The XeF_2–MF_5 (M = Sb, Ta, or Nb) Systems: Vibrational Spectra of Solid Xenon Difluoride Adducts [1]

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The i.r. and Raman spectra of the compounds $2XeF_2\cdot MF_5$ (M = Sb or Ta), $XeF_2\cdot MF_5$, and $XeF_2\cdot 2MF_5$ (M = Sb, Ta, or Nb) have been measured, and it has been shown that, although the spectra are best interpreted in terms of ionic formulations involving $[XeF]^+$ and $[Xe_2F_3]^+$, there is increasing covalent character in the series, $XeF_2\cdot SbF_5 < XeF_2\cdot TaF_5 < XeF_2\cdot NbF_5$, $XeF_2\cdot 2SbF_5 < XeF_2\cdot 2TaF_5 < XeF_2\cdot 2NbF_5$ and $2XeF_2\cdot SbF_5 < 2XeF_2\cdot TaF_5$.

Weight-loss *versus* time-of-pumping studies on the products of reaction of large excesses of XeF_2 with the pentafluorides have shown that, in addition to the simple 2 : 1, 1 : 1, and 1 : 2 compounds, species with compositions $[2XeF_2\cdot Xe_2F_3]^+[SbF_6]^-$, $[XeF_2\cdot XeF]^+[TaF_6]^-$, and $[XeF_2\cdot XeF]^+[NbF_6]^-$ are also formed.

ADDUCTS of xenon difluoride with pentafluorides were amongst the first noble-gas compounds to be discovered.[2] Most preparative methods have yielded adducts having $XeF_2 : MF_5$ mole ratios of 2 : 1, 1 : 1, and 1 : 2.[2-5] Differential thermal analytical (d.t.a.) investigations have produced, in addition, evidence for other, more complex, stoicheiometries.[6-8] Interestingly, the first d.t.a. study [6] produced no evidence for $2XeF_2\cdot SbF_5$ and the more recent investigations on the tantalum and niobium systems [8] failed to detect $2XeF_2\cdot TaF_5$ or $XeF_2\cdot NbF_5$.

Recently d.t.a. investigations have shown that chemical equilibria in the systems are established rather slowly.[9] We have found that kinetic factors are very important in the formation of xenon difluoride–pentafluoride adducts, especially in those where the xenon difluoride content is high. The results of dynamic d.t.a. methods must, therefore, be treated with the utmost caution.

The present work is in two parts. In the first 2 : 1, 1 : 1, and 1 : 2 adducts of xenon difluoride with the pentafluorides of antimony, tantalum, and niobium have been prepared by the direct combination of stoicheiometric amounts of the components and their vibrational spectra have been investigated in detail. The work includes the first preparation of $2XeF_2\cdot TaF_5$ and the first study of the vibrational spectra of this, $XeF_2\cdot TaF_5$, and $XeF_2\cdot NbF_5$. Clear evidence of a gradation of ionic character in the series of adducts has been obtained. In the second part detailed examination of Raman data on the products formed in the reaction of excess of xenon difluoride with each pentafluoride and the subsequent stepwise decomposition of the products *in vacuo* has enabled us to characterize new adducts which may be conveniently formulated as $[2XeF_2\cdot Xe_2F_3]^+[SbF_6]^-$, $[XeF_2\cdot XeF]^+[TaF_6]^-$, and $[XeF_2\cdot XeF]^+[NbF_6]^-$. All efforts to prepare a niobium fluoride adduct richer in xenon difluoride than $XeF_2\cdot NbF_5$ have failed.

RESULTS AND DISCUSSION

Products of the Stoicheiometric Reactions.—Gravimetric determination, X-ray powder photography, and vibrational spectroscopy confirmed the nature of the adducts produced. $2XeF_2\cdot TaF_5$ Has not been reported before and no vibrational spectroscopic data are available for this, $XeF_2\cdot TaF_5$, or $XeF_2\cdot NbF_5$.

$2XeF_2\cdot SbF_5$ *and* $2XeF_2\cdot TaF_5$. There is similarity between the X-ray diffraction patterns of these compounds but they are not isostructural. The solid-state i.r. and Raman spectra (Table) confirm the overall structural relationship.

The main features of our recorded Raman spectrum for $[Xe_2F_3]^+[SbF_6]^-$ agree well with those of other authors,[10,11] except that one peak in the strong doublet associated with the Xe–F stretching mode appears at 595 cm^{-1} rather than at 591 cm^{-1}. This discrepancy might be explained by the presence of 25—30% of $[2XeF_2\cdot Xe_2F_3]^+[SbF_6]^-$ [which has peaks in the Raman spectrum at 590·5 (100) and 576 (8·3) cm^{-1}] in their samples. However, they do not report the related shift at 518 cm^{-1} for $[2XeF_2\cdot Xe_2F_3]^+[SbF_6]^-$ which should have a relative intensity of *ca.* 5 in their spectra. We can find no evidence in the i.r. spectrum for the strong band at 617 cm^{-1} reported by Russian workers.[12]

The Raman and i.r. spectra of $[Xe_2F_3]^+[TaF_6]^-$ correlate well with those of $[Xe_2F_3]^+[SbF_6]^-$. In the Raman, further splitting of the high-frequency component of the Xe–F stretching mode occurs, probably

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as a result of the presence of crystallographically non-equivalent sites or weak intermolecular coupling. There is little doubt that the peak at 571 cm^{-1} is attributable to an Xe–F stretch. Although it is possible that deviation from the purely ionic formulation may lead to a breakdown of the mutual exclusion rule so that the ν_3 vibration of $[TaF_6]^-$ might appear in the Raman, the peak observed is far too strong. The peak at 428 cm^{-1} is attributed to the stretching mode of the weak Xe···F bonds in $[Xe_2F_3]^+$ In $2XeF_2\cdot SbF_5$ an equivalent but very weak band has been reported, as expected, at lower frequency.[10]

Infrared and Raman spectra of solid xenon difluoride–pentafluoride adducts (frequencies in cm^{-1} with intensities in parenthesis)

$2XeF_2\cdot SbF_5$ Raman Freq.	Infrared Freq.	$2XeF_2\cdot TaF_5$ Raman Freq.	Infrared Freq.	Assignment	$XeF_2\cdot SbF_5$ Raman Freq.	Infrared Freq.	$XeF_2\cdot TaF_5$ Raman Freq.	Infrared Freq.	$XeF_2\cdot NbF_5$ Raman Freq.	Infrared Freq.	Assignment
159 (24)		155 (13)					122 (9)		123 (9)		lattice modes
172 (10)		164 (25)		$\delta(F-Xe\cdots F)$	140 (22)		179 (4)		151 (12)		$\delta(F-Xe\cdots F)$
183 (5)		182 (19)							193 (6)		
282 (12)		271 (8)		$\nu_5(MF_6^-)$	273 (10)						$\nu_3(F^-{-}SbF_6)$
294 (3)					290 (13)		288 (10)		286 (9)		$\nu_9(F^-{-}SbF_6)$
		428br(2)		$\nu(Xe\cdots F)$			318(45)				$\nu(Xe\cdots F)$
	438sh		438sh				352 (2)				$\nu_{11}(F^-{-}TaF_5)$
	460m		454m	$\nu(M\cdots F)$			396 (2)				$\nu_3(F^-{-}TaF_5)$
	490br				473 (14)	450sh	461 (10)	468br, m		456sh	
			577vs	$\nu(TaF_6^-)$		476br	468 (18)			470w	$\nu_4(F^-{-}MF_5)$
583 (100)	570m	571 (70)					472 (11)			490m	
595 (60)	595m	585 (73)	586w				580 (10)	578 vs	587 (14)	582m, s	$\nu_2(F^-{-}MF_5)$
		592 (100)	592w	$\nu(Xe-F)$	592 (12)						$\nu_5(F^-{-}SbF_5)$
		598 (85)	600w		610sh (98)	608m	600 (83)	603s	596 (100)	602s	
649 (24)				$\nu_1(SbF_6^-)$	615 (100)		607 (100)		691 (95)		$\nu(Xe-F)$
			652br, w		617 (100)		614 (53)				
	660vs						640 (5)	619s		641s	$\nu_8(F^-{-}MF_6)$
	690sh			$\nu_3(SbF_6^-)$	645 (20)	652vs		652br, m?	667 (8)		$\nu_2(F^-{-}SbF_5)$
		693 (38)		$\nu_1(TaF_6^-)$	665 (55)						$\nu_1(F^-{-}SbF_5)$
			712w				675 (4)		667 (8)		$\nu_5(F^-\ MF_5)$
					681 (9)	690s					$\nu_8(F^-{-}SbF_5)$
							714	713m	711 (58)	710m	$\nu_1(F^-{-}MF_5)$
						707w?					

$XeF_2\cdot 2SbF_5$ Raman Freq.	Infrared Freq.	$XeF_2\cdot 2TaF_5$ Raman Freq.	Infrared Freq.	$XeF_2\cdot 2NbF_5$ Raman Freq.	Infrared Freq.	Assignment
111vvw						lattice modes
131 (15)		115 (5)		152 (3)		$\delta(F-Xe\cdots F)$
		147 (10)				
229 (10)		200 (4)		216 (8)		
		218 (6)		253 (16)		
		240sh (10)		271 (5)		$\nu(M_2F_{11}^-)$
		253 (21)				
		270 (7)				
271 (8)		294 (6)		297 (5)		
				322 (3)		$\nu(Xe\cdots F)$
				339 (3)		
296 (7)						$\nu(Sb_2F_{11}^-)$
				353? (1)		
				410(3)		$\nu(Nb\cdots F)$
		434 (5)				$\nu(Ta\cdots F)$
		460 (3)				
484 (5)	455sh					
	470m					$\nu(Sb\cdots F)$
	480sh					
528 (15)	526m		491br, w	504 (3)	500br, m. w	
			564sh	545 (3)		$\nu(M_2F_{11}^-)$
			576s	583sh (11)		
			581sh			
611sh (18)	611w	605 (75)	608br, s	600 (100)	600m	
619 (100)	626w	610 (100)				$\nu(Xe-F)$
		614 (80)				
652 (44)	650vs	628 (13)	667m	649 (4)	638s	
661 (7)	690m	646 (5)	669m, w	665 (12)	662sh	
681 (19)	724sh	654 (4)	724sh	682 (6)	671sh	
691 (53)		667 (7)	735sh	716 (6)	701m, w	$\nu(M_2F_{11}^-)$
704 (3)		680 (8)	752sh	725 (18)	730m, w	
		698 (6)		740 (66)	752sh	
		726 (75)		752 (3)	760sh	
		738 (40)		767 (8)	780sh	

Our Raman assignments were made on the basis of O_h symmetry for isolated octahedral $[MF_6]^-$ anions. This is reasonable in view of the appearance of the Raman-active modes, ν_1 and ν_5, and the absence of the Raman-inactive modes, ν_3 and ν_4, in each case. The splitting of ν_5 in the case of $[Xe_2F_3]^+[SbF_6]^-$ is either a result of slight cation–anion interaction or factor-group splitting. The i.r. spectra of both adducts are dominated by the strong i.r.-active mode, ν_3, which confirms the Raman assignments.

$XeF_2\cdot SbF_5$, $XeF_2\cdot TaF_5$, *and* $XeF_2\cdot NbF_5$. *X*-Ray powder diffraction patterns show that $XeF_2\cdot TaF_5$ and $XeF_2\cdot NbF_5$ are isostructural but $XeF_2\cdot SbF_5$ differs. The solid-state i.r. and Raman spectra, however, indicate an overall structural similarity and are compared in the Table. Our spectrum for $XeF_2\cdot SbF_5$ is in close agreement with that of Gillespie and Landa.[10]

The spectrum of $XeF_2\cdot SbF_5$ has been interpreted on the basis of O_h symmetry for the anion.[10] Definitive assignment of the anion modes in our spectra is difficult since, in the cases of the antimony and tantalum adducts, more than six anion modes are observed. An alternative to assuming that the compounds are ionic species $[XeF]^+[MF_6]^-$ (in which the anion has O_h

symmetry) is to formulate them as fluorine-bridged structures Xe–F$^+ \cdots$ F$^-$–MF$_5$ in which the anion can be regarded as distorted from O_h to C_{4v} symmetry.[13] For C_{4v} symmetry eleven normal modes of vibration are expected which are related to the six vibrational modes of the [MF$_6$]$^-$ anion of O_h symmetry (Figure 1). In particular the frequencies of the normal modes for the C_{4v} molecule, $\nu_1(a_1)$, $\nu_2(a_1)$, $\nu_8(e)$, $\nu_3(a_1)$, and $\nu_7(b_2)$, should correspond closely to those of the respective normal modes of the O_h molecule, $\nu_1(a_g)$, $\nu_2(e_g)$, $\nu_3(t_{1u})$, $\nu_4(t_{1u})$, and $\nu_5(t_{2g})$.

Recent force-field calculations for the hexafluoro-anions, [MF$_6$]$^-$ (M = Sb, Ta, and Nb),[14] and the correlation diagram (Figure 1) allow the ready assignment of $\nu_1(a_1)$ and $\nu_9(e)$ for each adduct. The bands in all the spectra in the 450—490 cm^{-1} region cannot reasonably be assigned to vibrations of octahedral [MF$_6$]$^-$ anions and must be assigned to additional ν(M $\cdots$ F)'s if O_h symmetry is invoked. With an assignment based on C_{4v} symmetry these bands are readily assigned to $\nu_4(a_1)$. The observation of this band in each of the spectra and of bands attributable to ν(Xe $\cdots$ F) in XeF$_2$·SbF$_5$[10] and XeF$_2$·TaF$_5$ is evidence for rather strong cation–anion interaction in the adducts. Thus, assignment on the basis of C_{4v} symmetry for the anion is easier than for O_h, which requires a breakdown of the mutual exclusion rule with respect to ν_3 in XeF$_2$·SbF$_5$ and ν_1 in XeF$_2$·TaF$_5$ and XeF$_2$·NbF$_5$ and factor-group splitting of ν_1 in XeF$_2$·SbF$_5$.

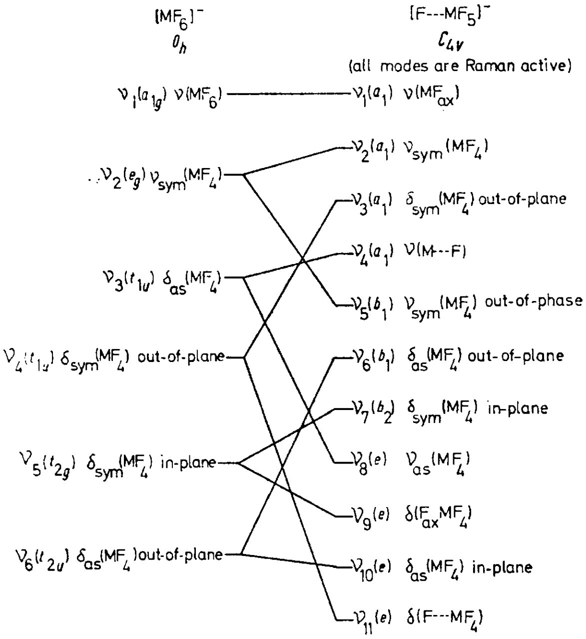
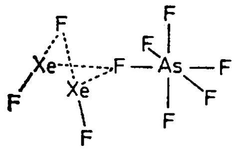


FIGURE 1 Vibrational modes and their correlations for O_h and C_{4v} molecules

XeF$_2$·2SbF$_5$, XeF$_2$·2TaF$_5$, *and* XeF$_2$·2NbF$_5$. *X*-Ray powder photography shows that the tantalum and niobium adducts are isostructural but that the antimony analogue has a different, but probably related, structure. The Raman for XeF$_2$·2SbF$_5$ and our i.r. data for the adduct and for Cs$^+$[Sb$_2$F$_{11}$]$^-$ further support earlier Raman assignments[10] (Table).

Our Raman spectra for XeF$_2$·2TaF$_5$ and XeF$_2$·2NbF$_5$ (see Table) differ significantly from those reported earlier.[10] We were able to resolve the single peak for ν(Xe–F) at 610 cm^{-1} in XeF$_2$·2TaF$_5$[10] into a triplet centred at 610 cm^{-1} and in XeF$_2$·2NbF$_5$ the strongest shift was at 600 cm^{-1} rather than at 596 cm^{-1}.[10] This is confirmed by the appearance of an absorption at 600 cm^{-1} in the i.r. region. The lower value reported by Gillespie and Landa[10] probably results from contamination with XeF$_2$·NbF$_5$ which has strong peaks at 596(100) and 601(95) cm^{-1}. The overall stoicheiometry may, nevertheless, have been preserved since their peak at 715(11) cm^{-1}[10] is twice as strong as ours and may indicate the presence of unchanged NbF$_5$. However, a much stronger shift at 766 cm^{-1} due to unreacted NbF$_5$ and a weaker one at 752 cm^{-1}[15] should also have been observed.

General Trends.—*X*-Ray crystallographic studies[16-18] and Raman spectroscopic examination[5,10] of representatives of the 2XeF$_2$·MF$_5$, XeF$_2$·MF$_5$, and XeF$_2$·2MF$_5$ classes of adduct indicate that they may be formulated [Xe$_2$F$_3$]$^+$[MF$_6$]$^-$, [XeF]$^+$[MF$_6$]$^-$, and [XeF]$^+$-[M$_2$F$_{11}$]$^-$. No Xe $\cdots$ F contact distance between the xenon atoms in [Xe$_2$F$_3$]$^+$ and the nearest fluorine of [AsF$_6$]$^-$ in [Xe$_2$F$_3$]$^+$[AsF$_6$]$^-$,[16] which presumably has structure (I), has been quoted, but the short fluorine-bridge bonds in XeF·Sb$_2$F$_{11}$ (2·35 Å)[17] and XeF·RuF$_6$ (2·18 Å)[18] testify against perfect salt-type formulations.



(I)

The fact that the spectra of the XeF$_2$·MF$_5$ adducts can be readily assigned on the basis of C_{4v} symmetry for the hexafluoro-anion is strong evidence for a significant lowering of the symmetry of the octahedral anion by fluorine bridging to the [XeF]$^+$ cation. The splitting of ν(Xe–F) in many of the adducts is attributed to factor-group splitting since ν(Xe–F) is totally symmetric. However, the mean value of the stretching frequencies associated with ν(Xe–F$^+$) for the XeF$_2$·2MF$_5$ and XeF$_2$·MF$_5$ series of adducts decrease SbF$_5$ >

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[13] G. J. Schrobilgen, Ph.D. Thesis, McMaster University, Canada 1973; B. Landa, Ph.D. Thesis, McMaster University, Canada, 1974; R. J. Gillespie and G. J. Schrobilgen, *Inorg. Chem.*, in the press; R. J. Gillespie, B. Landa, and G. J. Schrobilgen, *Inorg. Chem.*, in the press.

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[15] I. R. Beattie, K. M. S. Livingston, G. A. Ozin, and R. J. Reynolds, *J. Chem. Soc.* (*A*), 1969, 958.

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$TaF_5 > NbF_5$ (see Figure 2) which indicates that the Xe–F bond length in $[XeF]^+$ is progressively lengthened. At the same time, comparison of the weak peaks assigned to ν(Xe · · · F) shows a progressive increase in the value of the mean frequency and this can be reasonably attributed to the increasing strength of the bridging bond. The observation of the bending modes of the fluorine bridge in the two series is also in accord with these results.

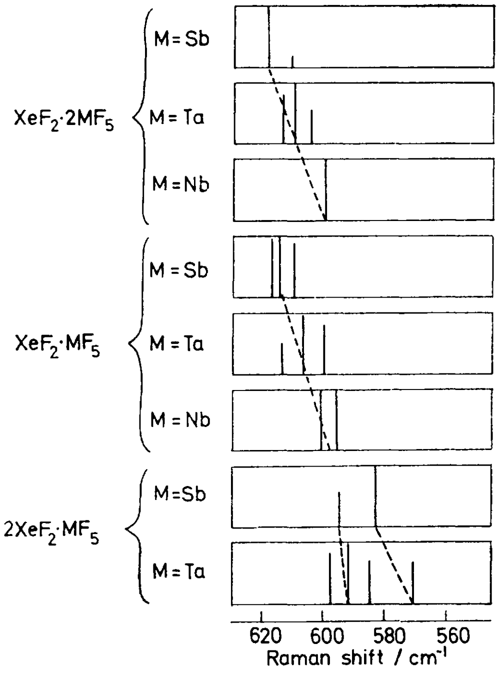

FIGURE 2 Stretching frequencies associated with ν(Xe–F)

The anionic parts of the molecules also reflect the covalent character of the species but establishment of clear trends to parallel those associated with $\nu(XeF^+)$ is more difficult. Comparison of the frequencies associated with the anionic parts of the $XeF_2{\cdot}2MF_5$ series, however, is interesting. Although no definitive assignments of absorption bands associated with $[M_2F_{11}]^-$ species have been made, Raman spectra for solid SbF_5,[19] TaF_5, and NbF_5 [15] have been reported and it appears that the shifts associated with the 'anionic' components in the series $XeF_2{\cdot}2SbF_5 \longrightarrow XeF_2{\cdot}2TaF_5 \longrightarrow XeF_2{\cdot}2NbF_5$ become progressively more pentafluoride-like as evidenced by the increasing number of bands in the high-frequency region of their spectra which can be correlated with the spectra of the pentafluorides.[15,19] MoF_5 [20] And NbF_5 [15] are the only solid pentafluorides with fully assigned spectra. NbF_5 Has bands in the high-frequency regions assigned as follows, $\nu(NbF)_{eq} = 766$vvs; $\nu(NbF)_{eq}$ or $\nu(NbF)_{ax} = 752$w; $\nu(NbF)_{eq} = 716$vs; $\nu(NbF)_{ax} = 668$w and $\nu(NbF)_{ax} = 656$.[15] $XeF_2{\cdot}2SbF_5$ Has five bands in this region, $XeF_2{\cdot}2TaF_5$ has eight, and $XeF_2{\cdot}2NbF_5$ also has eight of which four correlate closely with the NbF_5 spectrum.

In $2XeF_2{\cdot}TaF_5$ the frequencies of ν(Xe–F) are higher (see Figure 2) and ν(Xe · · · F) lower than in the analogous antimony adduct. Although, in this case, the Xe · · · F stretching frequency is not only associated with a fluorine bridge to the $[MF_6]^-$ ion but with bonds in the $[Xe_2F_3]^+$ ion itself, the changes lead to the conclusion that the cation has more electron density withdrawn in the tantalum case. This presumably occurs because of its closer involvement with the anion through some secondary bridging to the xenon atoms in $[XeF_3]^+$ by the fluorines of the $[TaF_6]^-$ ion.

Reactions of an Excess of Xenon Difluoride with the Pentafluorides SbF_5, TaF_5, *and* NbF_5 *and the Products of Decomposition*.—Monitoring of the reaction mixtures has shown that the same series of adducts can be obtained by the stepwise decomposition of the highest xenon difluoride-containing species. The products are less pure than those produced by stoicheiometric combination. Species with compositions $[2XeF_2{\cdot}Xe_2F_3]^+$-$[SbF_6]^-$, $[XeF_2{\cdot}XeF]^+[TaF_6]^-$, and $[XeF_2{\cdot}XeF]^+[NbF_6]^-$ are also formed and equilibria between these, the simpler adducts and the component molecules occur.

The $XeF_2{\cdot}SbF_5$ *System*.—In a typical reaction 11·75 mmol of XeF_2 with 2·00 mmol of SbF_5 was taken to completion by holding the mixture at 115 °C for 100 min when it melted to a clear, deep yellow, solution. The composition of the eutectic melt at this point was close to $5XeF_2{\cdot}SbF_5$ (*cf*. ref. 7). The mixture was quenched and pumped at room temperature for 250 min when the weight-loss *versus* time-of-pumping curve levelled off at the composition $2XeF_2{\cdot}SbF_5$.

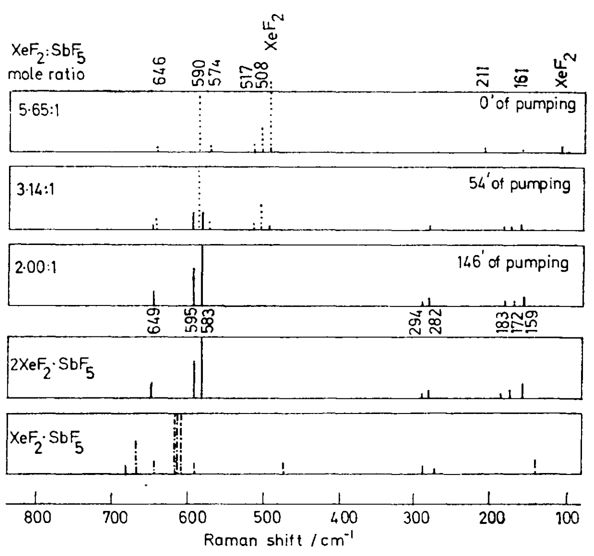

FIGURE 3 Raman spectra of the solids during the vacuum decomposition of the mixture XeF_2–SbF_5 at room temperature

The Raman spectrum of the quenched melt before pumping is entirely different from the spectra of $2XeF_2{\cdot}SbF_5$ and $XeF_2{\cdot}SbF_5$. The spectrum, however, is related to that of $2XeF_2{\cdot}SbF_5$ (see Figure 3). The

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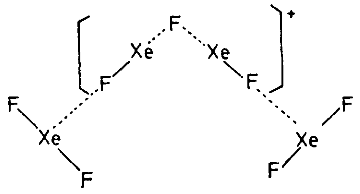
[19] P. A. W. Dean and R. J. Gillespie, *Canad. J. Chem.*, 1971, **49**, 1736.

[20] J. B. Bates, *Spectrochim. Acta*, 1971, **27A**, 1255.

peak associated with ν_1 of $[SbF_6]^-$ is shifted to slightly lower frequency and those associated with $\delta(F{-}Xe\cdots F)$ are also displaced. The most significant differences are that the doublet characteristic for $[Xe_2F_3]^+$ is changed in relative intensity and shifted towards lower frequencies and, in addition, there are new bands above $\nu(Xe{-}F)$ in free XeF_2.[21] This can be interpreted in terms of a loosening of the xenon–fluorine bonds in the $[Xe_2F_3]^+$ ion due to partial withdrawal of electrons by the weak association of XeF_2 molecules. Since the Raman spectrum at the composition $3{\cdot}1XeF_2{\cdot}SbF_5$ (see Figure 3) indicates that the new complex is already giving way to $[Xe_2F_3]^+[SbF_6]^-$ it seems reasonable to suppose that two XeF_2 molecules are involved in a weak association with the $[Xe_2F_3]^+$ unit (II).



(II)

In addition to the peaks already discussed the original spectrum indicates the presence of free xenon difluoride.[21]

The weakly associated XeF_2 can be easily removed at room temperature, without the appearance of inflexions in the pumping curve, until the composition $2XeF_2{\cdot}SbF_5$ is reached. The Raman spectrum then coincides with that of the sample produced by reaction of the stoicheiometric quantities of XeF_2 and SbF_5 (see Figure 3). Hence the first part of the weight-loss *versus* time-of-pumping curve can be explained by the following equation:

$$nXeF_2 + SbF_5\ (n > 4) \longrightarrow [2XeF_2{\cdot}Xe_2F_3]^+[SbF_6]^- + (n-4)XeF_2 \longrightarrow [Xe_2F_3]^+[SbF_6]^- + (n-2)XeF_2$$

$[Xe_2F_3]^+[SbF_6]^-$ Is stable at room temperature even in a dynamic vacuum. At 100 °C it loses xenon difluoride to give $[XeF]^+[SbF_6]^-$ after 18 h of pumping. This cannot be decomposed further in a dynamic vacuum but volatilizes unchanged at 150 °C.

Because of the practical difficulties in examining the higher temperature decomposition of $[Xe_2F_3]^+[SbF_6]^-$ we have not monitored the decomposition for other loosely bound species. However, examination of the spectra of the melt[22] shows that $[XeF_2{\cdot}XeF]^+[SbF_6]^-$ might be formed.

The XeF_2–TaF_5 *System.*—Mixtures of xenon difluoride and tantalum pentafluoride in mole ratios $XeF_2 : TaF_5 = 2{\cdot}14 : 1$ form clear yellow melts at *ca.* 70 °C. The spectrum of the quenched melt is a combination of the spectra of $[Xe_2F_3]^+[TaF_6]^-$ and $[XeF]^+[TaF_6]^-$ with additional peaks at 507 and 516 cm^{-1} due to weakly associated XeF_2. In view of the overall stoicheiometry it seems most probable that the XeF_2 is involved with $[XeF]^+$ rather than $[Xe_2F_3]^+$. The Raman spectra of quenched melts having the composition $XeF_2 : TaF_5$, 2 : 1, which have been prepared *in vacuo* also contain the same three adducts. If, however, the melt is prepared and quenched under one or more atmospheres pressure of xenon or nitrogen, which prevents significant escape of free xenon difluoride from the hot zone, the formation of $[XeF_2{\cdot}XeF]^+[TaF_6]^-$ and $[XeF]^+[TaF_6]^-$ is minimized and $[Xe_2F_3]^+[TaF_6]^-$ is essentially the only product. It can, therefore, be reasonably postulated that an equilibrium, $[Xe_2F_3]^+[TaF_6]^- \rightleftharpoons [XeF_2{\cdot}XeF]^+[TaF_6]^- \rightleftharpoons [XeF]^+[TaF_6]^- + XeF_2$ occurs in melts[22] containing $XeF_2 : TaF_5$ in mole ratios greater than 2 : 1.

$[Xe_2F_3]^+[TaF_6]^-$ Has an appreciable decomposition pressure at room temperature in a dynamic vacuum as the above equilibrium suggests. It decomposes readily in a dynamic vacuum at room temperature to yield $[XeF]^+[TaF_6]^-$ and xenon difluoride. Raman spectra run during the decomposition of $[Xe_2F_3]^+[TaF_6]^-$ to $[XeF]^+[TaF_6]^-$ show that the intermediate adduct is present only in mixtures with the two limiting compounds.

The XeF_2–NbF_5 *System.*—Mixtures of xenon difluoride and niobium pentafluoride in mole ratios $XeF_2 : NbF_5 = >2{\cdot}00 : 1$ melt at *ca.* 50 °C but an excess of xenon difluoride can only be brought into solution at about 110 °C. An eutectic is formed at composition $3{\cdot}8XeF_2{\cdot}NbF_5$. Raman spectra of these quenched melts provide no evidence of $[Xe_2F_3]^+$. Only peaks associated with free and loosely bound XeF_2 together with the expected spectrum for $[XeF]^+[NbF_6]^-$ are observed and this in interpreted in terms of the presence of the adduct $[XeF_2{\cdot}XeF]^+[NbF_6]^-$ (see Figure 4). The adduct appears to be stable only in the presence of an excess of xenon difluoride. It decomposes readily in a dynamic vacuum at room temperature and no points of inflexion are observed in the weight-loss *versus* time-of-pumping curve until the 1 : 1 adduct composition is reached.

General Discussion.—These results indicate the formation of $[2XeF_2{\cdot}Xe_2F_3]^+[SbF_6]^-$, $[XeF_2{\cdot}XeF]^+[TaF_6]^-$, and $[XeF_2{\cdot}XeF]^+[NbF_6]^-$ in the systems studied.

We have written the formulae of the new adducts as $[2XeF_2{\cdot}Xe_2F_3]^+[SbF_6]^-$, $[XeF_2{\cdot}XeF]^+[TaF_6]^-$, and $[XeF_2{\cdot}XeF]^+[NbF_6]^-$ since this conveniently differentiates the loosely bound xenon difluoride from that more closely associated with the pentafluoride, but this is merely a formalism.

The identification of these new adducts in the xenon difluoride–pentafluoride systems means that attempts to prepare the simple 2 : 1, 1 : 1, and 1 : 2 adducts by the combination of the exact mole ratios of the constituents, if carried out under conditions which allow one of them to be partially removed from the heating or

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[21] P. Tsao, C. C. Cobb, and H. H. Claassen, *J. Chem. Phys.*, 1971, **54**, 5247.

[22] B. Frlec and J. H. Holloway, *J. Inorg. Nuclear Chem.*, in the press.

quenching zone, will result in equilibria being shifted and adduct mixtures being formed. D.t.a. studies, in which the substances are held at high temperatures for several hours will, in some cases, give rise to mixtures which will include the species we have identified. Indeed, Raman spectroscopic examination of the molten adducts [22] have shown that equilibria involving the simple adducts and species containing loosely bound XeF_2 do occur. The existence of these equilibria can also plausibly be used to explain the unusually large divergence of reported values of the melting points for the 2 : 1, 1 : 1, and 1 : 2 adducts.[4,7,22]

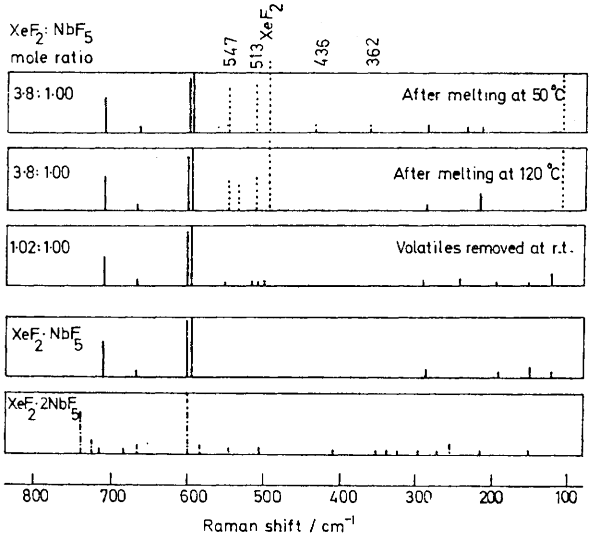

FIGURE 4 Raman spectra of the solids in the XeF_2–NbF_5 system

EXPERIMENTAL

Starting Materials.—XeF_2 Was prepared by pressure synthesis in a nickel vessel at 300 °C with the starting ratio Xe : F_2 equal to 2 : 1. It was purified by repeated trap-to-trap sublimation in a dynamic vacuum and checked for purity by i.r. spectroscopic examination of the vapour and Raman spectroscopy on the solid.

SbF_5, NbF_5, and TaF_5 Were all prepared from the elements by pressure synthesis in a nickel vessel and purified subsequently by a repeated trap-to-trap sublimation in dynamic vacuum.

X-*Ray Diffraction Measurements.*—*X*-Ray diffraction studies were carried out by the powder technique. Specimens were mounted in evacuated Pyrex capillaries and photographed on a Philips 11·64 cm diameter camera with Cu-K_α filtered radiation.

Raman Spectra.—Raman spectra were recorded using Coderg modified PH1 or T800 spectrometers. Exciting radiation was the blue 4880 Å line of a Coherent Radiation Laboratories model 52 ion laser used at *ca.* 250 mW. The Raman shifts were estimated to be accurate to at least 1 cm^{-1}. Samples were examined directly in a square cross-sectioned (7 × 7 mm) extension of the Pyrex reaction U traps, or were sealed in Pyrex capillaries.

I.r. Spectra.—I.r. spectra of pulverized solids sandwiched between two KBr or AgCl plates were recorded using a Perkin-Elmer 225 Grating Infrared Spectrometer.

Preparation of the Samples.—Pyrex glass U tubes with extended bottoms and equipped with TF2/13 Rotaflo Teflon valves were used for the preparations. SbF_5 Was transferred into the reaction vessels by sublimation in dynamic vacuum, whilst NbF_5 and TaF_5 were loaded into the reaction vessels in a dry box (Lintott Engineering Limited, Horsham, Essex). XeF_2 Was added from a Kel-F container by sublimation in dynamic vacuum. All-metal vacuum lines combined with glass and Kel-F attachments were used in preparations and surfaces were pretreated with F_2 or ClF_3 and evacuated prior to use. Weight balance was followed very carefully throughout the experiments. Raman spectra of the reaction products were recorded and intermediates obtained during the decomposition experiments were also monitored by Raman spectroscopy.

$2XeF_2{\cdot}MF_5$, $XeF_2{\cdot}MF_5$, *and* $XeF_2{\cdot}2MF_5$ *Stoicheiometric Preparations.*—The required amount of XeF_2 was added to MF_5 (*ca.* 10 mmol) contained in a reaction vessel and topped with 300 mm of Xe or dry N_2 to prevent XeF_2 escaping during the melting. The reactants were warmed up until a clear melt was obtained. This was then quenched and pumped at room temperature until constant weight was attained.

Reactions of an Excess of XeF_2 *with the Pentafluoride and Thermal Decompositions of Products.*—Xenon difluoride and the pentafluoride were mixed in the ratio $XeF_2 : MF_5$ of $>2 : 1$. Although in each case the mixtures reacted together slowly at room temperature,[4] the reactions do not go readily to completion without heating and so, in each case, the mixture was heated under 1 atm pressure of xenon or nitrogen until a clear melt was obtained. After quenching the mixture was pumped in a dynamic vacuum and the weight loss was observed and the mass balance checked. The Raman spectrum of the solid reaction mixture was run directly in the reactor at suitable times during the decomposition and Raman spectroscopy and *X*-ray crystallography were used to examine the products at points of inflexion on the weight-loss *versus* time-of-pumping curves.

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