Co-condensation Reactions of Uranium Tetrafluoride and Hexafluoride with Alkali Metals and Alkali-metal Fluorides in Low-temperature Argon Matrices

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The compounds UF_4 and UF_6, co-condensed with various alkali metals and alkali-metal fluorides, have provided i.r. spectroscopic evidence for the formation of MUF_4, MUF_5, MUF_6, M_2UF_6, and MUF_7 species. The bands are discussed in terms of the anion symmetry and the interactions between the alkali-metal and uranium ions.

THE gas-phase i.r. spectrum of UF_6 has recently been reported,[1] as well as the spectra of matrix-isolated UF_4,[2] UF_5,[3,4] and UF_6.[5] The present work has been carried out in an attempt to obtain i.r. spectra of an analogous series of uranium fluoride anions, $[UF_4]^-$, $[UF_5]^-$, $[UF_6]^-$, and $[UF_7]^-$. These species are present in various macroscopically available salts which are not expected to be easily volatilized. Gas-phase spectra are therefore not available. However, dilute, frozen, argon matrices containing these anions should provide a reasonable model of the gaseous state. The anions can be generated in the matrix by reaction of the uranium fluorides with either alkali metals or alkali-metal fluorides in argon at cryogenic temperatures.

EXPERIMENTAL

The matrix-isolation apparatus has been described previously.[6] Uranium tetrafluoride was obtained from ROC/RIC Chemical Corp. and was used as received. Uranium hexafluoride was prepared by direct fluorination of UF_4 in a nickel flow reactor at 300 °C. The gaseous product was trapped in a copper U tube cooled with a solid CO_2–acetone slush. The UF_6 was pumped on at liquid-nitrogen temperatures to remove volatile impurities. Vaporization of UF_6 was controlled by maintaining the copper U tube at 0 °C using an ice-bath, and by means of a needle valve connecting the UF_6 container with the matrix chamber. To remove trace amounts of HF, the UF_6 was passed over NaF. No impurities were detected in the i.r. spectra after this procedure. In experiments with UF_4, the reactant was vaporized at *ca.* 740 °C. The alkali metals Li, Na, and K were vaporized from stainless-steel cells at 350, 180, and 150 °C respectively. Cs was generated from a mixture of Li and CsI in a graphite cell heated to 300 °C. The salts NaF, KF, and CsF were vaporized from graphite cells at 920, 770, and 500 °C respectively. The trapping surfaces were maintained at 10—15 K during deposition under an argon pressure of 2.5×10^{-5} mmHg.† The matrix gas was passed through a liquid-nitrogen trap to remove impurities. Deposited surfaces were annealed by warming to 30 K for 5 min and then recooling. Successive stepwise annealings were usually performed, with i.r. spectra being recorded after each warm-up–cool-down cycle. The relative amounts of uranium fluoride and alkali metal or alkali-metal fluoride were varied by changing the furnace temperature in the case of solids or the needle-valve setting in the case of UF_6.

RESULTS AND DISCUSSION

UF_4 + *Alkali Metals*.—Condensation of ^7Li with UF_4 in an argon matrix produced four new bands in the i.r. spectrum together with those of unchanged UF_4 (Figure 1). It is likely that UF_4 was reduced by Li to give a Li^+,UF_4^- species, for which square-pyramidal (C_{4v}), trigonal-bipyramidal (C_{3v}), and the two lithium-bridged (C_{2v} and C_{3v}') structures are possible. The associated i.r.-active stretching modes are $2A_1 + E$ (C_{4v}), $2A_1 + E$ (C_{3v}), $3A_1 + 2B_1 + B_2$ (C_{2v}), and $3A_1 + 2E$ (C_{3v}'). Substitution of ^6Li for ^7Li yields a spectrum in which the band at 514.0 cm^{-1} seems to shift to a position under the UF_4 region, while a band at 553.8 cm^{-1} moves to 570.8 cm^{-1} (Figure 1). The remaining bands of Li^+,UF_4^-

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† Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa; 1 cal = 4.184 J.

[1] R. S. McDowell, L. B. Asprey, and R. T. Paine, *J. Chem. Phys.*, 1974, **61**, 3571.

[2] K. R. Kunze, R. H. Hauge, D. Hamill, and J. L. Margrave, *J. Phys. Chem.*, 1977, **81**, 1664.

[3] (*a*) R. T. Paine, R. S. McDowell, L. B. Asprey, and L. H. Jones, *J. Chem. Phys.*, 1976, **64**, 3081; (*b*) L. H. Jones and S. Ekberg, *ibid.*, 1977, **67**, 2591.

[4] K. R. Kunze, R. H. Hauge, D. Hamill, and J. L. Margrave, *J. Chem. Phys.*, 1976, **65**, 2026.

[5] W. B. Lewis, L. B. Asprey, L. H. Jones, R. S. McDowell, S. W. Rabideau, A. H. Zeltmann, and R. T. Paine, *J. Chem. Phys.*, 1976, **65**, 2707.

[6] J. W. Hastie, R. H. Hauge, and J. L. Margrave, *High Temperature Sci.*, 1969, **1**, 76.

shift by much smaller amounts. If one alternatively assumes that the band at 514.0 cm^{-1} for ^{7}Li and 570.8 cm^{-1} for ^{6}Li comprises a Li^+–UF_4^- stretching mode, with the remaining product bands belonging to U–F stretches, then the apparent shift gives a $\nu^6 : \nu^7$ ratio well in excess of the maximum limit of 1.08 : 1 calculated on the basis of a point-mass representation of Li^+ and UF_4^-. Thus a shift from 514.0 to 570.8 cm^{-1} is too large, making the hypothesis of a second band in the ^{6}Li spectrum necessary and reasonable. The observation of major lithium isotope shifts of two bands precludes the square-pyramidal (C_{4v}) and trigonal-bipyramidal (C_{3v}) structures which would be expected to exhibit only one major lithium-sensitive mode shift. Both Li–F bridged structures would exhibit two i.r.-active Li–F stretching bands, but the C_{2v} structure would have four i.r.-active U–F stretching modes as opposed to three for the C_{3v}' structure. Assuming a C_{3v}' configuration, one of the U–F modes may have too low an intensity to be seen or may be obscured. A C_{2v} structure cannot be dismissed, however, for two bands may have escaped detection for the same reasons. It is interesting to note that neon-matrix work on Li[AlF_4] gave evidence for a C_{2v} structure for that molecule.[7,8] Lithium isotope shifts for Li[AlF_4] approximate those observed in the present study.

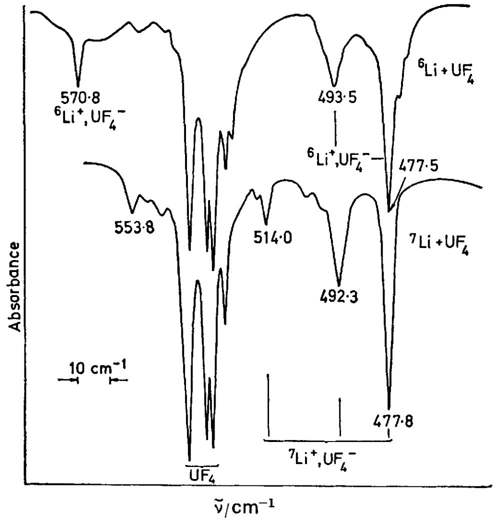

FIGURE 1 Infrared spectra of the reaction product of co-condensation of ^{7}Li and ^{6}Li with UF_4

The trapping of UF_4 with Na and K yielded bands at 485.8 and 470.5, and 480.8 and 466.3 cm^{-1}, spectroscopic evidence for an interaction similar to that observed for Li. The Na^+–UF_4^- and K^+–UF_4^- stretching modes are expected to be at too low a frequency to be seen within the lower limit of the spectrometer at 400 cm^{-1}. The small frequency shifts of the two correlated bands below 500 cm^{-1}, witnessed by progressing from ^{6}Li to K, support the contention that they arise from U–F stretching modes. Trapping ^{7}Li with UF_4 in a nitrogen matrix provided no additional insight into the band positions of Li^+,UF_4^-. Absorptions at 467.0 and 453.0 cm^{-1} may be correlated with those found at 492.3 and 477.8 cm^{-1} in argon, but the Li^+–UF_4^- frequency was not apparent, either because of low intensity or concealment by the UF_4 region. The spectrum of the product species in the nitrogen medium tended to be broad and ill resolved.

UF_6 + *Alkali Metals.*—The reactions of alkali metals with UF_6 in argon matrices produced the i.r. spectra shown in Figure 2. Some possible relations between the bands of the several systems are given in Table 1, in which correlated bands are assumed to arise from similar structures.

TABLE 1

UF_6 + Alkali metals

^{6}Li	^{7}Li	Na	Cs
(*a*) M^+ and $[UF_6]^-$ Free ions			
520.7	520.8	520.2	520.1
		525.4	526.3
(*b*) M^+,UF_6^- Contact pair			
446.1	444.8	449.9	
506.7	506.0		
525.5	526.2	521.9	
549.6	548.2	538.7	
570.8	569.6	557.2	
469.4(Li)	452.5(Li)		
(*c*) $2M^+$, UF_6^{2-} Dimetal contact pair			
408.1	411.3		
423.8	427.3		
		416.7	
			406.6
		433.8	
			417.7
		444.4	
			423.3
			426.8
			434.5
(*d*) Unassigned			
460.9	459.1		
		464.7	
			449.7
			457.7
			472.6
	504.7		
	556.7	545.7	537.1

A strong single new band common to all the systems and invariant in position among them occurs at 520 cm^{-1}, suggesting that this species is an isolated octahedral $[UF_6]^-$ anion essentially free from any metal-ion influence. Annealing tends to decrease the intensity of this band relative to others, lending support to the above assignment. In addition, a previous solid-state spectroscopic study of Cs[UF_6] has given 503 cm^{-1} as the ν_3 stretching frequency.[9] The discrepancy of 17 cm^{-1} can be attributed to solid-state effects. Closer to our value is the stretch at 526 cm^{-1} observed for [N_2H_6][UF_6]$_2$.[10]

Other bands at 444.8, 506.0, 526.2, 548.2, and 569.6 cm^{-1} formed with lithium are attributed to a single species and can be best explained by the assumption of a Li^+,UF_6^- contact pair in which the lithium serves as a

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[7] A. Buchler and J. B. Berkowitz-Mattuck, *Adv. High-temperature Chem.*, 1967, **1**, 129.

[8] S. J. Cyvin, B. N. Cyvin, D. Bhogeswara Rao, and A. Snelson, *Z. anorg. Chem.*, 1971, **380**, 212.

[9] M. J. Reisfeld and G. A. Crosby, *Inorg. Chem.*, 1965, **4**, 65.

[10] B. Frlec and H. Hyman, *Inorg. Chem.*, 1967, **6**, 2233.

bridge between two fluorines. The resulting C_{2v} symmetry would have the effect of activating the previously i.r.-inactive A_{1g} stretching mode, splitting and activating the degenerate E_{1g} mode, and splitting the degeneracy of the T_{1u} stretching mode to give six expected bands. Bands derived from the symmetric modes of octahedral symmetry are expected to be weak, while those originating from previously active modes under O_h symmetry are expected to be more intense. Hence, fewer absorptions than the maximum predicted are likely to be actually observed, as in the case with the present work, in which five are visible in the Li spectra. The frequencies expected to have low oscillator strength consist of an A_1 mode and an $A_1 + B_2$ set, grouped according to their respective origins in i.r.-inactive O_h, A_{1g}, and E_g modes. As one moves from a ^{6}Li to a ^{7}Li system a shift of the band of ^{6}Li at 469.4 cm^{-1} to 452.5 cm^{-1} is evident (Figure 3), indicating that this band involves a lithium stretching mode, in agreement with expectations based on a C_{2v} stretching model. However, one would expect to see two lithium stretching modes for the proposed model. The other band is probably below our lower limit of 400 cm^{-1} based on frequency differences of over 100 cm^{-1} for similar difluoride-bridged systems.[8] The shift of the band of ^{6}Li at 469.4 cm^{-1} seems to rob the band at 506.7 cm^{-1} of intensity, while contributing to the intensity of the band at 444.8 cm^{-1}. This intensification of one absorption by another arises by a coupling mechanism among vibrational modes of the same molecule. In general, modes close to each other in frequency will couple more strongly than modes with greatly separated frequencies. That the ^{6}Li mode couples with the mode at 506.7 cm^{-1}, intensifying it, is reasonable if one considers that both the M–F stretching frequencies are of the proper symmetry, A_1 and B_2, to permit coupling with a low-intensity U–F mode. Only like-symmetry modes will couple, thus precluding interaction between an M–F B_2 mode and a U–F A_1 mode and *vice versa*. The same mechanism intensifies the peak at 444.8 cm^{-1} in the ^{7}Li system, at the expense of the peak at 506.7 cm^{-1}.

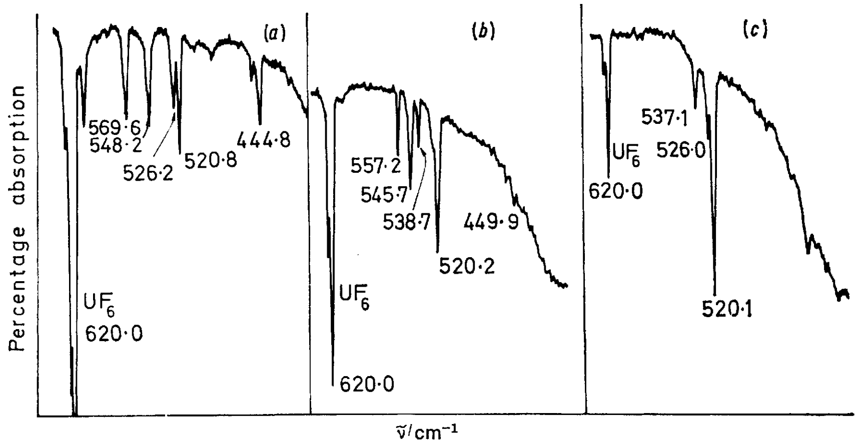

FIGURE 2 Infrared spectra of M–UF_6 reaction products in argon matrices: M = ^{7}Li (*a*), Na (*b*), and Cs (*c*)

When Na is used in place of Li a new band at 545.7 cm^{-1} is found between the two bands at 557.2 and 538.7 cm^{-1} which are correlated to those at 569.6 and 548.2 cm^{-1} in the lithium system. The region below 520 cm^{-1} lacks one of the bands seen for Li, displaying a weak absorption at 449.9 cm^{-1} which is believed to arise from the C_{2v} monosodium product. The presence of this peak at low sodium concentrations lends support to the foregoing conclusion. We may suppose that in the lithium system the bands below 520 cm^{-1} gain intensity both from interaction with the lithium stretching mode and the more perturbing nature of the smaller polarizing lithium. With Na, the stretching frequency of the alkali

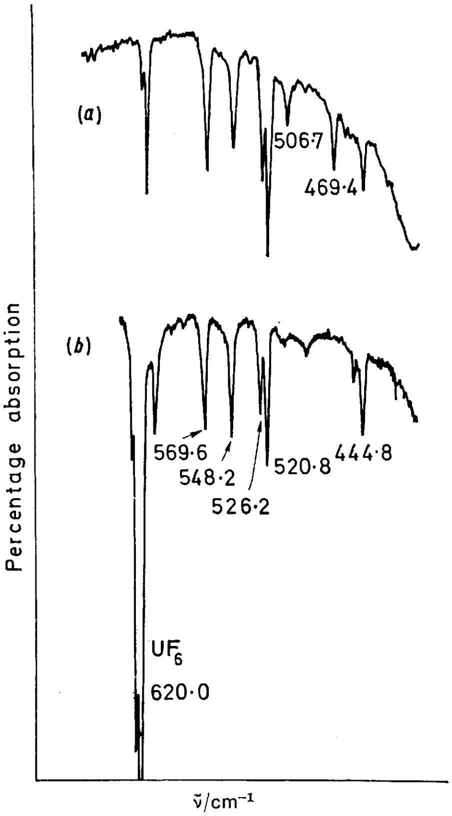

FIGURE 3 Infrared spectra of (*a*) ^{6}Li–UF_6 and (*b*) ^{7}Li–UF_6 in argon matrices

metal is too distant from the lower U–F stretching frequencies for interaction to occur. In addition, sodium is less polarizing than lithium, therefore the splitting of the triply degenerate stretching mode should decrease. This is borne out by the disappearance of one of the five bands, and the diminutive strength of that at 449.9 cm^{-1}.

Even less detail is to be seen in the spectra of the Cs–UF$_6$ system. The bands attributed to a C_{2v} bridging structure in the lithium and sodium cases are not evident here. The larger size and lower polarizing ability of Cs probably account for the absence of an interaction strong enough to remove the degeneracy of some modes and activate others. The $[UF_6]^-$ ion is not reduced in symmetry by Cs in the same manner as was observed in the lithium and sodium cases, leaving the feature at 520 cm^{-1} as the predominant one. However, a new single band is present at 737.1 cm^{-1} which seems to be correlated with the one previously referred to at 545.7 cm^{-1} in the sodium system. This particular absorption is not seen in Li–UF$_6$ systems on initial trapping and i.r. scanning. However, on annealing, bands at 556.7 and 504.7 cm^{-1} do appear in the lithium systems (Figure 4). The band at 556.7 cm^{-1} is believed to be correlated with those at 545.7 and 537.1 cm^{-1} for Na and Cs respectively. The particular species represented by these absorptions seems to gain stability as one progresses from Li to Cs. For Li, only annealing produces the species, whereas for Cs the species occurs without annealing and in the absence of the bands attributed to a C_{2v} structure. The frequency of these bands decreases from Li to Cs, possibly indicating a greater degree of reduction. Annealing strongly intensifies the band at 545.7 cm^{-1} in the sodium system while having little effect on that at 537.1 cm^{-1} in the caesium system. The positions are too high to be attributable to alkali-metal stretching modes or the $[UF_6]^{2-}$ species, but may arise from $[UF_6]^-$ in a different matrix environment.

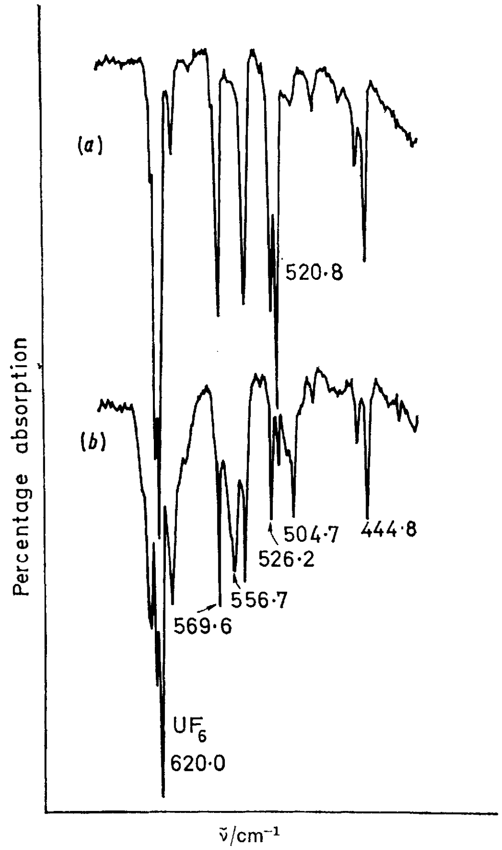

FIGURE 4 Growth of new bands on annealing of ^{7}Li–UF$_6$ trapped in argon: (*a*) before annealing, (*b*) after annealing

A weak band at 525.4 cm^{-1} decreases on annealing the Na–UF$_6$ system while one at 526.3 cm^{-1} in the Cs–UF$_6$ system disappears. The absorption positions at 525.5 and 526.2 cm^{-1} in the ^{6}Li and ^{7}Li systems which were assigned to the C_{2v} structure do not behave similarly and are much sharper and stronger. They do, however, have shoulders which may be representative of the same species giving rise to the bands at 525.4 and 526.3 cm^{-1} with Na and Cs. A tentative assignment of the bands at 525.4 (Na) and 526.3 cm^{-1} (Cs) to matrix site effects is not unreasonable, although speculative.

TABLE 2

UF_4 + Alkali-metal fluorides

	NaF	KF	CsF
(*a*) M$^+$, UF$_5$$^-$ Contact pair *			
			439.3
			447.7
	464.2	447.3	454.0
		453.3	457.0
	503.8		491.5
	507.1		497.5
	509.8	*502.8*	*501.0*
			506.1
(*b*) 2M$^+$, UF$_6$$^{2-}$ Dimetal contact pair			
	433.8		
		412.2	
	437.8		
		419.5	
	442.7		
		422.5	
			407.2
		431.3	
			418.2
			423.5
			427.1
			434.9
(*c*) Unassigned			
		482.2	480.2

* The most intense bands are in italics.

The lower-frequency peaks which gain intensity at higher alkali-metal concentrations and after matrix annealing are listed in Table 1. Assignments in this region are difficult owing to the greater number of absorptions and the greater possible variety of products as polymers and multiple-metal species. The presence of dimetal $[UF_6]^{2-}$ species can be hypothesized on the basis of concentration and annealing studies. In addition, as will be expanded below, alkali-metal fluoride–uranium tetrafluoride systems give similar bands in many of the same positions. Solid-state spectra of $K_2[UF_6]$ exhibit a

ν_3 absorption at 401 cm^{-1},[11] which, although somewhat below our results, indicates the region in which these bands are to be expected. Besides the free ion and the monometal contact species, several possible geometrical permutations exist for the dimetal contact pair. On the basis of similarity to absorptions in the MF–UF_4 systems (Table 2), assignments to the dimetal contact pair $2M^+,UF_6^{2-}$ are made in Table 1. There is a disparity between the lithium isotope bands in Table 1 of several cm^{-1} due to the broadness of these bands which may reflect a series of matrix sites close to each other in energy. The data suggest that in each system the same species is formed but by a different mechanism, *i.e.* by addition of alkali metal to UF_6 or by addition of alkali-metal fluoride to UF_4. The latter mechanism is believed to produce only contact species through a process in which the metal is involved in the transition states intermediate to $[UF_6]^{2-}$, while the former is believed to be capable of producing an M^+,UF_6^{2-} species in which only one metal atom is in contact with $[UF_6]^{2-}$, in addition to the dimetal contact molecule. This M^+,UF_6^{2-} product would arise by electron transfer from a remote metal atom, followed by further reduction by a proximate metal donor. Since the MF–UF_4 spectra are only expected to exhibit dimetal contact species, the matching bands in the M–UF_6 species are also believed to represent dimetal contact species. The remaining bands in Table 1 are unassigned.

UF_4 + *Alkali-metal Fluorides*.—Co-condensation of the alkali-metal fluorides NaF, KF, and CsF with UF_4 yielded matrices whose spectra showed an abundance of new bands as in Figure 5. Possible products are M^+,UF_5^- and $2M^+,UF_6^{2-}$ both species of which have been shown to exist on a macroscopic scale,[11,12] but for which isolated molecular i.r. spectra are lacking.

In Table 2 we have attempted to correlate bands among the several reactions on the basis of their behaviour on annealing. Addition of one NaF molecule to one UF_4 molecule is expected to produce the Na^+,UF_5^- contact pair. A C_{4v} structure may be hypothesized, in which the fluorine atoms are disposed in a manner similar to that of UF_5,[4,13] and the metal occupies an axial position above the axial fluorine. The band sets assigned to $[UF_5]^-$ are listed in Table 2 for the three alkali-metal fluorides used. A band at 470.7 cm^{-1} in the NaF–UF_4 system is observed to be also present in spectra of reactions of sodium metal with UF_4: it arises from reaction with metallic sodium produced by reduction of NaF in the furnace. The third band expected for a C_{4v} $[UF_5]^-$ structure may be too weak to be seen, as was supposed in the UF_5 case. The relative intensities of the doublets resemble those of the UF_5 spectra recorded earlier.[3,4] In the spectra of each of the MF–UF_4 reactions the $[UF_5]^-$ doublets show multiplicity attributed to small differences in geometry imposed by matrix site effects. These absorptions are grouped together in Table 2, the most intense band being in italics. A band in the CsF–UF_4 system at 480.2 cm^{-1} is believed to be related to the relatively weaker band at 482.1 cm^{-1} in the KF–UF_4 spectrum. This absorption is not apparent in the NaF–UF_4 spectrum, thus establishing a trend which indicates that the species represented by it forms readily in the CsF system, less readily in the KF system, and not at all in the NaF system. This may arise from a different geometry of M^+,UF_5^- for which the remaining bands are too weak to be seen.

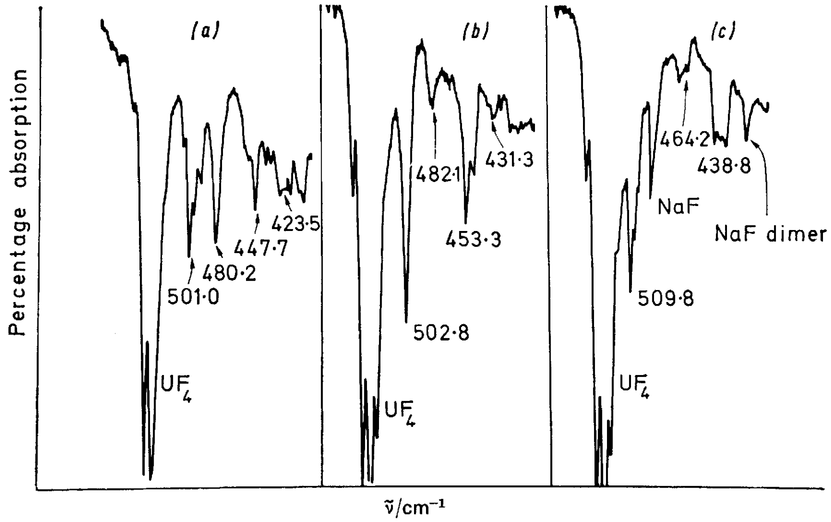

FIGURE 5 Infrared spectra of MF–UF_4 systems in argon matrices: M = Cs (*a*), K (*b*), and Na (*c*)

A band system below 437 cm^{-1} in the UF_4–CsF spectrum (Table 2), similar to that observed in matrix reactions of UF_6 with Cs mentioned above, is believed to represent the species $2Cs^+,UF_6^{2-}$. This set of bands is not present in spectra taken at low CsF concentrations and grows in intensity on annealing, lending further support to the above assignment. Band systems below

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[11] I. V. Tananaev, N. P. Galkin, G. S. Savchenko, and V. M. Sutyagin, *Zhur. neorg. Khim.*, 1962, **7**, 1675.

[12] K. Ohwada, *J. Chem. Phys.*, 1973, **58**, 4051.

[13] J. Krohn, W. B. Person, and J. Overend, *J. Chem. Phys.*, 1976, **65**, 969.

436 and 445 cm^{-1} in the KF– and NaF–UF_4 systems, respectively, exhibit similar behaviour and are assigned to the $2M^+,UF_6^{2-}$ contact pairs. The band at 417.0 cm^{-1} in the NaF system has previously been assigned to the linear dimer of NaF.[14]

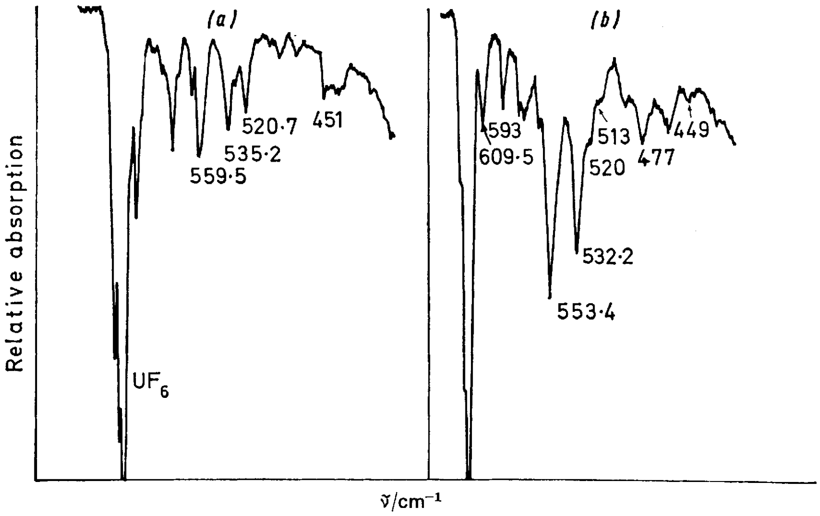

FIGURE 6 Infrared spectra of MF–UF_6 systems in argon matrices: M = K (*a*) and Cs (*b*)

A progressive red shift can be discerned for the M^+,UF_5^- bands in going from M = Na to Cs, reflecting the increasing electron density on $[UF_5]^-$ as the alkali metal becomes less electronegative.

UF_6 + *Alkali-metal Fluorides*.—No reaction was observed for the NaF–UF_6 system apart from the previously described Na–UF_6 reaction, the sodium atoms for which were probably furnished by reduction of NaF by the carbon furnace liner. In the KF–UF_6 experiment, however, two strong bands at 559.5 and 535.2 cm^{-1} appeared which may be tentatively attributed to a K^+,UF_7^- species (Figure 6). The band at 579.8 cm^{-1} arises from an unidentified impurity. A band of medium intensity at 457.5 cm^{-1} is also believed to arise from a $K[UF_7]$ product.

Caesium fluoride reacts with UF_6 in argon to yield strong features at 553.4 and 532.2 cm^{-1} (Figure 6), similar to those observed in the KF–UF_6 system. On annealing, bands at 513 and 477 cm^{-1} grow in intensity (Figure 7). The former pair, again, is assigned to the $[UF_7]^-$ species. The latter pair of bands which exhibits growth on annealing could represent either a $2K^+,UF_8^{2-}$ product or a polymeric species. Other bands at 457 and 491 cm^{-1} may belong to the set assigned to K^+,UF_7^-; their origin in higher-order products is improbable based on their relative insensitivity to annealing. Rather, they appear to grow only because they flank the band at 477 cm^{-1}. Under severe annealing, *i.e.* six successive annealings each of 4 min at 30 K, the band system centred at 477 cm^{-1} and the band at 513 cm^{-1} became increasingly strong and broad, possibly due to formation of crystalline non-isolated products. Bands at 520 cm^{-1} in both spectra are due to alkali-metal reactions from reduced alkali-metal fluorides which have reacted to form $[UF_6]^-$.

Both M^+,UF_7^- and $2M^+,UF_8^{2-}$ have been prepared on a macroscopic scale, and some vibrational data, both in the solid and solution states, have been reported.[15] The bands observed in the matrix for the KF–UF_6 experiments seem to correspond to those observed at 456 and 535 cm^{-1} in the acetonitrile solution work, with

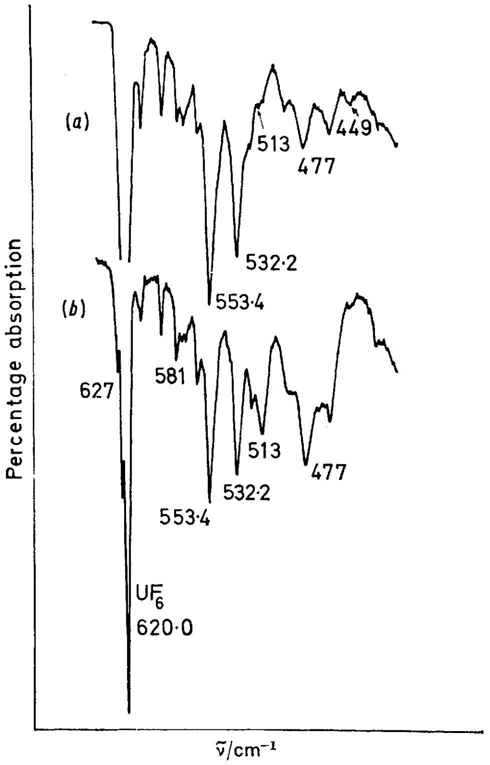

FIGURE 7 Growth of bands on annealing of the CsF–UF_6 system in an argon matrix: (*a*) before annealing, (*b*) after annealing

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[14] Z. K. Ismail, R. H. Hauge, and J. L. Margrave, *J. Inorg. Nuclear Chem.*, 1973, **35**, 3201.

[15] R. Bougon, P. Charpin, J. P. Desmoulin, and J. G. Malm, *Inorg. Chem.*, 1976, **15**, 2352.

the weak band at 617 cm^{-1} of ref. 15 possibly concealed beneath that of UF_6. Of particular interest is the band at 559.5 cm^{-1} which is seen in the matrix work but is absent from the solution spectrum. However, consideration of the low-temperature (−140 °C) solid-state Raman spectrum reported in ref. 15 suggests that a band at 545 cm^{-1}, which becomes Raman active in the low-temperature modification, might be correlated with the matrix feature at 559.5 cm^{-1}. In the low-symmetry (C_{2v} or below) form postulated for $[UF_7]^-$, Raman and i.r. activity are not mutually exclusive, indeed many modes are expected to be simultaneously active. A red shift from the matrix to the solid is also to be expected. In the crystalline state the reduction of symmetry is attributed to a decrease in thermal averaging of the fluorines and crystal-imposed symmetry, while $[UF_7]^-$ in the matrix is expected to be perturbed by the presence of the alkali metal. No i.r. spectra of $Cs[UF_7]$ in solution are available, but this system is expected to behave in a similar manner.

TABLE 3

Approximate gas-phase stretching frequencies ($\tilde{\nu}$/cm^{-1}) of uranium fluoride ions together with matrix frequencies of neutral uranium fluoride species

$[UF_4]^-$	UF_4 [a]	$[UF_5]^-$	UF_5 [b]	$[UF_6]^-$	UF_6 [c]	$[UF_7]^-$
465	532 (ν_3)	448	560	520 (ν_3)	620 (ν_3)	532
480		501	584			553
			647			

[a] Ref. 2. [b] Ref. 3 and 4. [c] Ref. 5.

Solid-state i.r. spectra for $Cs_2[UF_8]$ exhibit two bands at 464 and 508 cm^{-1} which are sharp and strong, respectively, and two bands at 578 and 586 cm^{-1} which are weak. The two bands in the CsF–UF_6 system which intensify on annealing may be tentatively assigned to the $2Cs^+$,-$UF_8{}^{2-}$ species on the basis of their proximity to the reported bands. The remaining weak features were not observed in the matrix spectra.

Conclusions.—It can be seen from the data that reduction of each of the uranium fluorides caused a shift to lower frequencies, *i.e.* a decrease of the force constant. This effect has been discussed in terms of the ionic character of the U–F bonds, an increase in ionic character resulting in a decrease in force constant.[16] Moreover, within any given series of alkali metal or alkali-metal fluoride reactions, the U–F frequencies of the reaction product usually decrease when descending the Periodic Table, reflecting the decrease in electronegativity of the metal. It is not intended to imply that the strength of the bonds decreases, as the force constant may decrease as a consequence of a broader valley of an ionic potential curve. Decreases in splittings of degenerate bands are also evident as heavier, less polarizing, alkali metals are used. On the basis of their intensity, the bands at 570.8, 548.8, and 526.2 (^7Li–UF_6) and 557.9, 539.2, and 521.9 cm^{-1} (Na–UF_6) are believed to be derived from the T_{1u} i.r.-active mode of a pure octahedral configuration. These three bands exhibit compression as well as a red shift on progressing from Li to Na. In the M–UF_4 systems, the bands are thought of as being derived from an i.r.-active T_2 mode of a tetrahedral configuration, again based on an intensity argument. In this case, however, the separation between the bands does not change appreciably on going from Li to K. This suggests that the metal atom is not responsible for the major splitting; more likely, the extra electron density is perturbing the structure from T_d symmetry and thus the free $[UF_4]^-$ ion is not expected to have tetrahedral symmetry.

The observation of an invariant band at 520 cm^{-1} among several M–UF_6 systems is explained as arising from a geometry in which the metal is separated by several angstroms from the $[UF_6]^-$ species by argon atoms. This distance is not great enough to prevent reduction of the UF_6. Electron transfer between separated atoms in molecular beams has been well established for alkali metal–halogen systems whereby the transfer occurs across a separation of 2—3 Å by a process known as ' harpooning '.[17] It can be pointed out that the electron affinity of UF_6 is 125 kcal mol^{-1},[18] which is much greater than that of the Cl atom (87.3 kcal mol^{-1}).[19] A similar type of mechanism to form separated $[UF_6]^-$ and M^+ is likely. In addition, the ionization potential of all alkali-metal atoms in solid argon is expected to be less than 125 kcal mol^{-1}; thus electron transfer at large distances is energetically allowed. A second electron cannot be added as easily, however, and a contact interaction may be required to form $2M^+,UF_6{}^{2-}$. Table 3 presents absorption positions which are expected to be close to free-ion gas-phase values for the uranium fluoride anionic species listed. Values were selected on the basis of invariance to metal species and on the assumption that the caesium fluoride- and potassium fluoride–uranium fluoride systems will give U–F frequencies closest to free-ion gas-phase values. Matrix frequencies are expected to be within 10 cm^{-1} of gas-phase frequencies, as demonstrated by UF_6 which exhibits a 6 cm^{-1} red shift from the gas phase to the matrix for ν_3.

The assumption of an octahedral $[UF_6]^-$ anion can be rationalized by a consideration of the orbital energy-level diagram of octahedral UF_6.[20] The lowest-lying unoccupied metal orbital is one of a_u symmetry, for which

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no Jahn–Teller distortion is expected following occupancy by the one electron from $[UF_6]^-$. The $[UCl_6]^{2-}$ anion, also possessing a non-degenerate ground state, has been shown to be essentially octahedral in solution.[21] For this molecule, however, there is a small pseudo-Jahn–Teller effect arising from vibronic coupling of the ground state with a degenerate excited state. This effect is not believed to be significant for analogous fluoro-complexes since the excited states are further removed from the ground state by the higher ligand-field strength of F^-. It must be remembered that, according to the Pauling criterion of percentage ionic character,[19] the electron added to UF_6 will not reside exclusively on the metal, but will distribute itself among the six fluorine atoms and uranium to give in this case a negative charge of 0.12 on each fluorine and 0.28 on the uranium. This rough calculation serves as nothing more than an illustration of a possible apportioning of the added electron.

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