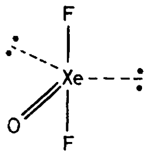
Preparation and Raman Spectra of $XeOF_2$, $XeOF_3^-$, and $XeO_2F_3^-$

By Ronald J. Gillespie* and Gary J. Schrobilgen
(*Department of Chemistry, McMaster University, Hamilton, Ontario* L8S 4M1, *Canada*)

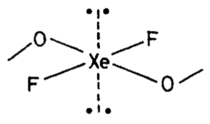
Summary The preparations of $XeOF_2$, $Cs^+XeOF_3^-$, and $Cs^+XeO_2F_3^-$ are described and Raman spectra are interpreted to provide information concerning the structures of these new oxyfluoro-species.

Evidence for $XeOF_2$ has been reported on two occasions[1,2] but in neither case was the compound isolated in a pure state nor was any evidence on its structure obtained. We have now isolated pure $XeOF_2$, obtained its Raman spectrum, and studied its fluoride-acceptor properties as well as its decomposition.

In order to effect the reaction of XeF_4 with water in HF solvent, it was first necessary to obtain the tetrafluoride in a finely divided form by dissolving crystalline XeF_4 in a minimum quantity of BrF_5 at 60 °C, quenching to −196 °C and distilling off the BrF_5 at −48 °C under reduced pressure. In a typical reaction, water (1·86 mmol) was syringed into an FEP reaction vessel containing the finely powdered XeF_4 (1·86 mmol) at −196 °C so that it froze above the XeF_4 without coming into contact with it. The tube and contents were then attached to a vacuum line and *ca.* 0·3 g of anhydrous HF was distilled in. The mixture was warmed to −63 °C at which temperature the water completely dissolved and finely divided XeF_4 remained insoluble. The reaction mixture was agitated frequently and the progress of the reaction was followed by observing the Raman spectrum of the solid at intervals after quenching the sample at −196 °C. As the reaction progressed, lines associated with XeF_4 diminished in intensity as those associated with $XeOF_2$ (also insoluble in HF at −63 °C) increased. After *ca.* 15 h, lines associated with solid XeF_2 [at 495 (100) cm^{-1}, ν ($\Sigma_g{}^+$), and 121 (15) cm^{-1}, an external mode], which precipitates from HF upon quenching, also began to appear and a slight O_2 pressure was observed in the reaction vessel. $XeOF_2$ presumably decomposes slowly at −63 °C to yield XeF_2 and oxygen. The reaction of XeF_4 with water was essentially complete after 24 h at −63 °C. XeF_2 and any traces of unchanged water were removed by addition of more HF followed by repeated extraction into the FEP sidearm of the reaction vessel at −78 °C. The sidearm was then heat-sealed under vacuum and the product pumped at −78 °C until the last traces of HF were removed. $XeOF_2$ is a light-yellow solid which decomposes explosively at *ca.* 0 °C. The Raman spectral assignments are given in the Table. According to the VSEPR theory, a monomeric $XeOF_2$ molecule would be expected to have structure (I). Alternatively, it could be an oxygen-bridged polymer such as (II) or the corresponding *cis*-structure.



(I)



(II)

On the basis of their isotopic dependence, the Xe–^{16}O and Xe–^{18}O stretching frequencies are readily assigned to the lines at 732 and 698 cm^{-1}, respectively. The Xe–^{16}O stretching frequencies of xenon(II) species containing a single Xe–^{16}O bond, such as $FXeOSO_2F$, occur in the range 400—474 cm^{-1}.[3] Thus, the Xe–O bond of $XeOF_2$ must have considerable double-bond character and the polymeric structure (II) may be ruled out. The Xe–^{16}O stretching frequency of $XeOF_2$ is somewhat lower than that of $XeOF_4$, XeO_2F_2, XeO_3, XeO_4, and XeO_3F^-, but this is consistent with the observation that Xe–F stretching frequencies generally decrease with decreasing oxidation state of xenon.[4]

The Xe–F symmetric stretch of $XeOF_2$, $\nu_3(a_1)$, is assigned to a strong band at 496 cm^{-1}. The Xe–F asymmetric stretch, $\nu_4(b_2)$, which is expected to be weak, was not observed.

A weak band observed at 275 (^{18}O) and 285 (^{16}O) cm^{-1} is assigned to $\nu_5(b_1)$, the $F_2Xe{=}O$ asymmetric bend (Xe–O wag). The $F_2Xe{=}O$ symmetric bend (pure in-plane XeF_2 bend), $\nu_3(a_1)$, and the XeF_2 out-of-plane bend, $\nu_6(b_2)$, which show no isotopic dependence are tentatively assigned to the bands at 186 and 197 cm^{-1}.

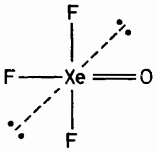
Table. Raman spectral data for $XeOF_2$, $XeOF_3^-$, and $XeO_2F_3^-$.

	Frequency/cm^{-1}			Assignment	
$F'XeF_2{}^{+a}$	$XeOF_2{}^{b-d}$	$F'XeOF_2{}^{-b}$	$F'XeO_2F_2{}^{-e}$	C_{2v}	Description
			861(16), 857(8)	b_2	Xe=^{16}O asym. str.
	732(8)	768(7)	834(100)	a_1	Xe=^{16}O sym. str.
	698(13)	727(32)		a_1	Xe=^{18}O sym. str.
643(100)		503(61)	541(2)	a_1	Xe–F′ str.
609(9)	Not observed	487(10)	514(18)	b_1	XeF_2 asym. str.
573(88)	496(100)[f]	464(100)	459(25)	a_1	XeF_2 sym. str.
		381(5)		b_2	F′–Xe=^{16}O o.p. δ
		370(6)		b_2	F–Xe=^{18}O o.p. δ
305(2)				b_1	$F_2Xe{-}F'$ asym. δ
		292(1)		a_1	sym. $F'F_2XeO$ i.p. δ
	285(4)	270(5)		b_1	Xe=^{16}O wag
	275(4)	260(8)		b_1	Xe=^{18}O wag
205(2)	186(8)			a_1	XeF_2 i.p. δ
	197(1)	219(1)		b_2	XeF_2 o.p. δ
		167(6)		b_1	Xe–F wag or XeF_2 i.p. δ

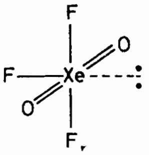
[a] R. J. Gillespie, B. Landa, and G. J. Schrobilgen, *Inorg. Chem.*, 1976, **15**, 1256. [b] $^{18}O:^{16}O$ = 1·62 : 1. [c] Low frequency lines, which show no ^{18}O—^{16}O dependence, have also been observed at 164(6), 128(5), and 64(4) cm^{-1} and are presumed to be external modes. [d] Ref. 2. [e] Only the ^{16}O-compound has been prepared. No assignments have been made for the low-frequency bending modes of this anion pending ^{18}O-data. The unassigned bands are at 436(12), 422(10), 380(20), 369(31), 339(13), 303(12), 300(17), 176(8), 167(14), and 137(40) cm^{-1}. [f] The XeF_2 symmetric stretch of $XeOF_2$ is very close in frequency to the symmetric stretch of XeF_2 [495(100) cm^{-1}], a possible contaminant in $XeOF_2$ preparations arising from decomposition of $XeOF_2$. The frequency and intensity of the XeF_2 symmetric stretch reported for $XeOF_2$ is for XeF_2-free material, as confirmed by the absence of the moderately strong band of XeF_2 at 121 cm^{-1} even under high gain conditions.

When CsF was added at −196 °C to solid $XeOF_2$ under a layer of HF, it dissolved upon warming to −78 °C Removal of the HF by pumping at −78 °C only resulted in a mixture of $Cs^+(HF)_xF^-$ and $XeOF_2$. However, upon slow warming of this mixture to 0 °C while pumping, $XeOF_2$ reacted rapidly with the $Cs^+(HF)_xF^-$ yielding $Cs^+XeOF_3^-$. The salt, $Cs^+XeOF_3^-$, is bright yellow and stable at room temperature for several hours. A small amount of a second oxygen-containing species was also formed. If the reaction mixture was allowed to warm slowly to room temperature followed by removal of HF under reduced pressure, no $XeOF_3^-$ was obtained, but the second oxygen-containing species was obtained in 100% yield. This second species was found to be $Cs^+XeO_2F_3^-$ which is formed by the disproportionation of $XeOF_2$. The tentative Raman spectral assignments for $XeOF_3^-$ (III) and $XeO_2F_3^-$ (IV) are given in the Table. On slow warming from −63 to 0 °C over a period of 20 h, pure $XeOF_2$ decomposes to XeF_2 and XeO_2F_2, which were identified by their characteristic Raman spectra.[5]

The Raman spectrum of $XeOF_3^-$ is assigned on the basis of C_{2v} symmetry [structure (III)]. The three Xe–F stretching modes expected for $XeOF_3^-$ are readily assigned by comparison with the Raman spectrum of the T-shaped XeF_3^+ cation. The F–Xe=O asymmetric bend is readily assigned by comparison with the corresponding mode in $XeOF_2$ and by the sensitivity of this mode to isotopic substitution. Assignments of the remaining modes are only tentative.



(III)



(IV)

Attempts to prepare the $XeOF^+$ cation have so far failed. Addition of AsF_5 to $XeOF_2$ under a layer of HF resulted in the rapid formation of O_2 and $XeF^+AsF_6^-$ which was identified by its Raman spectrum.[3] In the absence of HF, $XeOF_2$ and AsF_5 explode upon contact at −78 °C.

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[1] J. S. Ogden and J. J. Turner, *Chem. Comm.*, 1966, 693.

[2] E. Jacob and R. Opferkuch, *Angew. Chem. Internat. Edn.*, 1976, **15**, 158: these workers haverecently reported the synthesis of $XeOF_2$ by co-condensation of H_2O and XeF_4 vapours. Although no attempt was made to assign the vibrational spectra of their product, these authors did report all the Raman lines we have observed except the bands at 197(1), 186(8), 165(5), 128(5), and 64(4) cm^{-1} which we have consistently observed in all our preparations (Table). Moreover, a comparison of their Raman spectral data with ours indicates that their product was not pure. It appears to contain at least one other oxygen-containing species as additional lines were reported at 751(19) and 714(30) ($Xe{=}^{16}O$ and $Xe{=}^{18}O$ stretches, respectively) and 469·5(100) (no isotopic dependence and presumed to be an Xe–F stretching mode) and ^{18}O—^{16}O dependent pairs of lines at 229·5(13) and 291(14), 171·5(24) and 161·5(25), and 111·5(35) and 104(35), and ^{18}O—^{16}O independent lines at 154 and 136(16) cm^{-1}.

[3] B. Landa and R. J. Gillespie, *Inorg. Chem.*, 1973, **12**, 1383.

[4] R. J. Gillespie, B. Landa, and G. J. Schrobilgen, *J. Inorg. Nuclear Chem.*, Supplement 1976, 179.

[5] H. H. Claassen, E. L. Gasner, H. Kim, and J. L. Huston, *J. Chem. Phys.*, 1968, **49**, 253.