Preparation of $2KrF_2,SbF_5$ and KrF_2,SbF_5: the $Kr_2F_3^+$ and KrF^+ Cations

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Summary The adducts $2KrF_2,SbF_5$ and KrF_2,SbF_5 have been prepared and characterized for the first time and their Raman spectra interpreted in terms of there being substantial contributions to the bonding from the ionic formulations $Kr_2F_3^+,SbF_6^-$ and KrF^+,SbF_6^-; evidence for KrF_2,KrF^+,SbF_6^- has also been obtained.

Recently we obtained Raman evidence for $Kr_2F_3^+$ in solutions of an excess of KrF_2 with TaF_5 in BrF_5 and qualitative evidence for KrF_2,SbF_5 from the direct combination of the component molecules.[1][†]

We have now shown that reaction of KrF_2 with solid $BrF_4^+,Sb_2F_{11}^-$ at room temperature gives BrF_5 and at −40° in BrF_5 solution $2KrF_2,SbF_5$ and BrF_5 are produced. The $2KrF_2,SbF_5$ can be obtained as a white solid by removal of the solvent and excessive KrF_2 at −40° and is stable at that temperature. The main shifts in its Raman spectrum are readily assigned to the $Kr_2F_3^+$ cation and the assignment correlates well with that of the related xenon difluoride adduct (see Figure) and our earlier evidence for $Kr_2F_3^+$ in solution.[1] The solubility of the adduct in BrF_5 at −40° is approximately 0·15 mmol/100 mg of the solvent.

$2KrF_2,SbF_5$ decomposes very slowly in a dynamic vacuum at −30° to yield white, crystalline KrF_2,SbF_5 which is stable at room temperature. Its Raman spectrum correlates well with that of KrF_2,TaF_5[1] (see Figure). The i.r. spectrum of the solid powder between silver chloride windows exhibits strong features at *ca.* 470 and 652 cm^{-1} which are characteristic of the SbF_6^- anion in xenon

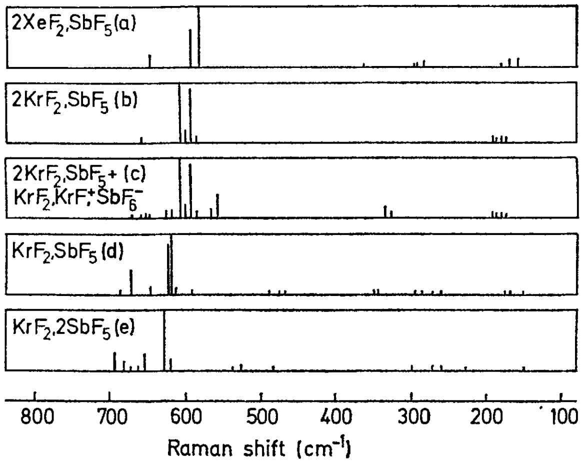

Figure. Raman spectra of solid krypton difluoride adducts. Relative intensities are given in parentheses.

(a) Bands assigned to $Xe_2F_3^+$ stretching modes are 583 (100) and 595 (60) cm^{-1}. (b) Bands assigned to the main $Kr_2F_3^+$ stretching modes are 595 (93) and 607 (100) cm^{-1} [these are about 12 cm^{-1} above the corresponding bands in $2XeF_2,SbF_5$; *cf.* (a)]. (c) In addition to the shifts due to $Kr_2F_3^+,SbF_6^-$ in (b) bands at 559 (40) and 565 (15) cm^{-1} can be correlated with loosely bound KrF_2 and those at 619 (17) and 623 (13) cm^{-1} can be attributed to KrF^+. (d) The doublet associated with KrF^+ stretching modes occurs at 618 (100) and 621 (85) cm^{-1}. The mean (619·5 cm^{-1}) coincides with the shift at 620 cm^{-1} in the contaminated $KrF_2,2SbF_5$ sample.[1] (e) The doublet associated with the KrF^+ stretch occurs at 627 (100) and 619 (20) cm^{-1}.

[†] *Added in proof:* soon after the appearance of our paper[1] preliminary data on $Kr_2F_3^+$ was presented by R. J. Gillespie, B. Landa, and G. J. Schrobilgen at the Assemblée générale annuelle de la Societé Chimique de France, Marseille, May 23—25, 1973 (R. J. Gillespie, personal communication).

difluoride complexes[2,3] and less pronounced absorptions in the 570—605 cm^{-1} region can be tentatively assigned to vibrations associated with the KrF$^+$ cation. The *X*-ray powder diffraction pattern shows a very close relationship to that of XeF_2,TaF_5 (or the isostructural XeF_2,NbF_5) but there is a more marked difference between that of KrF_2,SbF_5 and its xenon analogue. The Raman data on KrF_2,SbF_5 have enabled us to show that our previously reported spectrum for $KrF_2,2SbF_5$[1] contains bands associated with KrF_2,SbF_5 contaminant. Our value for ν(Kr–F$^+$) in KrF_2,SbF_5 coincides with the value predicted by Liu and Schaefer[4] and in $KrF_2,2SbF_5$ (see Figure) with that previously reported by Bartlett *et al.*[5] Decomposition of KrF_2,SbF_5 occurs in a dynamic vacuum at temperatures in excess of 35° as follows:

$$2KrF_2,SbF_5 \rightarrow KrF_2 + KrF_2,2SbF_5;$$

$$KrF_2,2SbF_5 \rightarrow Kr + F_2 + 2SbF_5.$$

In our earlier attempts to prepare KrF_2,SbF_5 by direct combination of the component molecules at room temperature[1] the adduct formed was partially decomposed by local overheating during the vigorous combination.

In the course of a systematic study of the vibrational spectra and conductivities of a variety of adducts of XeF_2 with the pentafluorides of antimony, tantalum and niobium we have isolated $2XeF_2,SbF_5$ and $2XeF_2,TaF_5$ but no equivalent NbF_5 adduct could be obtained.[3] Characteristic frequencies in the Raman spectra of these solids can be assigned to the $Xe_2F_3^+$ and MF_6^- (M = Sb or Ta) ions. Raman spectra of quenched melts of large excesses of XeF_2 with the pentafluorides indicate, in addition, the presence of the adducts $2XeF_2,Xe_2F_3^+,SbF_6^-$, XeF_2,XeF^+,TaF_6^-, and XeF_2,XeF^+,NbF_6^- since, in each case, two bands in the 505—550 cm^{-1} region superimposed on a slightly modified adduct spectrum can be attributed to XeF_2 loosely associated with the adduct. Spectra of slightly decomposed $Kr_2F_3^+,SbF_6^-$ exhibit similar additional shifts at 559 (40) and 565 (15) cm^{-1} which can be similarly interpreted in terms of the formation of the intermediate KrF_2,KrF^+,SbF_6^- (see Figure).

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