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New Syntheses and Properties of XeO_2F_2, $Cs^+XeO_2F_3^-$, and $NO_2^+[XeO_2F_3{\cdot}nXeO_2F_2]^-$

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Alkali-metal nitrates and N_2O_5 are useful reagents for the stepwise replacement of two fluorine atoms by one oxygen atom in xenon fluorides or oxyfluorides. Thus, the reaction of an excess of XeF_6 with $CsNO_3$ yields $XeOF_4$, FNO_2, and $CsXeF_7$ in high yield. With $CsNO_3$ in excess, the primary products are $CsXeOF_5$ and FNO_2, and after longer reaction times some $CsXeO_2F_3$ is also formed. The reaction of $CsNO_3$ with an excess of $XeOF_4$ produces FNO_2 and XeO_2F_2 in quantitative yield with a mixture of CsF and $CsXeOF_5$ as the byproducts. Recrystallization of this CsF–$CsXeOF_5$–XeO_2F_2 mixture from anhydrous HF provides a convenient synthesis for $CsXeO_2F_3$. The reaction of N_2O_5 with an excess of $XeOF_4$ results in XeO_2F_2 and FNO_2, thus providing a new safe synthesis for XeO_2F_2. Vibrational spectra of liquid, solid, and Ar-matrix-isolated XeO_2F_2 are reported. With FNO_2, xenon dioxide difluoride forms an unstable $NO_2^+[XeO_2F_3{\cdot}nXeO_2F_2]^-$ adduct, which was characterized by Raman spectroscopy. The vibrational spectra of $CsXeO_2F_3$ were recorded and assigned. It is shown that the two oxygen atoms in $XeO_2F_3^-$ are cis and not trans to each other and that the Raman spectrum previously attributed to $Cs^+XeO_2F_3^-$ is due to a $Cs^+[XeO_2F_3{\cdot}nXeF_2]^-$ adduct.

Introduction

In a prevous paper[1] it was shown that the nitrate ion is an excellent reagent for substituting one oxygen atom for two fluorine ligands in BrF_5. During a study of the general utility of this reagent, the reactions of NO_3^- with xenon fluorides were also studied, and the results are summarized in this paper.

The controlled, stepwise substitution of two fluorines by one oxygen in XeF_6 was of particular interest because the previously used methods for the synthesis of XeO_2F_2 involved the highly explosive XeO_3, either as a starting material[2] or as a potential byproduct.[3,4] In view of this explosion hazard, it is not surprising that the previous literature on XeO_2F_2 is rather limited. The compound was first prepared by Huston[2] from XeO_3 and $XeOF_4$ and was characterized by him and his co-workers by vibrational spectroscopy,[5] neutron diffraction,[6] and an ^{18}F radiotracer study.[7] The only other reports on XeO_2F_2 chemistry are by Schrobilgen and co-workers. They prepared XeO_2F_2 by hydrolysis of XeF_6 in HF solution[3,4] and recorded its NMR[4] and Raman[4,8] spectra. Furthermore, they showed that XeO_2F_2 is a good fluoride ion donor and can form 1:1 and 1:2 adducts with SbF_5 that contain the XeO_2F^+ cation.[3,8-10] Although the direct complexation of XeO_2F_2 with alkali-metal fluorides was not studied, they obtained, by the disproportionation of $XeOF_2$ in the presence of CsF in anhydrous HF, a solid that, on the basis of its Raman spectrum, was attributed to $Cs^+[$*trans*-$XeO_2F_3]^-$.[11]

In addition to the synthesis of XeO_2F_2, we have also studied its fluoride ion donor and acceptor properties. In this paper, the adduct formation of XeO_2F_2 with CsF and FNO_2 is included, while data on the new adducts $XeO_2F^+AsF_6^-$ and $FO_2XeFXeO_2F^+AsF_6^-$ are given elsewhere.[12]

Experimental Section

Caution! The reaction of $XeOF_4$ with an excess of nitrate produces highly explosive XeO_3. Liquid mixtures of XeO_2F_2 and XeO_3, when cooled with liquid nitrogen, tended to flash followed within seconds by explosions. Therefore, for the $XeOF_4$ and XeO_2F_2 syntheses the xenon-containing starting materials should always be used in excess, and appropriate safety precautions should be taken.

Apparatus and Materials. The vacuum lines, handling techniques, and spectrometers used in this study have been described elsewhere.[12,13] $CsNO_3$ was prepared from Cs_2CO_3 and HNO_3 and dried in a vacuum oven at 120 °C for 1 day. FNO_2 was obtained as a byproduct from the reactions of nitrates with either XeF_6, $XeOF_4$, or BrF_5[1] and was purified by fractional condensation through two cold traps kept at −142 and −196 °C, with the material retained at −196 °C being used. CsF was dried by fusion in a platinum crucible, followed by immediate transfer of the hot clinker to the dry N_2 atmosphere of a glovebox. XeF_6 was prepared from Xe and F_2 and purified by complexing with NaF and subsequent vacuum pyrolysis of the adduct.[14,15] $XeOF_4$[13] and N_2O_5[16] were prepared by literature methods, and HF was dried with BiF_5 as previously described.[17]

Reaction of $CsNO_3$ with an Excess of XeF_6. A 30-mL stainless steel cylinder was loaded in the drybox with $CsNO_3$ (2.44 mmol). On the vacuum line, XeF_6 (20.51 mmol) was added at −196 °C. The cylinder was heated to 56 °C for 4 h and then cooled to −196 °C. It did not contain any material noncondensable at −196 °C. The material volatile at 25 °C was separated by fractional condensation through traps kept at −78 and −196 °C. The −196 °C trap contained FNO_2 (1.85 mmol), and the −78 °C trap had XeF_6, $XeOF_4$, and some FNO_2. To separate all of the FNO_2 from XeF_6 and $XeOF_4$, the contents of the −78 °C trap were fractionated three more times as described above and yielded an additional 0.55 mmol of FNO_2 in the −196 °C trap for a total of 2.4 mmol. XeF_6 and $XeOF_4$ were separated by complexing XeF_6 with a large excess of NaF in a Monel cylinder at 70 °C for 2 h, followed by pumping off the unreacted $XeOF_4$ at 25 °C and collecting it in a U-trap at −78 °C. The collected material (546 mg; weight calculated for 2.44 mmol of $XeOF_4$ 545 mg) was shown by its vapor pressure and infrared spectrum to be pure $XeOF_4$. The solid nonvolatile residue from the $CsNO_3$–XeF_6 reaction (976 mg; weight calculated for 2.44 mmol of $CsXeF_7$ 969 mg) was identified by infrared and Raman spectroscopy as $CsXeF_7$.[18]

Reaction of XeF_6 with an Excess of $CsNO_3$. A mixture of $CsNO_3$ (6.06 mmol) and XeF_6 (1.12 mmol) was heated in a 30-mL stainless steel cylinder for 16 h to 54 °C. The cylinder was cooled to −196 °C and contained no noncondensable material. The material volatile at 25 °C was separated by fractional condensation through traps kept at −78 and −196 °C. The −196 °C trap contained FNO_2 (1.13 mmol), while the −78 °C trap had $XeOF_4$ (0.03 mmol). The solid, off-white residue (1.369 g; weight calculated, for 1.09 mmol of $CsXeOF_5$, 0.03 mmol of CsF, and 4.94 mmol of $CsNO_3$ 1.376 g) was identified by vibrational spectroscopy as $CsNO_3$ and $CsXeOF_5$[19] containing small amounts of $CsXeO_2F_3$ and $CsXeF_7$[18] and a trace amount of XeO_2F_2.

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When the reaction time for the XeF_6 plus excess $CsNO_3$ system was increased to 2 weeks or more, the yield of FNO_2 increased and $CsXeO_2F_3$ became a major reaction product besides $CsXeOF_5$, $CsXeF_7$, and unreacted $CsNO_3$.

Reaction of $CsNO_3$ with an Excess of $XeOF_4$. Finely powdered $CsNO_3$ (1.28 mmol) was loaded into a prepassivated 10-mL stainless steel cylinder in the drybox. The cylinder was evacuated on the vacuum line, and $XeOF_4$ (4.97 mmol) was added at −196 °C. The cylinder was kept in an oven at 45 °C for 24 h, then reconnected to the vacuum line, and cooled to −196 °C. It did not contain any significant amount of gas noncondensable at −196 °C. The material volatile at 25 °C was separated by fractional condensation in a dynamic vacuum through traps kept at −78 and −196 °C. The −78 °C trap contained $XeOF_4$ (3.18 mmol), and the −196 °C trap, FNO_2 (1.22 mmol). The white solid residue (569 mg; weight calculated for 1.28 mmol of XeO_2F_2, 0.77 mmol of CsF, and 0.51 mmol of $CsXeOF_5$ 566 mg) was identified by vibrational spectroscopy. The Raman bands due to XeO_2F_2 (884 m, 852 sh, 849 vs, 501 m, 489 ms, 354 w, 207 w cm^{-1}) deviated somewhat from those of the neat solid XeO_2F_2 but in their general appearance resembled those of XeO_2F_2 mixtures with other compounds (see Results and Discussion).

Preparation of $Cs^+XeO_2F_3^-$. The solid product obtained from the $CsNO_3$ plus excess $XeOF_4$ reaction, when recrystallized from anhydrous HF, was converted almost quantitatively to $Cs^+XeO_2F_3^-$ with simultaneous $XeOF_4$ evolution. A remaining trace of free XeO_2F_2, detectable by its Raman bands at 881, 850, and 497 cm^{-1}, could be converted to $CsXeO_2F_3$ by the addition of a small amount of extra CsF before the recrystallization.

Preparation of XeO_2F_2. A sample of freshly prepared N_2O_5 (3.95 mmol) was transferred on the vacuum line under a dynamic vacuum into a 0.75-in-o.d. Teflon-FEP U-trap that was equipped with two stainless steel valves and kept at −45 °C. The Teflon U-trap was cooled to −196 °C, and $XeOF_4$ (8.71 mmol) was added. The mixture was allowed to slowly warm to ambient temperature in an empty cold Dewar flask and was kept at this temperature for 90 min. The U-tube was cooled to −196 °C and contained no noncondensable material. The material volatile at room temperature was pumped off briefly through two traps cooled to −78 and −196 °C. The trap at −196 °C contained FNO_2 (7.4 mmol), while the one at −78 °C had $XeOF_4$ (4.75 mmol). The liquid residue in the Teflon U-trap (827 mg; weight calculated for 3.95 mmol of XeO_2F_2 and 0.49 mmol of FNO_2 827 mg) was shown by Raman spectroscopy to be predominantly ionic $NO_2^+[XeO_2F_3 \cdot nXeO_2F_2]^-$. Complete removal of FNO_2 together with some XeO_2F_2 was achieved by prolonged pumping on the sample at ambient temperature. The resulting pure XeO_2F_2 was a white solid melting at 31 °C and was characterized by its vibrational spectra.[4,5,8]

The XeO_2F_2–FNO_2 System. FNO_2 (3.86 mmol) was added at −196 °C to a sapphire tube containing XeO_2F_2 (1.32 mmol). The mixture was allowed to warm to ambient temperature. At first the product was liquid, but after several hours at 25 °C it was converted to a white solid, which was shown by Raman spectroscopy to be an NO_2^+ salt of $[XeO_2F_3 \cdot nXeO_2F_2]^-$. The tube was cooled to −78 °C, and unreacted FNO_2 (3.21 mmol) was pumped off, establishing the composition of the white solid as $NO_2^+[XeO_2F_3 \cdot 1.03XeO_2F_2]^-$. The dissociation pressure above 0.65 mmol of this solid in a 27.2-mL volume at 22.4 °C was found to be 96 Torr of FNO_2. Upon removal of FNO_2 by brief pumping at 25 °C, the white solid residue melted to a clear colorless liquid that had lost most of its FNO_2. As described above for the preparation of pure XeO_2F_2, the complete removal of FNO_2 was achieved with some loss of XeO_2F_2.

Results and Discussion

Reactions of NO_3^- with XeF_6 and Synthesis of $XeOF_4$. The reaction of $CsNO_3$ with a large excess of XeF_6 at temperatures above the melting point of XeF_6 (49.5 °C) proceeds quantitatively according to (1) and (2). If in (1) the excess of XeF_6 is reduced

$$CsNO_3 + XeF_6 \rightarrow CsF + XeOF_4 + FNO_2 \qquad (1)$$

$$CsF + XeF_6 \rightarrow CsXeF_7 \qquad (2)$$

to less than 100%, some of the CsF can react with $XeOF_4$ to form $Cs^+XeOF_5^-$.[19] Substitution of $CsNO_3$ by $NaNO_3$ in (1) provides the following advantages, a more detailed description of which is reported elsewhere:[13] (i) $NaNO_3$ is commercially readily available and less expensive than $CsNO_3$; (ii) NaF does not form a stable adduct with $XeOF_4$, and therefore, only a small excess of XeF_6 is required for (1) without loss of $XeOF_4$; (iii) the formed NaF complexes the small excess of XeF_6 used as $NaXeF_7$. This results in $XeOF_4$ and FNO_2 as the only volatile products, which can be separated readily by fractional condensation due to their vastly different volatilities.

If in the $CsNO_3$–XeF_6 reaction an excess of $CsNO_3$ is being used, most of the XeF_6 is converted to $XeOF_4$, which reacts with CsF according to (3). In this case, the major reaction products

$$CsF + XeOF_4 \rightarrow CsXeOF_5 \qquad (3)$$

are FNO_2 and $CsXeOF_5$, with small amounts of CsF, $CsXeF_7$, $CsXeO_2F_3$, and XeO_2F_2 also being formed. With long reaction times of several weeks at 54 °C, the secondary reactions (4) and (5) gain in importance, and $CsXeO_2F_3$ becomes a major reaction product.

$$CsNO_3 + XeOF_4 \rightarrow CsF + FNO_2 + XeO_2F_2 \qquad (4)$$

$$CsF + XeO_2F_2 \rightarrow CsXeO_2F_3 \qquad (5)$$

Reaction of $CsNO_3$ with $XeOF_4$ and Synthesis of XeO_2F_2. The reaction of $CsNO_3$ with a large excess of $XeOF_4$ results in the quantitative formation of FNO_2 and XeO_2F_2 according to (4), with about 60% of the CsF reacting with excess $XeOF_4$ according to (3) to give $CsXeOF_5$. Since XeO_2F_2 is of low volatility and is difficult to remove from the other solid products, i.e. CsF and $CsXeOF_5$, the $CsNO_3$ in (4) was replaced by N_2O_5 which, in the solid state, has the ionic structure $NO_2^+NO_3^-$.[16,20] In this manner, instead of nonvolatile CsF, volatile FNO_2 is formed as in (6), and XeO_2F_2 is the only low-volatility reaction product, thus facilitating product separation. While most of the FNO_2 byproduct can

$$NO_2^+NO_3^- + XeOF_4 \rightarrow 2FNO_2 + XeO_2F_2 \qquad (6)$$

readily be pumped off from XeO_2F_2 at ambient temperature, complete removal of FNO_2 becomes increasingly more difficult and requires prolonged pumping. Since pure XeO_2F_2 melts at 31 °C[2], solidification of the initially liquid reaction product at ambient temperature serves as a good indication that removal of the FNO_2 byproduct is essentially complete.

The use of an excess of N_2O_5 in (6) should be avoided because XeO_2F_2 can react further with N_2O_5, producing FNO_2 and highly explosive XeO_3. This was experimentally verified but not further pursued due to the pronounced sensitivity of the resulting liquid XeO_2F_2–XeO_3 mixture. This mixture, when cooled with liquid nitrogen, tended to flash followed by explosive decomposition.

In summary, the reaction of N_2O_5 with $XeOF_4$ provides a convenient, scalable, and safer new synthesis for XeO_2F_2, provided that an excess of $XeOF_4$ is used in the reaction. The previous methods used either $XeOF_4$ and the explosive XeO_3 as starting materials[2] or the hydrolysis of XeF_6 in HF solution, which has also been described as hazardous.[4]

Synthesis of $XeO_2F_3^-$ Salts. The solid product obtainable from the reaction of $CsNO_3$ and an excess of $XeOF_4$ (see above) consists of a mixture of CsF, $CsXeOF_5$, and XeO_2F_2. Recrystallization of this mixture from anhydrous HF solution results in an essentially complete conversion of CsF and $CsXeOF_5$ to $CsXeO_2F_3$ according to (5) and (7). The fact that the pseudo-trigonal-bipyramidal

$$CsXeOF_5 + XeO_2F_2 \xrightarrow{HF} CsXeO_2F_3 + XeOF_4 \qquad (7)$$

XeO_2F_2 (Xe has one sterically active free valence electron pair in its Xe(VI) compounds) is a stronger Lewis acid than pseudooctahedral $XeOF_4$ and, therefore, displaces it from its salts is not surprising. Since $XeOF_4$ has a vapor pressure of 29 torr at 23 °C, it can readily be pumped off from the $CsXeO_2F_3$ product, which is isolated as a stable white solid.

The only previous report concerning the existence of an $XeO_2F_3^-$ salt was a statement that, in an HF solution containing CsF, $XeOF_2$ disproportionates according to (8) to give $CsXeO_2F_3$.[11]

$$2XeOF_2 + CsF \xrightarrow{HF} CsXeO_2F_3 + XeF_2 \qquad (8)$$

The product from (8) was characterized by its Raman spectrum, which was interpreted in terms of an $XeO_2F_3^-$ anion in which the two oxygen atoms are trans to each other.[11] However, the Raman spectrum (trace B, Figure 1) of our $CsXeO_2F_3$, prepared according to (7), significantly differs in the region of the Xe–F vibrations from that previously reported.[11] This discrepancy was resolved.

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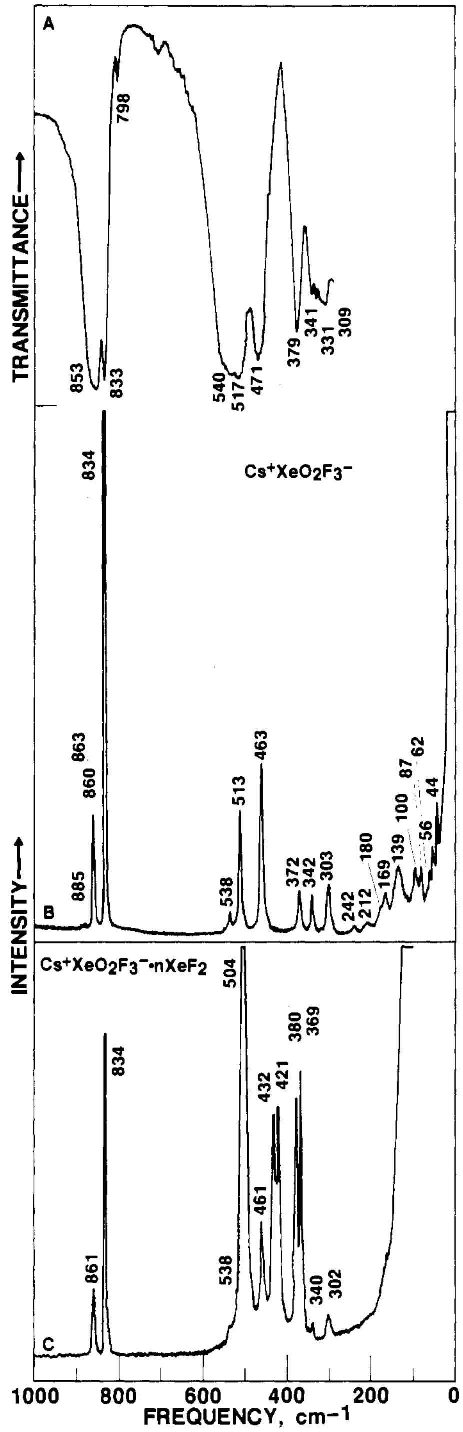

Figure 1. Traces A and B: infrared and Raman spectra, respectively, of solid $CsXeO_2F_3$ at 25 °C. Trace C: Raman spectrum of $CsXeO_3F_2{\cdot}nXeF_2$ at 25 °C.

It was shown that a mixture of XeF_6 and XeF_4, when reacted with $CsNO_3$, yields a product that contains XeF_2 in addition to $CsXeO_2F_3$ and exhibits a Raman spectrum (see trace C of Figure 1) that is similar to that previously reported.[11] Therefore, the material previously ascribed[11] to $CsXeO_2F_3$ was most likely a $CsXeO_2F_3{\cdot}nXeF_2$ adduct. This is not surprising in view of the known tendency of XeF_2 to form molecular adducts with other pseudooctahedral xenon or iodine species such as XeF_4,[21] $XeOF_4$,[22] XeF_5^+,[23,24] or IF_5[24] and the fact that XeF_2 is a byproduct in (8).

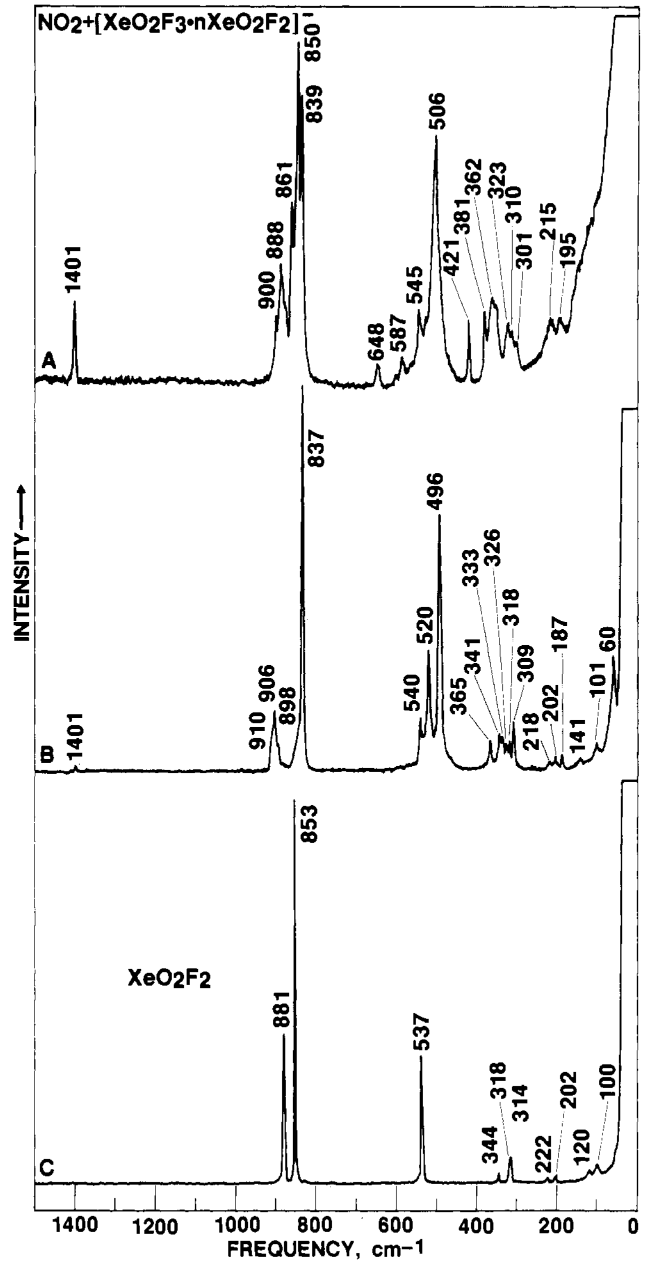

Figure 2. Trace A: Raman spectrum of solid $NO_2^+[XeO_2F_3{\cdot}nXeO_2F_2]^-$ recorded at 25 °C under an FNO_2 pressure of 2 atm. Trace B: Raman spectrum of a sample of XeO_2F_2 containing a small amount of residual FNO_2, recorded as a solid at −100 °C. Trace C: Raman spectrum of the XeO_2F_2 residue after complete removal of all FNO_2, recorded as a solid at 25 °C.

In the case of the reaction of $CsNO_3$ with XeF_4 containing XeF_6, the formation of $CsXeO_2F_3{\cdot}XeF_2$ is readily explained by the sequence of reactions 9–12. Reaction 10 has previously been shown[25] to occur readily at temperatures above −15 °C. A detailed discussion of the vibrational spectra of $CsXeO_2F_3$ will be given below.

$$CsNO_3 + XeF_4 \rightarrow CsF + FNO_2 + XeOF_2 \tag{9}$$

$$2XeOF_2 \rightarrow XeO_2F_2 + XeF_2 \tag{10}$$

$$CsF + XeO_2F_2 \rightarrow CsXeO_2F_3 \tag{11}$$

$$CsXeO_2F_3 + XeF_2 \rightarrow CsXeO_2F_3{\cdot}XeF_2 \tag{12}$$

The sluggishness of FNO_2 removal from XeO_2F_2 (see above) and the observation of a Raman signal at 1401 cm^{-1}, which is characteristic for NO_2^+,[16] suggested that XeO_2F_2 and FNO_2 might

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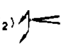
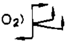
Table I. Vibrational Spectra of XeO_2F_2 and Their Assignment in Point Group C_{2v}

assgnt			obsd freq, cm^{-1} (rel intens)			
			solid, -110 °C	Ar matrix	liquid	
			Ra	IR	Ra	IR
A_1	ν_1	$\nu_{sym}(XeO_2)$	853 (100)	849 mw	845 (100) p	841 s
	ν_2	$\nu_{sym}(XeF_2)$	537 (33)	537 w	495 (35) p	500 sh
	ν_3	$\delta_{sym}(XeO_2)$	344 (2.5)	331 sh	334 (21)	
	ν_4	δ(XeF) 	202 (1.4)	202 w	200 (5)	
A_2	ν_5	$\tau(XeO_2)$	318 (~1)	329 sh		
B_1	ν_6	$\nu_{as}(XeO_2)$	881 (39)	906 s	901 (15) dp	895 vs
	ν_7	δ(XeF_2) 	222 (1.2)		220 sh	
B_2	ν_8	$\nu_{as}(XeF_2)$	578 (0+)	585 vs	575 sh, dp	575 s
	ν_9	$\delta_{rock}(XeO_2)$ 	314 (6)	324 m	312 sh	

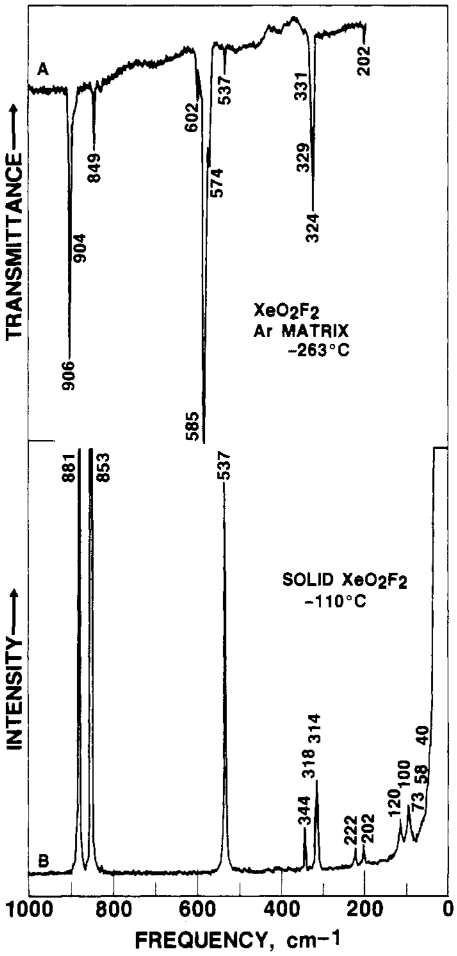


Figure 3. Trace A: infrared spectrum of XeO_2F_2, isolated in an Ar matrix at -263 °C. Trace B: Raman spectrum of solid XeO_2F_2 recorded at -110 °C.

form an unstable adduct. This was confirmed by showing that XeO_2F_2, when combined with an excess of FNO_2 at room temperature, retained at -78 °C about 0.5 mol of FNO_2/mol of XeO_2F_2. The Raman spectrum (trace A, Figure 2) of the resulting adduct showed the 1401-cm^{-1} band characteristic[16] of NO_2^+ and was not a composite of the spectra of free $XeO_2F_3^-$ (trace B, Figure 1) and solid XeO_2F_2 (trace C, Figure 2). Therefore, it is attributed to an NO_2^+ salt of a $[XeO_2F_3 \cdot nXeO_2F_2]^-$ polyanion. The $FNO_2 \cdot 2XeO_2F_2$ adduct, which was isolated by FNO_2 removal at -78 °C, was an unstable white solid with an FNO_2 dissociation pressure of at least 96 Torr at 22.4 °C. Complete removal of all FNO_2 could be achieved by prolonged pumping at 25 °C. Raman spectra at different stages of FNO_2 removal are shown in Figure 2, traces A-C, and indicate that the presence of even small amounts of NO_2^+ causes pronounced association effects and complexity of the spectra for XeO_2F_2.

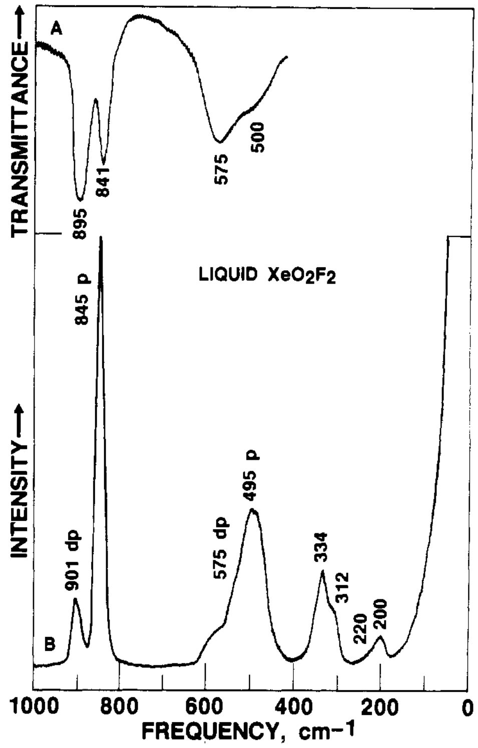
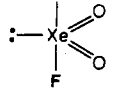


Figure 4. Trace A: infrared spectrum of liquid XeO_2F_2 between AgCl disks. Trace B: Raman spectrum of liquid XeO_2F_2 recorded at 35 °C; p and dp are abbreviations for polarized and depolarized bands, respectively.

Vibrational Spectra. XeO_2F_2. Although most of the fundamental vibrations of XeO_2F_2 were known from previous studies[4,5] and a normal-coordinate analysis had been carried out,[26] the marginal quality of some of the reported spectra[5] and questions concerning the assignments of some of the deformation modes prompted us to redetermine the vibrational spectra. The results are shown in Figures 3 and 4, , and the revised assignments are summarized in Table I. The structure of XeO_2F_2 has been



established by a neutron diffraction study.[6] It is a pseudo trigonal bipyramid of symmetry C_{2v} in which one of the equatorial positions is occupied by a free valence electron pair. Of the nine fundamentals the four A_1 modes, $\nu_6(B_1)$, and $\nu_8(B_2)$ have been firmly assigned.[4,5,26]

The modes in question are the XeO_2 torsion mode, $\nu_5(A_2)$, the XeF_2 bending mode, $\nu_7(B_1)$, and the XeO_2 rocking mode, $\nu_9(B_2)$.

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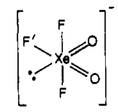
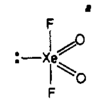
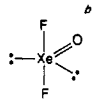
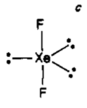
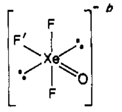
(26) Willet, R. D.; LaBonville, P.; Ferraro, J. R. *J. Chem. Phys.* **1975**, *63*, 1474.

Table II. Vibrational Spectra of $Cs^+XeO_2F_3^-$ Compared to Those of Closely Related Compounds

assgnt for $XeO_2F_3^-$ in point group C_s			obsd freq, cm^{-1} (rel intens)								assgnt for $XeOF_3^-$ in point group C_s		
					 [a]		 [b]	 [c]		 [b]			
			Ra	IR	Ra	IR		Ra	IR				
A′	ν_1	$\nu_{as}(XeO_2)$	863 (18)	853 vs	881 (39)	906 s	732 (8)			768 (7)	A′	ν_1	$\nu(XeO)$
	ν_2	$\nu_{sym}(XeO_2)$	834 (100)	833 m	853 (100)	849 mw							
	ν_3	$\nu(XeF')$	513 (20)	517 vs						503 (61)		ν_2	$\nu(XeF')$
	ν_4	$\nu_{sym}(XeF_2)$	463 (29)	471 s	537 (33)	537 w	496 (100)	509 (100)		464 (100)		ν_3	$\nu_{sym}(XeF_2)$
	ν_5	$\delta_{sciss}(XeO_2)$	372 (7)	379 m	344 (2.5)	331 sh							
	ν_6	$\delta(F'XeO)$	303 (8)	309 m						270 (5)		ν_4	$\delta(F'XeO)$
	ν_7	$\delta_{sciss}(XeF_2)$ 	212 (1.5)		222 (1.2)		197 (1)		213 vs	219 (1)		ν_5	$\delta_{sciss}(XeF_2)$
	ν_8	$\delta_{sciss}(XeF_2)$ 	169 (5)		202 (1.4)	202 w	186 (8)			167 (5)		ν_6	$\delta_{sciss}(XeF_2)$
A″	ν_9	$\nu_{as}(XeF_2)$	538 (3)	540 vs	578 (0+)	585 vs			560 vs	487 (10)	A″	ν_7	$\nu_{as}(XeF_2)$
	ν_{10}	$\tau(XeO_2)$		331 w	318 (~1)	329 sh	285 (4)			381 (5)		ν_8	$\delta_{rock}(XeO)$
	ν_{11}	$\delta_{rock}(XeO_2)$	342 (6)	341 w	314 (6)	324 m							
	ν_{12}	$\delta_{rock}(XeF')$	242 (1)							292 (1)		ν_9	$\delta_{rock}(XeF')$

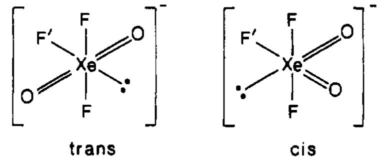
[a] Data from this work (Table I). [b] Data from ref 11. [c] Data from ref 27.

It should be noted that, in the previous normal-coordinate analysis,[26] the ν_7 and ν_9 modes have been assigned to the wrong symmetry blocks and must be exchanged. Although the choice of the B_1 and B_2 block for such a C_{2v} molecule is arbitrary, all modes within a given block must be symmetric with respect to the same plane of symmetry.

For the assignments of ν_5, ν_7, and ν_9, three frequencies, 318, 314, and 222 cm^{-1} (Ra (Raman) values of the solid), are available. Since the $\nu_7(B_1)$ and the $\nu_4(A_1)$ XeF_2 bending modes should be almost degenerate, their frequencies and relative intensities should be similar. Since $\nu_4(A_1)$ has been firmly assigned to the 202-cm^{-1} band,[4,5,21] $\nu_7(B_1)$ is assigned to the 222-cm^{-1} band. Of the remaining two yet unassigned vibrations, the XeO_2 rocking mode should have higher infrared and Raman intensities than those for the XeO_2 torsion. The rocking mode, therefore, is assigned to the 314-cm^{-1} band, leaving the very weak 318-cm^{-1} band for the torsional mode.

The $XeO_2F_3^-$ Anion. As mentioned above, the Raman spectrum previously attributed[11] to $CsXeO_2F_3$ is that of a $CsXeO_2F_3 \cdot nXeF_2$ adduct. The vibrational spectra of $CsXeO_2F_3$ free of XeF_2 are shown in Figure 1, traces A and B, and their assignments are summarized in Table II.

The Xe atom in $XeO_2F_3^-$ possesses a free valence electron pair, and therefore, the structure of the anion should be that of a pseudooctahedron. In such a structure the two oxygen ligands could be either cis or trans with respect to each other, and the vibrational spectra should allow one to distinguish between these two isomers.


trans cis

For simplicity, let us assume isolated linear and bent (90°) OXeO groups. A linear OXeO group has a center of symmetry, and therefore, the symmetric and the antisymmetric stretching vibrations should be mutually exclusive in the infrared and the Raman spectra. Furthermore, the coupling between the antisymmetric and the symmetric stretching modes should be at a maximum, resulting in a maximal separation of their frequencies.[28] On the other hand, for a right-angled OXeO group both the antisymmetric and the symmetric stretching vibrations should be of significant intensity in both the infrared and the Raman spectra. Furthermore, their frequency separation should be at a minimum since their potential energy terms (G matrix terms) become identical.[28]

These arguments can be nicely supported by the known examples[29] of *cis*- and *trans*-$IF_4O_2^-$, which are also pseudooctahedral and have atomic masses very similar to those in $XeO_2F_3^-$. Thus, in *trans*-$IF_4O_2^-$ the symmetric and the antisymmetric OIO stretching modes are mutually exclusive in the infrared and Raman spectra and exhibit a frequency separation of 61 cm^{-1}. By contrast, in *cis*-$IF_4O_2^-$ both OIO stretching modes are infrared and Raman active (Ra (cm^{-1} (relative intensity)) ν_{as} 875 (14), ν_{sym} 856 (100); IR (cm^{-1}) ν_{as} 875 vs, ν_{sym} 855 vs) and their frequency separation is only 20 cm^{-1}.

Inspection of Figure 1 and Table II reveals for $XeO_2F_3^-$ a frequency separation of about 29 cm^{-1} and significant Raman intensity for the antisymmetric OXeO stretch and infrared intensity for the symmetric OXeO stretch. Furthermore, these observations for $XeO_2F_3^-$ closely resemble those for solid XeO_2F_2 ($\Delta\nu = 28$ cm^{-1}; Ra (cm^{-1} (relative intensity)) ν_{as} 881 (39), ν_{sym} 853 (100)), which was shown by neutron diffraction[6] to have an OXeO bond angle of 106°.[30] Consequently, the oxygen atoms in $XeO_2F_3^-$ must be cis with respect to each other, and their bond angle should be similar to that in XeO_2F_2. The same arguments hold for the $CsXeO_2F_3 \cdot nXeF_2$ adduct, which exhibits almost identical XeO_2 stretching frequencies and intensities.

The vibrational assignments for *cis*-$XeO_2F_3^-$ are based to a large extent on correlations with the known spectra of the closely related XeO_2F_2, $XeOF_2$,[11] and XeF_2[27] molecules and the $XeOF_3^-$ anion[11] (see Table II). Compared to those of XeO_2F_2, the $XeO_2F_3^-$ vibrations involving the XeO_2 group exhibit only minor frequency shifts, with the stretching modes being somewhat lower and the deformation modes being somewhat higher than their counterparts in XeO_2F_2. The frequency increases of the deformation modes are attributed to the addition of the fluoride ion, resulting in increased crowding of the ligands in the equatorial plane and concomitant resistance toward angle deformation. On the other

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(27) Bartlett, N.; Sladky, F. O. In *Comprensive Inorganic Chemistry*; Bailar, J. C., Emeleus, H. J., Nyholm, R., Trotman-Dickenson, A. F., Eds.; Pergamon: Oxford, U.K., 1973; Vol. 1, p 255.

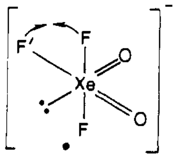
(28) Weidlein, J.; Muller, U.; Dehnicke, K. In *Schwingungsspektroskopie*; Thieme: Stuttgart, West Germany, 1982; p 53.

(29) Christe, K. O.; Wilson, R. D.; Schack, C. J. *Inorg. Chem.* **1981**, *20*, 2104.

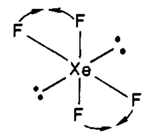
(30) The small (106°) O–Xe–O bond angle in solid XeO_2F_2 is due to oxygen bridging with neighboring molecules. In matrix-isolated XeO_2F_2, the O–Xe–O bond angle must be significantly larger than 106° and should approximate the 120° value expected for an ideal trigonal bipyramid. This is supported by the increased frequency separation of 57 cm^{-1} observed for the two XeO_2 stretching modes in matrix-isolated XeO_2F_2. A trans configuration of the oxygens in matrix-isolated XeO_2F_2 can be ruled out from the significant intensities of $\nu_{as}(XeO_2)$ in the Raman and of $\nu_{sym}(XeO_2)$ in the IR spectra.

hand, all vibrations involving the two axial fluorine atoms show pronounced frequency decreases. This is not surprising because the formal negative charge, created by the addition of the extra F^- ligand, generally resides in this type of molecule on the highly electronegative fluorine ligands. Therefore, the axial Xe–F bonds become more ionic and weaker.

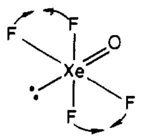
The addition of the F^- ion to XeO_2F_2 creates three extra fundamentals. These are the equatorial Xe–F′ stretching mode, ν_3, the F′XeO bending mode, ν_6, and the XeF′ rocking mode, ν_{12}. The assignment of the Xe–F′ stretching mode to the 513-cm^{-1} Raman band is clear-cut. The frequency of the F′XeO deformation mode involves a singly bonded fluorine and a doubly bonded oxygen and, therefore, should be intermediate between those of the XeO_2 deformations (380–330 cm^{-1}) and the XeF_2 deformations (170–220 cm^{-1}). It is, therefore, assigned to the Raman band at 303 cm^{-1}. The remaining XeF′ rocking mode (ν_{12}) is assigned to the last, yet unassigned Raman band at 242 cm^{-1}. The frequency of this mode appears plausible from a comparison with the closely related XeF_4 and $XeOF_4$ molecules. The XeF′ rocking mode in $XeO_2F_3^-$ involves a motion similar to that of the symmetric in-plane deformations in XeF_4 and $XeOF_4$, which have frequencies of 235 and 233 cm^{-1}, respectively. Similarly, the frequency of the axial XeF_2 scissoring mode, ν_8(A′), of $XeO_2F_3^-$ correlates well with that of the antisymmetric XeF_4 deformation mode, ν_9(E), of $XeOF_4$.



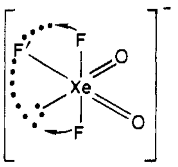
ν_{12}(A″), 242 cm^{-1}



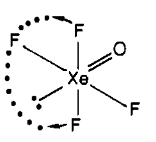
ν_3(B$_{2g}$), 235 cm^{-1}



ν_6(B$_2$), 233 cm^{-1}



ν_8(A′), 169 cm^{-1}



ν_9(E), 161 cm^{-1}

The assignments given in Table II for $XeOF_3^-$ are tentative since at present it is not known whether the oxygen atom is cis or trans with respect to the equatorial fluorine ligand. For $CsXeO_2F_3\cdot nXeF_2$ (trace C, Figure 1) no detailed analysis is made at this time, except for the obvious assignments of the bands at 861, 834, 538, 461, 340, and 302 cm^{-1} to $XeO_2F_3^-$ and of the 504-cm^{-1} band to XeF_2. Similarly, a detailed analysis of the $NO_2^+[XeO_2F_3\cdot nXeO_2F_2]^-$ spectrum (trace A, Figure 2) is not warranted. Some obvious assignments are as follows: 1401 cm^{-1}, $\nu_{sym}(NO_2^+)$; 900, 888, and 879 cm^{-1}, $\nu_{as}(XeO_2)$; 861, 850, and 839 cm^{-1}, $\nu_{sym}(XeO_2)$; 506 cm^{-1}, $\nu_{sym}(XeF_2)$.

Conclusion. The usefulness of nitrates as a reagent for the substitution of two fluorine ligands for a doubly bonded oxygen has been extended from bromine fluorides[1,31] to xenon fluorides.

In the previous work on BrF_5 it was suggested[1] that the fluorine–oxygen reaction involves an $M^+F_5BrONO_2^-$ intermediate, which for M = Li or Na decomposes to MF, and an unstable F_4BrONO_2, which then decomposes to FNO_2 and BrF_3O. For M = K, Rb, or Cs, which can form stable BrF_4O^- salts, the direct formation of $M^+BrF_4O^-$ by FNO_2 elimination from $M^+F_5BrONO_2^-$ was postulated. In this study, the formation of free XeO_2F_2 was observed for the $CsNO_3$ plus $XeOF_4$ reaction, in spite of the stability of $Cs^+XeO_2F_3^-$. It, therefore, appears that in these exchange reactions, regardless of the nature of the M^+ cation, MF and the free oxyfluoride are generated first and that the formation of the alkali-metal oxyfluoride salts is a secondary reaction of variable conversion.

Furthermore, the present study demonstrates that N_2O_5, which in the solid state has the ionic composition $NO_2^+NO_3^-$, can serve as a substitute for the alkali-metal nitrates. When the desired oxyfluoride has little or no volatility, the use of N_2O_5 is of particular advantage because volatile FNO_2 is the only byproduct, thereby facilitating the product separation.

Finally, the nitrate method provided an improved synthesis of XeO_2F_2 that allowed a better characterization of its properties and reaction chemistry, in particular with respect to its Lewis acid and base characteristics.

Acknowledgment. We are grateful to Dr. C. J. Schack and R. D. Wilson for their help, to Dr. G. J. Schrobilgen for providing us with copies of his original XeO_2F_2 Raman spectra, and to the Office of Naval Research for financial support.

Registry No. $CsNO_3$, 7789-18-6; XeF_6, 13693-09-9; FNO_2, 10022-50-1; $XeOF_4$, 13774-85-1; $CsXeF_7$, 19033-04-6; $CsXeOF_5$, 12191-01-4; $CsXeO_2F_3$, 65014-03-1; XeO_2F_2, 13875-06-4; N_2O_5, 10102-03-1; $NO_2^+[XeO_2F_3]^-$, 116025-38-8.

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