Photolysis of Noble Gas–Fluorine Mixtures; Dimorphism in Krypton Fluoride Chemistry

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The UV photolysis of krypton–fluorine mixtures at −196 °C readily affords KrF_2. Variable-temperature Raman studies on this material indicate a temperature-dependent phase transition at −80 °C. The low-temperature UV photolysis of krypton–fluorine mixtures in the presence of Lewis acids (AsF_5 or SbF_5) only affords KrF_2. Variable-temperature Raman studies on the resulting mixtures show that $Kr_2F_3^+SbF_6^-$, α- and β-$KrF^+Sb_2F_{11}^-$, $KrF^+AsF_6^-$ and $KrF^+As_2F_{11}^-$ are formed on warming the mixtures.

Preparative krypton chemistry has steadily progressed from the first isolation of KrF_2 in 1965[1] to the reaction of the difluoride with a range of Lewis acids and the isolation and characterisation of the cationic krypton fluorides KrF^+, $KrF^+\cdot xKrF_2$, $Kr_2F_3^+$ and $Kr_2F_3^+\cdot xKrF_2$.[2–4] Recently one of us (G. J. S.) has identified the first examples of krypton bonded to an element other than fluorine in the synthesis of the $[RC{\equiv}N{-}Kr{-}F]^+$ cation (R = H, CF_3, C_2F_5 or C_3F_7).[5] The low thermal stability of many of these krypton fluorides ($Kr_2F_3^+$ salts rapidly decompose at 0 °C while the krypton nitriles decompose above −60 °C) suggested to us that advances in krypton fluoride chemistry could be made by minimising reaction temperatures. Following the observation by Slivnik *et al.*[6] that KrF_2 could be obtained in high yields by the UV irradiation of krypton in liquid fluorine at −196 °C, we have attempted the photolysis of noble gas–fluorine mixtures in the presence and absence of Lewis acids, and report here for the first time the preparation of $KrF^+As_2F_{11}^-$ and the presence of two solid-state forms of KrF_2 and $KrF^+Sb_2F_{11}^-$.

Although polymorphism is a well known phenomenon throughout synthetic inorganic chemistry, it has only been verified once previously in krypton chemistry when Gillespie and Schrobilgen[2] identified high- and low-temperature phases of $KrF^+AsF_6^-$ which may be interconverted merely by warming/cooling.

Experimental

All manipulations were carried out on a metal vacuum line with facilities to connect Teflon FEP and Pyrex reaction vessels as described previously.[3] Krypton (B.O.C. or Matheson) and fluorine (Matheson or Air Products) were used as received. Arsenic and antimony pentafluorides were prepared by literature routes.[7,8]

Raman spectra were recorded using either a Coderg modified PH1 or T800 (with triple monochromator) spectrometer. Exciting radiation was the blue 4880 Å line of a Coherent Radiation Laboratories model 52 argon-ion laser. Spectra at −196 °C were recorded with the solids in the reaction tubes partially immersed in liquid nitrogen contained in a transparent Pyrex Dewar. Variable-temperature spectra were recorded on samples held in a stream of cold nitrogen gas from a heated liquid nitrogen source. Varying the rate of liquid nitrogen boil off allowed temperatures from −160 to +10 °C to be obtained. Samples were allowed to equilibrate at each temperature for 20 min before spectra were recorded. Complete equilibrium was checked by recording multiple spectra, at each temperature.

Preparation of KrF_2.—Krypton difluoride was prepared by the photolysis of krypton–fluorine mixtures using medium-pressure mercury lamps (RPR-3500 Å) (Southern New England Ultraviolet Company, USA).

In a typical preparation fluorine (1.5 mmol) and krypton (1.5 mmol) were condensed from a nickel manifold into a prepassivated Teflon FEP reactor (6 cm^3 total volume) at −196 °C. The mixture was photolysed for 17 h during which a white solid, only slightly soluble in liquid fluorine, was obtained in the bottom of the reactor. The reactor was then pumped at −196 and −183 °C to remove unreacted fluorine and krypton, respectively. The Raman spectrum was obtained for this solid at −196 °C. The solid was then warmed briefly to room temperature and the Raman spectrum recorded again at −78 °C.

Photolysis of Kr, F_2 *and* SbF_5 *Mixtures.*—Antimony pentafluoride (0.15 g, 0.7 mmol) was condensed into a prepassivated Teflon FEP reactor and F_2 (1.5 mmol) and Kr (1.5 mmol) condensed on top when the SbF_5 remained undissolved. After photolysis for 17 h, the excess of F_2 and Kr was removed and the Raman spectrum recorded at −196 °C and then at various temperatures up to −25 °C.

A further 1:1 mixture of F_2 (1.5 mmol) and Kr (1.5 mmol) was condensed onto this sample and the photolysis at −196 °C repeated. After removal of unreacted F_2 and Kr, the sample was warmed briefly to −10 °C before the Raman spectrum was recorded again at −78 °C.

Photolysis of Kr, F_2 *and* AsF_5 *Mixtures.*—Arsenic pentafluoride (42.5 mg, 2.5×10^{-4} mol) was condensed into a prepassivated Pyrex reactor and F_2 (1.5 mmol) and Kr (1.5 mmol) condensed on top when the AsF_5 remained undissolved. After photolysis for 8 h, the excess of F_2 and Kr were removed and the Raman spectrum recorded at −196 °C and then at various temperatures up to −40 °C.

Discussion

The Raman spectrum (recorded at −196 °C) of the white solid from the krypton–fluoride photolysis shows unequivocally that this is the same material as that described by Claassen *et al.*[9] from electric discharge experiments and we obtain a 28% yield of KrF_2 after 8 h of photolysis. The single Raman-active Kr–F stretch at 465.5 cm^{-1} is comparable to the single Raman-active Xe–F stretch at 515 cm^{-1} for XeF_2. However, on warming the sample to room temperature and quenching the sample at −78 °C, the Raman spectrum of KrF_2 changes. Using variable-

Table 1 Factor-group analysis for crystalline KrF_2 and XeF_2

	$KrF_2(D_{4h}^{14}, Z^1 = 2)^a$					$XeF_2(D_{2h}^{17}, Z^1 = 1)$				
$D_{4h}{}^b$	$N_T{}^b$	T_A	T	R	ν_i	N_T	T_A	T	R	ν_i
A_{1g}	1	—	—	—	1	1	—	—	—	1
A_{2g}	1	—	—	1	—	—	—	—	—	—
B_{1g}	1	—	—	1	—	—	—	—	—	—
B_{2g}	1	—	—	—	1	—	—	—	—	—
E_g	1	—	—	1	—	1	—	—	1	—
A_{1u}	—	—	—	—	—	—	—	—	—	—
A_{2u}	2	1	—	—	1	2	1	—	—	1
B_{1u}	2	—	1	—	1	—	—	—	—	—
B_{2u}	—	—	—	—	—	—	—	—	—	—
E_u	4	1	1	—	2	2	1	—	—	1

[a] Z^1 = Number of molecules in primitive cell. [b] N_T = Total number of modes of primitive cell; T_A = acoustic modes; T = optic branch translatory modes; R = rotatory modes; ν_i = internal modes of molecules.

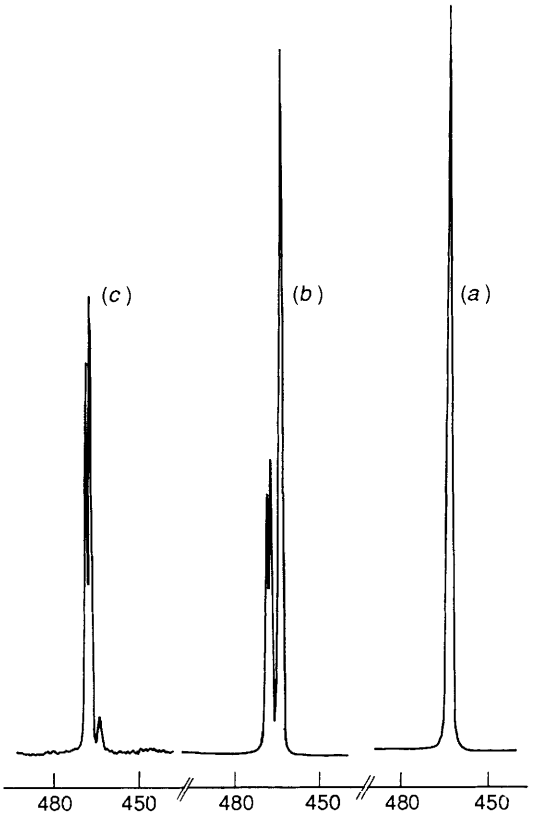


Fig. 1 Raman spectra of solid KrF_2 recorded at −196 °C. (*a*) Prepared at −196 °C, (*b*) after warming to −80 °C for 30 s, (*c*) after warming to −80 °C for 3 min

temperature Raman experiments we have fully investigated these changes. At temperatures between −196 °C and −85 °C, the Raman spectrum for KrF_2 is unaltered. Holding the sample at −80 °C, the band at 465.5 cm^{-1} decreases in intensity and additional features at 469.5 and 468.6 cm^{-1} are observed (Fig. 1). After only 3 min at this temperature, the band at 465.5 cm^{-1} had almost completely disappeared. At first, it was believed that these new bands might be assignable to a *new* krypton fluoride, but the absence of the bands in the Raman spectrum at −196 °C and the fact that their appearance is reversible with respect to temperature suggests that KrF_2 undergoes a phase change at *ca.* −80 °C. For simplicity we refer to the low-temperature (−196 °C) phase as α-KrF_2 and the higher temperature (−78 °C) phase as β-KrF_2.

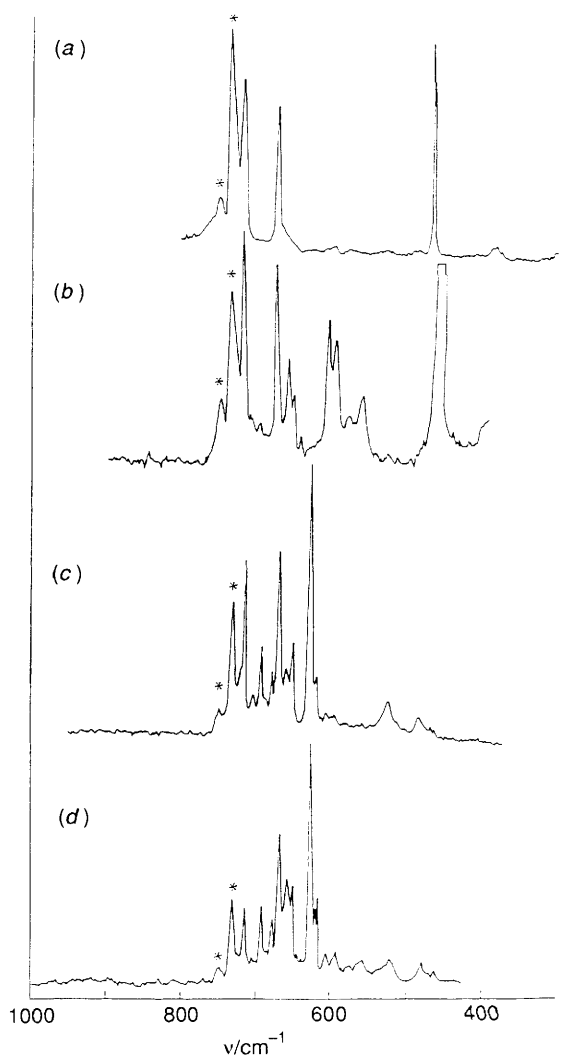


Fig. 2 Raman spectra of the products from the reaction of KrF_2 with SbF_5. (*a*) At −196 °C, unreacted α-KrF_2 and SbF_5. (*b*) At −95 °C, $Kr_2F_3{}^+SbF_6{}^-$, unreacted α-KrF_2 and SbF_5. (*c*) At −25 °C, α-$KrF^+Sb_2F_{11}{}^-$. (*d*) At −10 °C, α- and β-$KrF^+Sb_2F_{11}{}^-$ (* Peaks due to Teflon FEP)

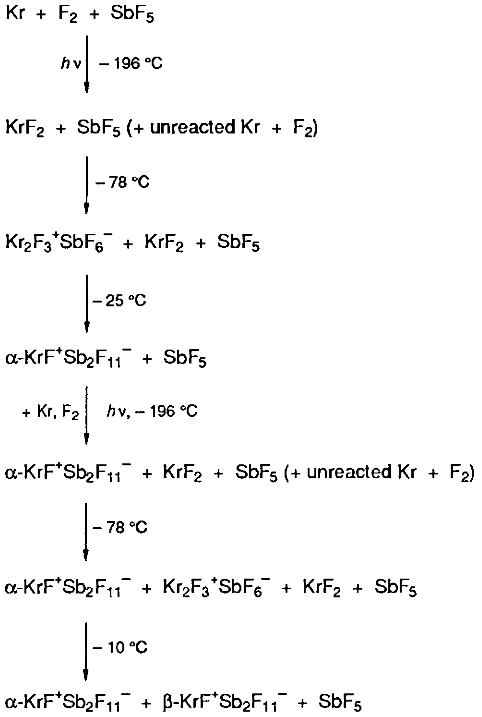
The temperature-dependent phase change is of considerable interest. The X-ray crystal structure of KrF_2 at −78 °C has been reported.[10] The molecule crystallises in the tetragonal space group $P4_2/mnm$ with two linear KrF_2 molecules per unit cell aligned in planes perpendicular to the tetrad axis. A factor-group analysis for this crystal has been reported incorrectly[11] and Table 1 gives the correct factor-group analysis with that of crystalline XeF_2[12] for comparison. As can be seen, the $\Sigma_g{}^+$ Raman-active stretch for gaseous, monomeric KrF_2 ($D_{\infty h}$) splits into 2 bands ($A_{1g} + B_{2g}$) in space group $P4_2/mnm$. This contrasts with that for crystalline XeF_2 for which only one band is predicted.

When these predictions are compared with our Raman data, it is clear that Falconer and co-workers[10] solved the X-ray crystal structure of β-KrF_2. Furthermore, the simplicity of our Raman spectrum at −196 °C and its similarity to that of XeF_2 suggests that α-KrF_2 probably crystallizes in the same space group as XeF_2. Definitive confirmation of this, however, must await an X-ray structural investigation of KrF_2 at liquid-nitrogen temperatures.

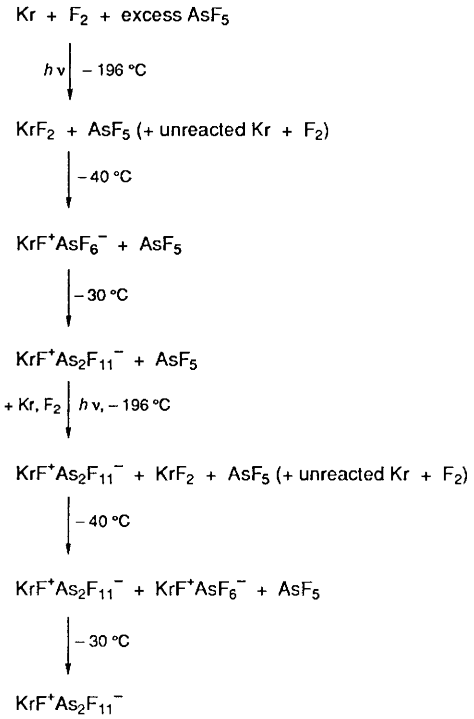
Photolysis of F_2–Kr–SbF_5 *Mixtures*.—The Raman spectroscopic data for the products formed during the photolysis and subsequent warming of F_2–Kr–KrF_2–SbF_5 mixtures are given

Table 2 Raman bands (cm^{-1}) and assignments for products of Kr + F_2 + SbF_5 reactions (with relative percentage intensities in parentheses)

	$Kr_2F_3^+SbF_6^-$		α- and β-$KrF^+Sb_2F_{11}^-$	α-$KrF^+Sb_2F_{11}^-$	β-$KrF^+Sb_2F_{11}^-$
$Kr_2F_3^+$	606 (100)	KrF^+	627 (100)	627 (100)	
	595 (91)		624 (18)		624 (100)
	559 (43)		620 (21)	619 (20)	
SbF_6^-	658 (45)	$Sb_2F_{11}^-$	694 (30)	694 (30)	
	652 (42)		680 (16)	680 (18)	
	645 (9)		677 (3)		675 (15)
	565 (8)		672 (13)	672 (11)	
			654 (30)	653 (27)	
			648 (6)		648 (26)
			523 (13)	524 (8)	591 (10)
			482 (10)	483 (5)	



Scheme 1 Reactions in the Kr–F_2–KrF_2–SbF_5 system



Scheme 2 Reactions in the Kr–F_2–KrF_2–AsF_5 system

in Table 2 and typical spectra in Fig. 2. A schematic representation of the reactions is given in Scheme 1.

When F_2–Kr–SbF_5 mixtures are photolysed at −196 °C, KrF_2 is formed but does not react further with F_2 or SbF_5 at this temperature. On warming to about −95 °C, KrF_2 reacts with SbF_5 to form $Kr_2F_3^+SbF_6^-$ in equilibrium with unreacted KrF_2 and SbF_5. Our Raman spectrum of $Kr_2F_3^+SbF_6^-$ is in good agreement with that in the literature.[2,3] Thus it appears that $Kr_2F_3^+SbF_6^-$ is the first product of the reaction of KrF_2 with SbF_5 at −95 °C whereas $KrF^+Sb_2F_{11}^-$ is the first product observed from the reaction of KrF_2 with SbF_5 at room temperature.[2,13]

On warming, $Kr_2F_3^+SbF_6^-$ reacts further with KrF_2 and SbF_5, and the Raman spectrum at −25 °C is in good agreement with the Raman spectrum of $KrF^+Sb_2F_{11}^-$ reported by Frlec and Holloway[3] in the presence of unreacted SbF_5. There is a disagreement in the literature regarding the Raman spectrum of $KrF^+Sb_2F_{11}^-$. This apparent discrepancy is explained below.

Addition of more fluorine (1.5 mmol) and krypton (1.5 mmol) to the sample of $KrF^+Sb_2F_{11}^-$–SbF_5 followed by photolysis and the removal of unreacted gases affords more KrF_2 which does not react with $KrF^+Sb_2F_{11}^-$ or SbF_5 at −196 °C. As the sample is warmed, and the Raman spectrum is recorded at various temperatures, bands due to $KrF^+Sb_2F_{11}^-$ are unchanged but at −95 °C bands due to $Kr_2F_3^+SbF_6^-$ again appear indicating that KrF_2 reacts initially with SbF_5 at −95 °C to yield the 2:1 adduct. On warming further to −10 °C, the bands due to $Kr_2F_3^+SbF_6^-$ decrease whilst those due to $KrF^+Sb_2F_{11}^-$ increase along with a number of other weaker bands (Table 2). The nature of these bands was initially unclear, but it appears that the bands correlate with the most intense bands of $KrF^+Sb_2F_{11}^-$ reported by Gillespie and Schrobilgen.[2] Therefore we suggest that, as with KrF_2 and $KrF^+AsF_6^-$ [2] there are two crystalline modifications (α and β) of $KrF^+Sb_2F_{11}^-$ which may be thermally related but which have been seen together for the first time in our variable low-temperature Raman experiments.

Photolysis of F_2–Kr–AsF_5 *Mixtures*.—The Raman spectroscopic data for the products formed during the photolysis and subsequent warming of F_2–Kr–KrF_2–AsF_5 mixtures are given in Table 3 and a schematic representation of the reactions in Scheme 2.

As for the F_2–Kr–SbF_5 mixtures, F_2–Kr–AsF_5 mixtures when photolysed at −196 °C yield KrF_2, which does not react further with F_2 or AsF_5 at this temperature. We observed no change in the Raman spectrum through a variable low-temperature experiment up to −40 °C when the 2:1 KrF_2–AsF_5 mixture reacted to form α-$KrF^+AsF_6^-$ and unreacted KrF_2, the Raman spectrum of which agrees with those in the

Table 3 Raman bands (cm^{-1}) for products of KrF_2 + AsF_5 reactions (with relative percentage intensities in parentheses)

	α-$KrF^+AsF_6^-$		$KrF^+As_2F_{11}^-$				
KrF^+	604 (100)		566 (8)		570 (28)		570 (41)
							566 (26)
	612 (100)		282 (7)		282 (9)		286 (10)
AsF_6^-	712 (11)	$As_2F_{11}^-$	798 (br)		798 (br)		798 (vbr)
			711 (3)		711 (4)		711 (10)
			692 (22)	$\xrightarrow{+KrF_2}$	692 (90)	$\xrightarrow{+KrF_2}$	692 (100)
			676 (6)		680 (14)		680 (18)
	421 (13)		647 (5)		647 (7)		
	385 (7)						
			373 (10)		373 (20)		373 (62)

literature.[1,2] We have found no evidence for a 2:1 KrF_2:AsF_5 adduct comparable to $Kr_2F_3^+SbF_6^-$.

In a separate experiment using a three-fold excess of AsF_5 the variable-temperature Raman experiment afforded initially at −40 °C α-$KrF^+AsF_6^-$, but when the mixture is warming to −30 °C this reacts with the excess of AsF_5. The peaks due to α-$KrF^+AsF_6^-$ decrease in intensity and a number of new bands appear. By repetition of the Kr–F_2 photolysis in the presence of the initial products and warming the sample to −30 °C, all the new bands increase at the same rate. Therefore, they can be identified with one new species, and we assign these bands to $KrF^+As_2F_{11}^-$ by comparison with the Raman spectra for α- and β-$KrF^+Sb_2F_{11}^-$ and $Na^+As_2F_{11}^-$.[14]

Conclusion

UV photolysis of liquid krypton–fluorine mixtures is a cheap convenient method for the preparation of KrF_2 in fair yield. During variable-temperature Raman experiments on KrF_2 we have identified a change in the Raman spectrum at −80 °C which can be explained in terms of a phase change in crystalline KrF_2. Krypton difluoride does not react with SbF_5 or AsF_5 under UV irradiation at −196 °C, but on warming KrF_2–SbF_5 mixtures, $Kr_2F_3^+SbF_6^-$ and α- and β-$KrF^+Sb_2F_{11}^-$ can be readily identified. Warming KrF_2–AsF_5 mixtures yields $KrF^+AsF_6^-$ and $KrF^+As_2F_{11}^-$.

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