The capillaries were plugged with Kel-F grease in the Dri-Lab and were immediately sealed upon removal by drawing down in a small flame. In preliminary studies Raman spectra were measured with a Cary 83 spectrometer (excitation at 4880 Å). However, the Raman data, enumerated in Table I and depicted schematically in Figures 1 and 2, were excited at 5145 Å and were recorded using a Spex 1401 monochromator and a photon-counting detector system. Dilute solutions of XeF_4 and $XeOF_4$ were also examined by Raman spectroscopy, using sealed quartz tubes of 2-mm internal diameter.

X-Ray Powder Photographs. Quartz capillaries of 0.5- or 0.3-mm diameter were filled in the Dri-Lab and sealed as for the Raman samples. Powder photographs were taken using a GE Precision camera, employing graphite-monochromatized Cu Kα radiation. Powder data for $XeF_4 \cdot SbF_5$, $XeF_4 \cdot 2SbF_5$, $XeOF_4 \cdot SbF_5$, and $XeOF_4 \cdot 2SbF_5$ are given in the microfilm version of this paper as Tables II–V.[19]

Results and Discussion

As well as providing distinctive fingerprints for the compounds detected in the XeF_4–SbF_5 and $XeOF_4$–SbF_5 systems, Raman spectroscopy afforded information about the nature of the species present. In no case do the spectra of the solids show the characteristic Raman lines of the parent molecular fluorides; by the same token, neither XeF_4 nor $XeOF_4$ is present as such in antimony pentafluoride solution, at least in an amount detectable by the Raman effect. Although we anticipated ionic structures containing XeF_3^+ or $XeOF_3^+$ cations, the relative complexity of the vibrational spectra prevented us from making a persuasive case, without some firm structural evidence for at least one of the adducts. We therefore undertook X-ray single-crystal analyses of the XeF_4–SbF_5 compounds. Our structure of the 1:2 compound[1] established the formulation $[XeF_3^+][Sb_2F_{11}^-]$; this provided a fixed point in the interpretation of the spectroscopic data. We were further aided in this task, and in assigning frequencies, by Raman data, either obtained in this laboratory or gleaned from the literature, for antimony pentafluoride adducts of other fluoride ion donors. (See footnotes in Table I.)

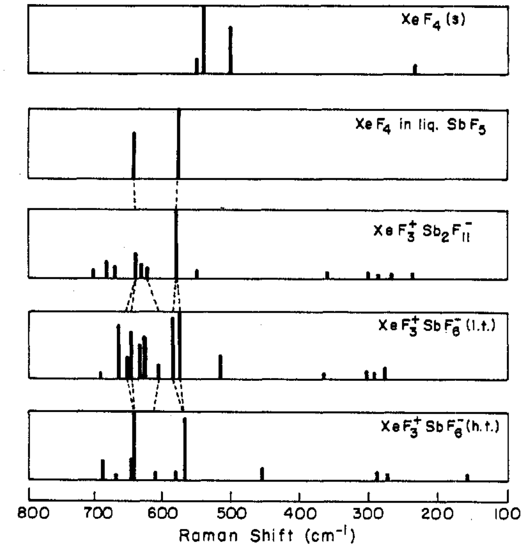


Figure 1. Raman spectra of XeF_4 and its SbF_5 salts. (Dotted lines connect bands due to related vibrations.)

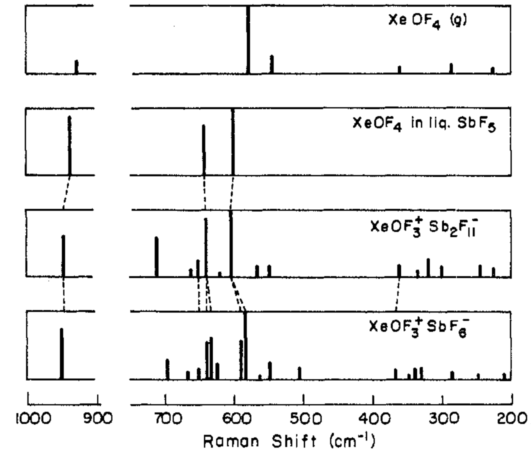


Figure 2. Raman spectra of $XeOF_4$ and its SbF_5 salts. (Dotted lines connect bands due to related vibrations.)

The problem of identifying cation and anion bands in the XeF_4–SbF_5 and $XeOF_4$–SbF_5 systems is by no means straightforward. Both cation and anion stretching fundamentals occur in the same region of the spectrum (450–750 cm^{-1}), while comparison with other compounds of this sort shows no truly characteristic spectroscopic pattern for either SbF_6^- or $Sb_2F_{11}^-$—the former anion commonly suffers severe distortions from O_h symmetry. Nevertheless, the solids and solutions examined displayed apt and consistent sets of Raman lines (joined by dots in the figures) attributable to XeF_3^+ or $XeOF_3^+$ cations. We were further encouraged in our assignments by the comparison of these frequencies with the corresponding fundamentals of related molecules derived from a trigonal-bipyramidal unit (Table VI). Given in the following paragraphs is the gist of the arguments which led us to what, in our estimation, is the most reasonable set of assignments.

Like the monomeric halogen trifluoride molecules,[20] the T-shaped XeF_3^+ cation has essentially C_{2v} symmetry and should display two strong, polarized Raman lines in the region associated with Xe–F stretching fundamentals. These

---

(19) Tables II–V, listings of X-ray powder data, will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-1722.

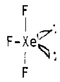
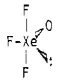
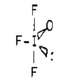
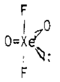
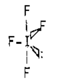
(20) H. Selig, H. H. Claassen, and J. H. Holloway, *J. Chem. Phys.*, 52, 3517 (1970).

Table I

XeF_3^+ in SbF_5	$XeF_3^+Sb_2F_{11}^-$	$XeF_3^+SbF_6^-$ (h.t.)	$XeF_3^+SbF_6^-$ (l.t)	$XeOF_3^+$ in SbF_5	$XeOF_3^+Sb_2F_{11}^-$	$XeOF_3^+SbF_6^-$	
Cation stretching features							
				939 p	944(63)	944(75)	$\nu(Xe{=}O)$
642 p	640(40)	645(100)	653(77) 646(56)	642 p	638(89)	635(55) 631(63)	$\nu(Xe{-}F_{eq})$
	618 sh	613(8)	608(12)		649(30)	621(19)	$\nu_{asymm}(Xe{-}F_2(ax))$
584 p	582(100)	569(98)	578(96) 569(100)	597 p	601(100)	586(58) 580(100)	$\nu_{symm}(Xe{-}F_2(ax))$
Other features							
(a)	(c)	(b)	(b)	(a)	(c)	(b)	
	713(9)						
	701(11)	689(27)	690(6)		708(60)	693(27)	$\nu(Sb{-}F)$
	681(23)	668(5)	665(62)		662 sh	663(9)	
	667(17)	652(20)	633(56)		620(5)	649(sh)	
	631(35)	581(3)	628(65)				
	550(13)		517(35)		565(18)	562(2)	
	487(5)	456(18)			546(19)	546(19)	
						505(15)	
	363(8)		.365(11)		358(17)	365(11)	$\delta(O{=}Xe{-}F)$ and $\delta(F{-}Xe{-}F)$
					333(11)	345(4) 337(14)	
	302(8)	290(9)	302(8)		316(30)	327(17)	$\delta(F{-}Xe{-}F)$ and $\delta(F{-}Sb{-}F)$
	285(5)	275(8)	292(10)		298(18)	283(12)	
	267(7)		275(16)		261(12)	245(12)	
	236(8)				245(19)	207(6)	
	220(sh)	160(4)			225(17)	195(5)	
	~160(2)	115(8)					
	103(10)						

[a] Solvent and anion bands omitted. [b] Raman lines for SbF_6^- (cm^{-1}): In $KSbF_6$(c): 661 (vs), 575 (s), 294 (m), 278 (m) [H. A. Carter and F. Aubke, *Can. J. Chem.*, **48**, 3456 (1970)]. In $[IF_4^+][SbF_6^-]$: 694 (7.2), 662 (27.5), 570 (7), 525 (6), 299 (4), 242 (0+) [ref 21]. In $[Xe_2F_3^+][SbF_6^-]$: 660 (2), 644 (27), 572 (10), 561 (15), 517 (1), 281 (12) [R. Mews and N. Bartlett, to be submitted for publication]. In $[BrF_2^+][SbF_6^-]$: 686 (9), 678 (43), 661 (1), 638 (41), 547 (35), 492 (9), 281 (7), 270 (16) [K. O. Christe and C. J. Schack, *Inorg. Chem.*, **9**, 2296 (1970)]. [c] Raman lines for $Sb_2F_{11}^-$: In $[KrF^+][Sb_2F_{11}^-]$: 693 (s), 679 (m), 670 (w), 651 (s), 619 (s), 521 (m), 481 (m), 298 (w), 270 (w), 230 (w) [N. Bartlett and D. E. McKee, unpublished observations]. In $[BrF_4^+][Sb_2F_{11}^-]$: 710 (11), 705 (11), 699 (23), 687 (5), 647 (80), 588 (8), 547 (27), 296 (11), 265 (10), 238 (13) [N. Bartlett, D. E. McKee, and C. J. Adams, unpublished observations].

Table VI

XeF_2 [a]	XeF_3^+ [b]	$XeOF_3^+$ [b]	IOF_3 [c,d]	XeO_2F_2 [e]	IF_4^+ [f]	TeF_4 [g]	
							
		939	878				ν, E=O
				822			ν_{symm}, EO_2
				850			ν_{asym}, EO_2
					733	695	ν_{symm}, eq. EF_2
					720	682	ν_{asym}, eq. EF_2
	640	642	651				ν, eq. E-F
557	618	649	545	585	645	588	ν_{symm}, ax EF_2
515	582	597	512	537	625 614	572	ν_{asym}, ax EF_2
213	363	358	351	324	389	333	Deformation, EF_2

[a] Values for vapor-phase molecule: P. Tsao, C. C. Cobb, and H. H. Claassen, *J. Chem. Phys.*, **54**, 5247 (1971); S. Reichman and F. Schreiner, *ibid.*, **51**, 2355 (1969). [b] This work. [c] Reference 25. [d] D. E. McKee and N. Bartlett, to be submitted for publication. [e] Reassignment of frequencies for matrix-isolated molecule reported by H. H. Claassen, E. L. Gasner, and H. Kim, *J. Chem. Phys.*, 49, 253 (1968). [f] Values for $[IF_4^+][SbF_6^-]$(s).[21] [g] Values for matrix-isolated molecule.[24]

lines are indeed observed at *ca.* 640 and *ca.* 575 cm^{-1} and are assigned respectively to $\nu_1(a_1)$, involving principally the equatorial Xe-F bond, and $\nu_2(a_1)$, associated with the symmetric stretching motion of the axial XeF_2 unit. The antisymmetric stretching fundamental of the XeF_2 unit, $\nu_4(b_1)$, is normally only weakly Raman active and is expected to lie at slightly higher frequency than $\nu_2(a_1)$ (BrF_3: $\nu_2(a_1)$ 552 cm^{-1}, $\nu_4(b_1)$ 612 cm^{-1};[21] see also Table VI); this fundamental is not observed for XeF_3^+ in solution in antimony pentafluoride but is identified with weak lines at *ca.* 614 cm^{-1} in the spectra of $XeF_4 \cdot SbF_5$ and $XeF_4 \cdot 2SbF_5$. A line at *ca.* 360 cm^{-1} is attributed to a deformation of the axial XeF_2 group. Some of the XeF_3^+ fundamentals occur as doublets in the room-temperature modification of $[XeF_3^+][SbF_6^-]$; a similar effect is noted for $[XeOF_3^+][SbF_6^-]$ and also for $[IF_4^+][SbF_6^-]$.[21]

The $XeOF_3^+$ cation is expected to be structurally akin to XeF_3^+, with the oxygen atom of the former situated at one of the equatorial lone-pair sites of the latter. A polarized Raman line at *ca.* 940 cm^{-1} is appropriately situated for an Xe–O stretching vibration, and the pattern of Xe–F stretches seen for $XeOF_3^+$ is remarkably like that of XeF_3^+. Polarized Raman lines occur at *ca.* 640 and *ca.* 590 cm^{-1} (*cf.* XeF_3^+: 640, 575 cm^{-1}) and are assigned like their XeF_3^+ counterparts, to the equatorial Xe–F and symmetric axial XeF_2 stretching motions, respectively. Unlike Gillespie, *et al.*,[12] who attributed Raman lines at *ca.* 550 cm^{-1} in $[XeOF_3^+][Sb_2F_{11}^-]$ to the antisymmetric stretching motion of the axial XeF_2 unit, we prefer to assign this fundamental above 600 cm^{-1}, prompted both by the comparison with XeF_3^+ and by the evidence of similar molecules which shows the antisymmetric stretch to lie higher than its symmetric counterpart. In passing, it should be noted that the comparison with solid IOF_3 which led Gillespie, *et al.*,[12] to their assignment may not be altogether valid. The crystallographic data[22] for this solid, interpreted in terms of discrete IOF_3 groups, are but poor and have never been fully reported. The testimony of related compounds, *e.g.*, TeF_4 (Table VI), suggests that the lattice should contain significant intermolecular interactions, which matrix-isolation studies[23,24] of SF_4, SeF_4, and TeF_4 suggest should considerably lower the frequencies of the axial stretching fundamentals. Moreover, the Raman spectrum of IOF_3 as reported by Carter and Aubke[25] displays more lines than may comfortably be accommodated by a molecular model.

Our vibrational data for the XeF_3^+ and $XeOF_3^+$ cations are not sufficiently complete, we feel, to allow worthwhile normal-coordinate analysis; the approximations necessary would be too severe. Nevertheless, if our assignments for the XeF_3^+ and $XeOF_3^+$, vibrational modes and our suppositions concerning the $XeOF_3^+$ shape are valid, we can predict the bond lengths in $XeOF_3^+$ with fair precision. Since the stretching frequency ν(Xe–O) is not very different for the cation (939 cm^{-1}) compared with the value in the parent molecule (923 cm^{-1}),[16] it is probably safe to assume that the Xe–O bond lengths will be similar (XeO in $XeOF_4$ = 1.70 (2) Å).[26] Moreover, comparison of the Xe–F distance will not differ greatly for the two cations (1.83 Å in XeF_3^+)[1] although the higher axial stretching fundamentals found for the Xe(VI) cation imply that the axial Xe–F bonds in $XeOF_3^+$ may be slightly shorter than in XeF_3^+ (1.88, 1.89 Å).[1]

It is of interest that no evidence for either $Xe_2F_7^+$ or $Xe_2O_2F_7^+$ was found in these studies, although both $Xe_2F_3^+$ [3] and $Xe_2F_{11}^+$ [27] have been established. This is consistent with XeF_4 and $XeOF_4$ being inferior F^- ion donors compared with either XeF_2 or XeF_6. The complex cations, in effect, involve fluoride ion donation by a neutral molecule to a daughter cation.

Finally, it should be noted that $XeOF_4$ and IF_5 are extremely similar in their fluoro acid-base chemistry. Both form 1:1 and 1:2 adducts with the F^- acceptor SbF_5, for which the following ionic formulations are appropriate: $[XeF_3^+][SbF_6^-]$, $[XeF_3^+][Sb_2F_{11}^-]$, $[IF_4^+][SbF_6^-]$,[21] $[IF_4^+][Sb_2F_{11}^-]$.[28] Molecular adducts $XeF_2 \cdot XeOF_4$[29] and $XeF_2 \cdot IF_5$[30] are given with xenon difluoride while cesium fluoride affords both 1:1 and 1:3 complexes with $XeOF_4$[31] and with IF_5.[32]

Registry No. $XeOF_4$, 13774-85-1; SbF_5, 7783-70-2; XeF_4, 13709-61-0; $[XeF_3^+][Sb_2F_{11}^-]$, 39797-62-1; $[XeF_3^+][SbF_6^-]$, 39797-63-2; $[XeOF_3^+][Sb_2F_{11}^-]$, 39797-64-3; $[XeOF_3^+][SbF_6^-]$, 39797-65-4.

Acknowledgments. C. J. A. carried out this work with the support of a Harkness Fellowship from the Commonwealth Fund. The work was otherwise supported by the U. S. Atomic Energy Commission.

---

(21) D. E. McKee, D. D. Gibler, C. J. Adams, and N. Bartlett, to be submitted for publication.

(22) J. H. Viers and H. W. Baird, *Chem. Commun.*, 1093 (1967).

(23) R. L. Redington and C. V. Berney, *J. Chem. Phys.*, 43, 2020 (1963).

(24) C. J. Adams and A. J. Downs, *Spectrochim. Acta, Sect. A*, 28, 1841 (1972).

(25) H. A. Carter and F. Aubke, *Inorg. Chem.*, 10, 2296 (1971).

(26) J. Martins and E. B. Wilson, Jr., *J. Mol. Spectrosc.*, 26, 410 (1968).

(27) K. Leary, A. Zalkin, and N. Bartlett, *J. Chem. Soc., Chem. Commun.*, 132 (1973); submitted for publication in *Inorg. Chem.*

(28) A. J. Edwards, personal communication.

(29) N. Bartlett and M. Wechsberg, *Z. Anorg. Allg. Chem.*, 385, 5 (1971).

(30) G. R. Jones, R. D. Burbank, and N. Bartlett, *Inorg. Chem.*, 9, 2264 (1971).

(31) D. E. McKee and N. Bartlett, unpublished observations.

(32) K. O. Christe, *Inorg. Chem.*, 11, 1215 (1972).