Notes

The Infrared Spectra of Alkali Metal Hexafluorouranates(V). An Example of Dependence of Molecular Geometry on Matrix Gas

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Potassium, rubidium, and caesium hexafluorouranates(V) are vaporised at temperatures of the order of 400 °C. The vapours are co-condensed with argon or nitrogen as matrix gases. Infrared spectra suggest a C_{3v} symmetry for the species isolated in argon and a C_{2v} symmetry in nitrogen. In the case of sodium hexafluorouranate(V) the spectra are complicated by decomposition reactions leading to uranium pentafluoride as one of the products.

In 1978 Kunze *et al.*[1] described the i.r. spectra of alkali metal UF_n^{m-} salts (obtained from the reaction of alkali metal atoms or alkali metal fluorides with uranium fluorides) in argon matrices. They commented that these compounds ' are not expected to be easily volatilised '. We were interested in the possibility of decomposing alkali metal hexafluorouranates(V) to yield *monomeric* uranium pentafluoride as the sole vapour phase species. We were also interested in the nature of the interaction of the octahedral hexafluorouranate(V) ion with an alkali metal ion, if vapour phase transport of the alkali metal hexafluorouranate(V) occurred. By analogy with earlier work[2] we expected the lighter alkali metal salts to yield more uranium pentafluoride (by decomposition) and the heavier alkali metal salts to favour vapour phase transport of alkali metal hexafluorouranate(V).

Results and Discussion

Preliminary experiments showed that heating $CsUF_6$ *in vacuo* at temperatures of the order of 400 °C led to a sublimate which gave an *X*-ray powder diffraction pattern identical to that of the starting material. Figure 1(*a*) shows a portion of the i.r. spectrum of $CsUF_6$ isolated in an argon matrix. The two bands shown occur in the region appropriate[3] to ν_3 (t_{1u}) of octahedral UF_6^- with an intensity ratio (higher : lower) of almost exactly 2 : 1. Closely similar spectra were obtained for the potassium and rubidium salts and from the Table it can be seen that there is a small but significant cation dependence for these bands. The only other bands observed in the uranium—fluorine stretching region were weak and occurred in the region[3] of ν_1 (*ca.* 620 cm^{-1}) and ν_2 (*ca.* 430 cm^{-1}) of octahedral UF_6^-. From these experimental observations we conclude that the interaction of the alkali metal ion with the initially octahedral UF_6^- ion has perturbed the octahedron so that the triple degeneracy of ν_3 has been partially lifted to yield an *a* and an *e* mode. The fact that both ν_1 and ν_2 are weak in the i.r. spectrum suggests that the perturbation is small. The splitting of approximately 20 cm^{-1} between the *a* and the *e* modes is of the order to be expected for the interaction of an alkali metal ion such as K^+, Rb^+, or Cs^+ with a large singly charged UF_6^- ion. The small splittings observed on the two principal bands are typical of matrix site effects. Finally, by analogy with oxoanions,[4] where no unidentate interactions have been found in the presence of one cation, we can confidently reject a unidentate C_{4v} (apical) interaction and assign a tridentate C_{3v} (or facial) structure.

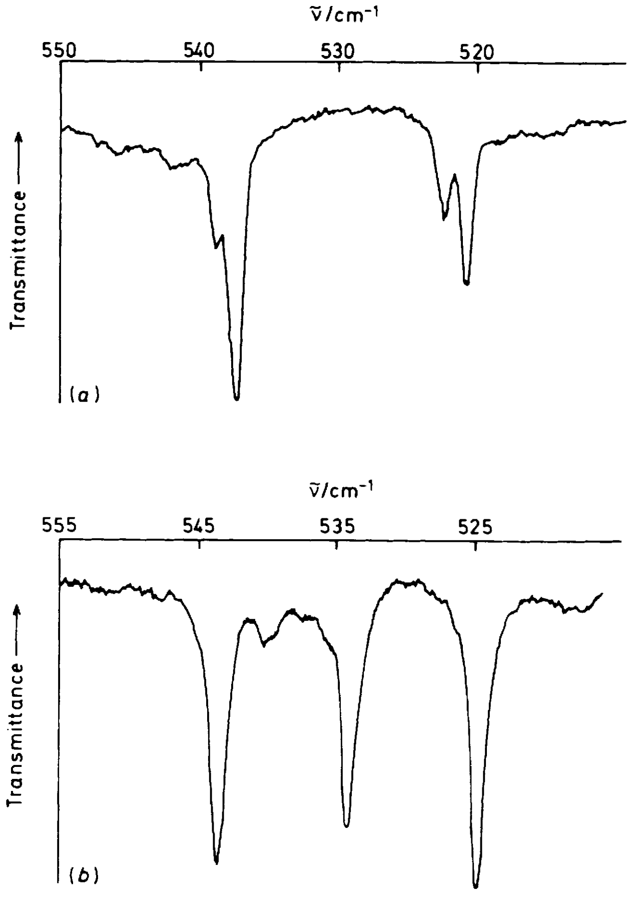

Figure 1. High-resolution i.r. spectra of (*a*) $CsUF_6$ in an argon matrix; (*b*) $CsUF_6$ in a nitrogen matrix

Isolation of the same salts in nitrogen led to an interesting result. Three bands of approximately equal intensity were formed giving an approximately regularly spaced triplet of lines. The overall splitting between the extremes of this triplet was of the order of 20 cm^{-1}, similar to the separation found between the *a* and *e* modes in argon matrices. We interpret these observations to mean that in nitrogen the triple degeneracy of ν_3 (t_{1u}) for octahedral UF_6^- has been fully lifted

Table. Observed i.r. frequencies ($\bar{\nu}$/cm^{-1}) for matrix-isolated MUF_6

$NaUF_6$			KUF_6		$RbUF_6$		$CsUF_6$		
Ar[a]	Ar	N_2	Ar[b]	N_2	Ar[c]	N_2	Ar[a]	Ar[d]	N_2
	620.3w	622.1w			617.0w			616.0w	616.4w
557.2	557.6s	557.3s[e]		547.4s		545.3s			543.6s
(545.7)	(545.3)[f]	(542.9)	540.7s		539.0s		537.1w	537.2s	
538.7	539.1s	539.6s		535.5s		534.6s			533.9s
			518.6m		522.4m			520.4m	
521.9	521.7s	525.8s		525.3s		525.0s			524.4s
[g] 525.4,							[g] 526.3,		
520.2							520.1		
		463.5w							463.1w
449.9					441vw			442vw	
		431vw							422.1vw

[a] Ref. 1. [b] Weak features at 526.4 and 528.6; shoulder 543.4 cm^{-1}. [c] Weak features at 543.5 and 517.0br; shoulder at 540.0 cm^{-1}. [d] Shoulders at 538.7 and 522.0 cm^{-1}. [e] Broader than 539.6 or 525.8 cm^{-1} features. [f] Broader feature of variable intensity, with shoulders. [g] Discrete UF_6^-.

to give $a_1 + b_1 + b_2$ in C_{2v} symmetry (with a bidentate or edge interaction).

We have previously shown that $CsClO_3$[4] isolated in an argon matrix shows a tridentate interaction between the anion and the cation. By contrast for the closely related $RbClO_4$ the interaction is bidentate in a nitrogen matrix. These two results, coupled with the present work, emphasise the small energy differences between bi- and tri-dentate interactions. Although we cannot prove unambiguously that the interpretation of the present work is correct, nonetheless the magnitudes of the frequency differences, the regularity of the triplet spacing, the observed intensity ratios, and the fact that the explanation offered accounts for all the observations leads us to conclude that we are observing a change in shape with matrix gas. Further, because we are studying the interaction between large (spherical) alkali metal ions and an almost spherical anion (which interact principally by coulombic forces) we would expect orientation effects to be at a minimum. In the vapour the alkali metal ions would 'roll around' the UF_6^- ion, initially *via* an edge/face/edge . . . progression. At higher temperatures this pathway would become less clearly defined.

For sodium hexafluorouranate(V) the picture is more complicated because decomposition occurred during the vaporisation process leading to uranium pentafluoride as one of the products. In argon matrices in the region 520—560 cm^{-1} (appropriate to UF_6^- species) three bands were always present in roughly 1 : 1 : 1 intensity ratio at 557.6 (557.2), 539.1 (538.7), and 521.7 (521.9 cm^{-1}). Figures in brackets refer to the earlier work of Kunze *et al.*[1] and as can be seen the agreement is excellent. We also agree with the assignment of C_{2v} (or lower) symmetry. It is interesting to note that, like Kunze *et al.*,[1] we observe a broader feature of variable intensity at 545.3 (545.7 cm^{-1}), although our experimental conditions are quite different from theirs. In nitrogen matrices three bands of approximately equal intensity can also be identified together with a weak feature at 542.9 cm^{-1}. It seems likely that the band at 545.3 cm^{-1} in argon correlates with the band at 542.9 cm^{-1} in nitrogen. Due to lack of isotopic data we are unable to decide from which species this band originates. [It should be noted that all three methods of preparation detailed for sodium hexafluorouranate(V) led to the observation of the band at 545.3 cm^{-1} in argon matrices.]

Our experimental results on MUF_6 (M = Na, K, Rb, or Cs) are summarised in the Table. In some cases matrix site effects are evident. The change in shape from a C_{3v} 'molecule' for the potassium, rubidium, and caesium salts to a C_{2v} 'molecule' for the sodium salt (both in argon matrices) can be rationalised on the basis of increased $M^+ \cdots U^{\delta+}$ repulsion terms as the size of the alkali metal ion decreases.

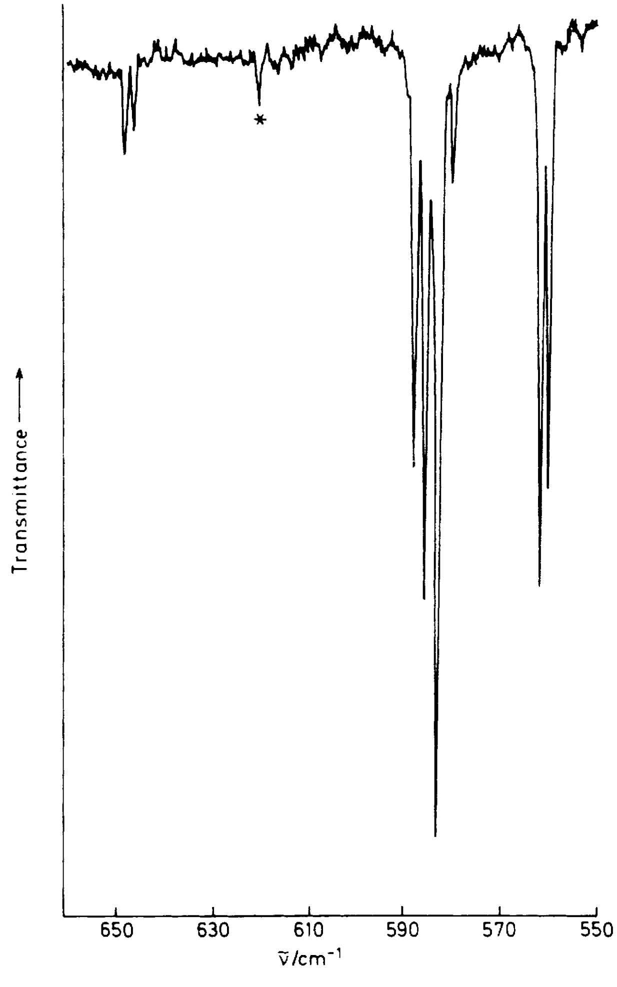

Figure 2. The i.r. spectrum of monomeric uranium pentafluoride isolated in an argon matrix (* uranium hexafluoride)

In view of the high quality of the uranium pentafluoride (monomer) spectra obtained, a number of related experiments was performed. These are documented in the Experimental section. Figure 2 shows the i.r. spectrum of uranium pentafluoride obtained by heating a mixture of U_3O_8 and UF_4 to approximately 650 °C in a platinum cell, and co-condensing the vapours with argon. Note the almost complete absence of any other bands. The occurrence of multiple sites under our trapping conditions is apparent. Annealing of the matrix showed growth of one band in each group: 646.5 (ν_1); 560.7 (ν_2); 583.5 cm^{-1} (ν_7). These frequencies agree to within 0.5 cm^{-1} with those quoted by Jones and Ekberg[5] for uranium pentafluoride obtained by the photolysis of uranium hexafluoride.

Experimental

Several different methods were used for the preparation of the alkali metal hexafluorouranate(V) species. (*a*) The direct reaction of stoicheiometric amounts of intimately ground alkali metal fluoride with uranium pentafluoride in previously fluorinated sealed monel (alloy of Cu and Ni) or aluminium containers at 350 °C for several days[6] (sodium and caesium). (*b*) The reaction between stoicheiometric amounts of alkali metal fluoride and uranium pentafluoride previously dissolved in 60% (by weight) hydrofluoric acid.[7] Either the precipitate was filtered off (caesium) or the solution was evaporated to dryness under reduced pressure (sodium). (*c*) The reaction of stoicheiometric amounts of alkali metal nitrate and nitrosyl hexafluorouranate(V) ground together followed by heating in a sealed preconditioned aluminium[8] container for several days at temperatures in excess of 300 °C (sodium, potassium, rubidium, and caesium). *X*-Ray powder diffraction studies of $NaUF_6$ and of $CsUF_6$ yielded spacings in good agreement with the literature[6] values for these compounds. Nitric oxide, carbon monoxide, and alkali metal nitrates and fluorides were all obtained commercially and used without purification. Nitrosyl hexafluorouranate(V)[9] and uranium pentafluoride[10] were prepared by established literature methods.

For spectroscopic studies, sodium or caesium fluoride heated (in the vaporisation cell) with uranium pentafluoride gave spectra identical to those obtained from the compounds prepared conventionally. It is also interesting to note that heating caesium fluoride and uranium tetrafluoride gave spectra consistent with the formation of $CsUF_6$ (which is expected to be the most volatile species in the Cs–U–F system). Matrix spectra from the vaporisation of $NaUF_6$ in alumina cells led to bands characteristic of AlF_3 and $NaAlF_4$[11] in addition to UF_5 and $NaUF_6$. Attempts to vaporise $CsUOF_5$[12] yielded spectra of UF_6.

Heating an intimately ground mixture of U_3O_8 and UF_4 (*with no attempt to exclude moisture* during the initial mixing process) led to high quality spectra of UF_5 monomer, when a platinum or copper container was used.

Details of the matrix isolation system have been described elsewhere.[13] The central window was of caesium iodide and during deposition the temperature of this window was of the order of 14 K. Spectroscopy was carried out on a Perkin-Elmer 225 i.r. spectrometer. Vaporisation was normally from monel or platinum cells.

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