Preparation of the KrF^+, $Kr_2F_3^+$, and BrF_6^+ Ions and their Characterisation by ^{19}F Nuclear Magnetic Resonance and Raman Spectroscopy

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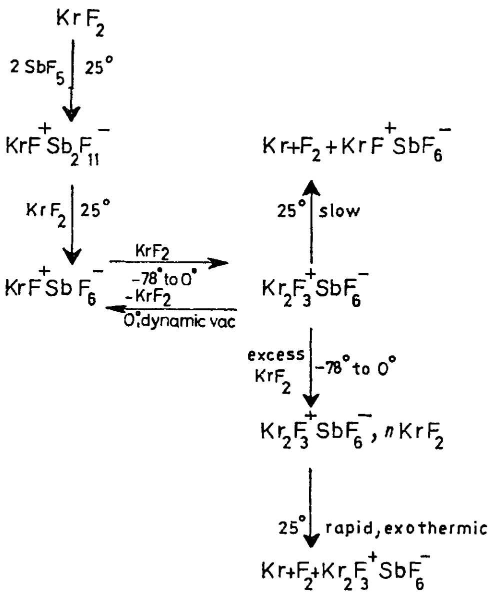
Summary New adducts of KrF_2 with AsF_5, SbF_5, and PtF_5 are shown by ^{19}F n.m.r. and Raman spectroscopy to be the ionic compounds $KrF^+MF_6^-$ (M = As, Sb, or Pt), $KrF^+Sb_2F_{11}^-$, $Kr_2F_3^+MF_6^-$ (M = As or Sb), and $Kr_2F_3^+MF_6^-,nKrF_2$(M = As or Sb); the gross structure of the new cation, $Kr_2F_3^+$, has been established and appears to be similar to that of $Xe_2F_3^+$; the new cation, BrF_6^+, has also been prepared by oxidation of $BrF_5$with $Kr_2F_3^+$.

The only previously characterised adduct of KrF_2 is the compound $KrF_2,2SbF_5$.[1,2] It also has been reported that KrF_2 forms a solid adduct with AsF_5 at −78°, but this solid has never been characterised.[1] Frlec and Holloway[3] have very recently reported the Raman spectra of $KrF_2,2MF_5$ (M = Ta, Nb, or Sb) and KrF_2,TaF_5 and have obtained Raman evidence which indicated the possible existence of the $Kr_2F_3^+$ ion.

We report here the preparation of the adducts KrF_2,MF_5-(M = As, Sb, or Pt), $2KrF_2,MF_5$(M = As or Sb), and $nKrF_2,MF_5$ (M = As or Sb and $n > 2$) and give the first conclusive evidence for the $Kr_2F_3^+$ cation in solution and in the solid phase.[4]



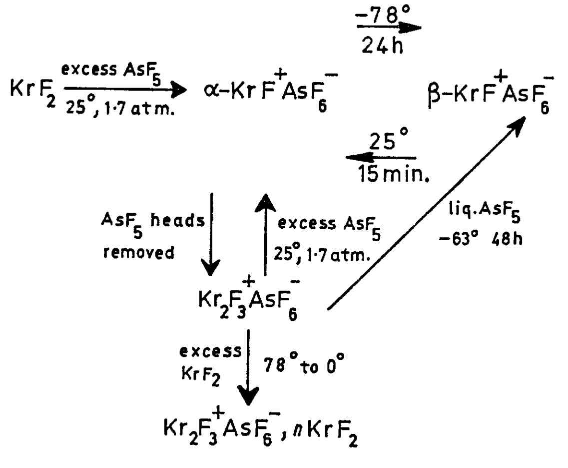
Scheme 1

Table 1. ^{19}F n.m.r. parameters for KrF_2, KrF^+, $Kr_2F_3^+$, their xenon analogues, and the BrF_6^+ cation

Species	Chemical shifts[a] (p.p.m.)	J/Hz	T/°C	Solutes (molar conc.)	Solvent
KrF_2	$-55{\cdot}6$		26	KrF_2 (*ca.* 0·1)	HF
KrF^+	22·6		-40	KrF_2(*ca.* 0·1) SbF_5 (*ca.* 0·5)	HF
$Kr_2F_3^+$	A $-19{\cdot}0$ X_2 $-73{\cdot}6$	$351(^{19}F_t{-}^{19}F_b)$	-66	KrF_2(*ca.* (1) SbF_5 (*ca.* 0·5)	BrF_5
XeF_2	199·6	$5665(^{129}Xe{-}^{19}F)$	-68	$XeF_2(-1)$	HF
XeF^+	289·8	$7210(^{129}Xe{-}^{19}F)$	26	XeF_2(0·34)	SbF_5
$Xe_2F_3^+$	A 184·7 X_2 252·0	$308(^{19}F_t{-}^{19}F_b)$ $4865(^{129}Xe{-}^{19}F_b)$ $6740(^{129}Xe{-}^{19}F_t)$	-62	$Xe_2F_3^+AsF_6^-$(0·67)	BrF_5
BrF_6^+	$-339{\cdot}4$	$1575(^{79}Br{-}^{19}F)$ $1697(^{81}Br{-}^{19}F)$	26	$BrF_6^+Sb_2F_{11}^{-b}$	HF

[a] Spectra recorded at 56·4 or 58·3 MHz and referenced to external $CFCl_3$. [b] Concentration unknown; $BrF_6^+Sb_2F_{11}^-$ was obtained as a mixture with $BrF_4^+Sb_2F_{11}^-$ and dissolved in HF solvent; ($BrF_n^+Sb_2F_{11}^-$) *ca.* 0·5 M.

The SbF_5 and AsF_5 adducts were formed by the series of reactions given in Schemes 1 and 2, respectively. Platinum hexafluoride reacts with KrF_2 according to equation (1) to give a yellow solid which can be formulated as $KrF^+PtF_6^-$ on the basis of its Raman spectrum.



Scheme 2

$$KrF_2 + PtF_6 \xrightarrow{0^\circ} KrF^+PtF_6^- + \tfrac{1}{2}F_2 \qquad (1)$$

Fluorine-19 n.m.r. evidence has been obtained for both KrF^+ and $Kr_2F_3^+$ in solution. The n.m.r. parameters are given in Table 1 and are compared with those of XeF^+ and $Xe_2F_3^+$. A solution of KrF_2 in HF gave a single resonance at $-55{\cdot}6$ p.p.m. from external $CFCl_3$, in good agreement with the previously reported value of -53 p.p.m.[5] Transfer of the solution to a sample tube containing an excess of SbF_5 with respect to KrF_2 gave a new signal to high field of KrF_2. This new signal can be assigned to KrF^+ and the high field shift is analogous to that observed when XeF_2 ionises to XeF^+. A solution containing a two-fold excess of KrF_2 with respect to SbF_5 in BrF_5 solution at low temperature gave an AX_2 spectrum which can be unambiguously assigned to the V-shaped fluorine-bridged structure (I) similar to that of $Xe_2F_3^+$.[6] It is noteworthy, however, that the terminal fluorine resonance of $Kr_2F_3^+$ occurs to low field of the bridging fluorine resonance while the opposite is true in the case of $Xe_2F_3^+$. The relatively large fluorine–fluorine coupling, which is the first observed for a krypton compound, is, however, similar to the value observed for $Xe_2F_3^+$.

The Raman spectra of the KrF^+ and $Kr_2F_3^+$ compounds are also consistent with the ionic formulation of these compounds. The spectra of the KrF^+ salts (Figure a–e) consist of a strong high frequency band(s) due to the Kr–F stretch, characteristic bands of the anion, a weak band at *ca.* 340 cm^{-1} which may be attributed to the stretching of the $F{-}Kr{-}{-}{-}FMF_5$ bridging bond and several bands in the region 100 to 200 cm^{-1} which may be reasonably assigned to bending and torsional modes of the F–Kr---F group. Unlike $KrF^+Sb_2F_{11}^-$, the Kr–F stretch in all the $KrF^+MF_6^-$ compounds appears as an intense doublet which is attributed to factor group splitting of this mode. In the case of the MF_6^- compounds the formally forbidden ν_3 and ν_4 vibrations of the anion were observed; this may be attributed to lowering of the octahedral symmetry of the MF_6^- anion by the fluorine bridge.

Table 2. Raman frequencies and assignments for $BrF_6^+AsF_6^{-a}$

Frequency (cm^{-1})	Assignment
679(41)	$\nu_1(a_{1g}),AsF_6^-$
668(28)	$\nu_2(e_g),BrF_6^+$
658(100)	$\nu_1(a_{1g}),BrF_6^+$
575(4)	$\nu_2(e_g),AsF_6^-$
405(34)	$\nu_5(t_{2g}),BrF_6^+$
367(6)	$\nu_5(t_{2g}),AsF_6^-$

[a] Spectrum recorded at -90°C; lines due to the FEP sample tube have been deleted.

The Raman spectra of $Kr_2F_3^+SbF_6^-$ and $Kr_2F_3^+AsF_6^-$ (Figure f—g) show the expected anion frequencies. In contrast to $Xe_2F_3^+$, however, it appears that the Raman spectrum of the $Kr_2F_3^+$ ion is best interpreted in terms of the unsymmetrical structure (II) which is effectively a KrF^+ ion fluorine bridged to a KrF_2 molecule. The KrF^+ stretch is observed at a slightly lower frequency than in the $KrF^+MF_6^-$ salts. Bands are observed at 555 and 456 cm^{-1} ($Kr_2F_3^+$-

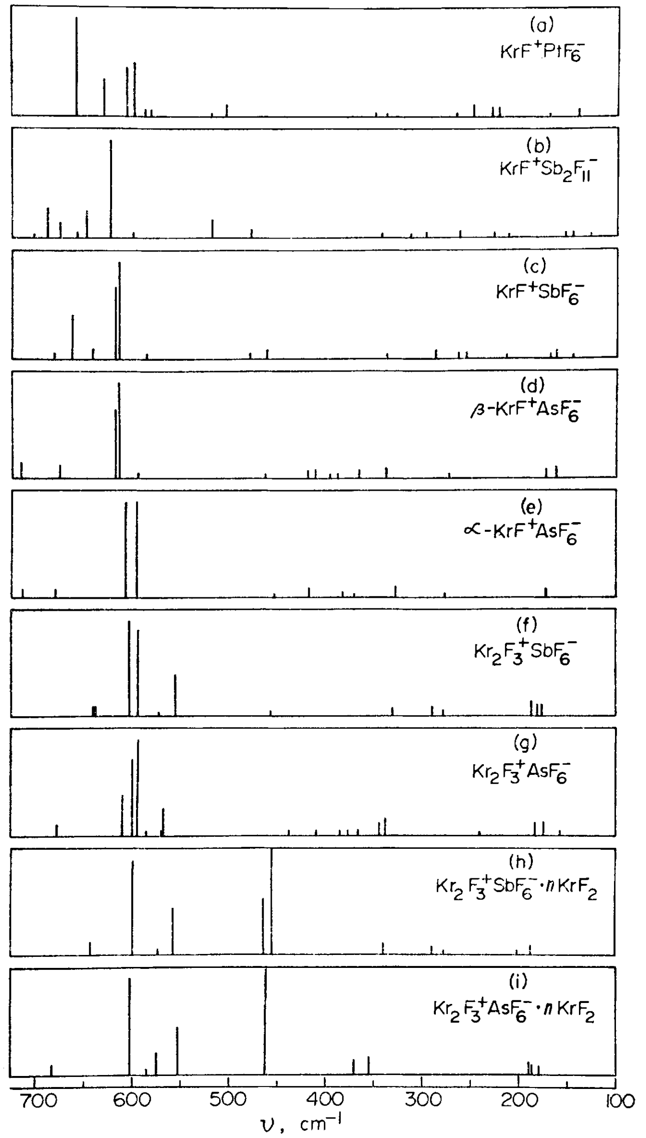
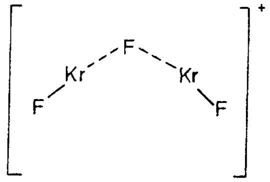
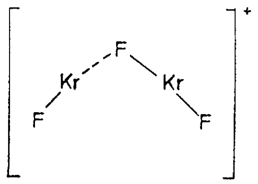


FIGURE. Raman spectra of KrF^+ and $Kr_2F_3^+$ salts. Spectra were recorded at $-90°C$; lines due to the FEP sample tube have been deleted. The Kr–F stretching frequencies of the KrF^+ salts occur at (a) 606(50) and 599(60) cm^{-1}, (b) 624(100) cm^{-1}, (c) 619(74) and 615(100) cm^{-1}, (d) 619(72) and 615(100) cm^{-1} (low temperature modification), (e) 607(100) and 596(100) cm^{-1} (high temperature modification). The Kr–F stretching frequencies of the asymmetric $Kr_2F_3^+$ cation occur at (f) 603(100) and 594(89) cm^{-1} (KrF^+), and 555(34) and 456(4) cm^{-1} (KrF_2); (g) 610(43), 600(80) and 594(100) cm^{-1} (KrF^+), and 437(5) and 567(31) cm^{-1} (KrF_2). The $Kr_2F_3^+,nKrF_2$ salts have strong lines that are assigned to Kr–F stretching modes at (h) 599(100), 557(50) and 466(60) cm^{-1}; (i) 602(100), 575(23) and 553(50) cm^{-1}. The strongest lines at 456 and 462 cm^{-1} are assigned to ν_1 of excess KrF_2 present in the samples.

SbF_6^-) and at 567 and 467 cm^{-1} ($Kr_2F_3^+SbF_6^-$) which may be assigned to ν_3 and ν_1 of the KrF_2 part of the ion [*cf.* ν_1 at 449 (Raman) and ν_3 at 588 (i.r.) for gaseous KrF_2]. The observation of the formally forbidden ν_3 vibration of KrF_2 in the Raman spectrum is consistent with a lowering of the symmetry of the molecule by the fluorine bridge. Finally, the stretching of the weaker and longer Kr---F bond is observed at 330 and 336, 347 cm^{-1} in the SbF^-_6 and AsF_6^- compounds, respectively. It is not entirely clear why $Kr_2F_3^+$ is symmetrical in solution in BrF_5, but apparently unsymmetrical in the solid state. It is possible that the lack of symmetry in the solid state is due to weak fluorine bridging with the anion.



(I)



(II)

The $Kr_2F_3^+$ salts react with further KrF_2 to give new adducts which are tentatively formulated as $Kr_2F_3^+MF_6^-$,-$nKrF_2$ (Figure h—i). The formation of these adducts is accompanied by further characteristic changes in the Raman spectra, but in view of a complete lack of any structural information on these compounds or any analogous compounds no attempt is made to analyse these spectra here.

Solutions of $Kr_2F_3^+SbF_6^-$ and $Kr_2F_3^+AsF_6^-$ in BrF_5 are not stable and on warming to room temperature rapidly decompose to give Kr, F_2, and the new cation, BrF_6^+.[7] The stable white salts $BrF_6^+AsF_6^-$ and $BrF_6^+Sb_2F_{11}^-$, the latter as a mixture with $BrF_4^+Sb_2F_{11}^-$, have been isolated from these solutions. The Raman spectrum of $BrF_6^+AsF_6^-$ is given in Table 2. As in the case of IF_6^+,[8] ν_2 of the octahedral BrF_6^+ ion occurs at higher frequency than ν_1.

The ^{19}F n.m.r. spectrum of the BrF_6^+ cation in HF solvent (Table 1) consists of two overlapping 1 : 1 : 1 : 1 quartets at very low field. These are assigned to $^{79}BrF_6^+$ and $^{81}BrF_6^+$ and arise from spin-spin coupling of six equivalent fluorines with ^{79}Br and ^{81}Br, both with $I = 3/2$, and represent the first reported case of a Br–F coupling. The observation of well-resolved Br–F spin–spin coupling indicates a spherically symmetric electric field about the bromine nucleus, confirming the expected O_h symmetry for the BrF_6^+ ion solution.

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[1] H. Selig and R. D. Peacock, *J. Amer. Chem. Soc.*, 1964, **86**, 3895.

[2] D. E. McKee, C. J. Adams, A. Zalkin, and N. Bartlett, *J.C.S. Chem. Comm.*, 1973, 26.

[3] B. Frlec and J. H. Holloway, *J.C.S. Chem. Comm.*, 1973, 370.

[4] R. J. Gillespie, B. Landa and G. J. Schrobilgen, paper presented at the Assemblée générale annuelle de la Société Chimique de France, Marseille, France, May 23—25, 1973.

[5] F. Schreiner, J. G. Malm, and J. C. Hindman, *J. Amer. Chem. Soc.*, 1965, **87**, 25.

[6] F. O. Sladky, P. A. Bulliner, N. Bartlett, B. G. De Boer, and A. Zalkin, *Chem. Comm.*, 1968, 1048.

[7] R. J. Gillespie, paper presented at the XXIVth International Congress of Pure and Applied Chemistry, Hamburg, Germany, Sept. 3—8, 1973; R. J. Gillespie and G. J. Schrobilgen, *Inorg. Chem.*, to be published.

[8] K. O. Christe and W. Sawodny, *Inorg. Chem.*, 1967, **6**, 1783.