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ELECTRONIC SOLUTION SPECTRA FOR URANIUM AND NEPTUNIUM IN
OXIDATION STATES (III) TO (VI) IN ANHYDROUS HYDROGEN FLUORIDE

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DISCLAIMER

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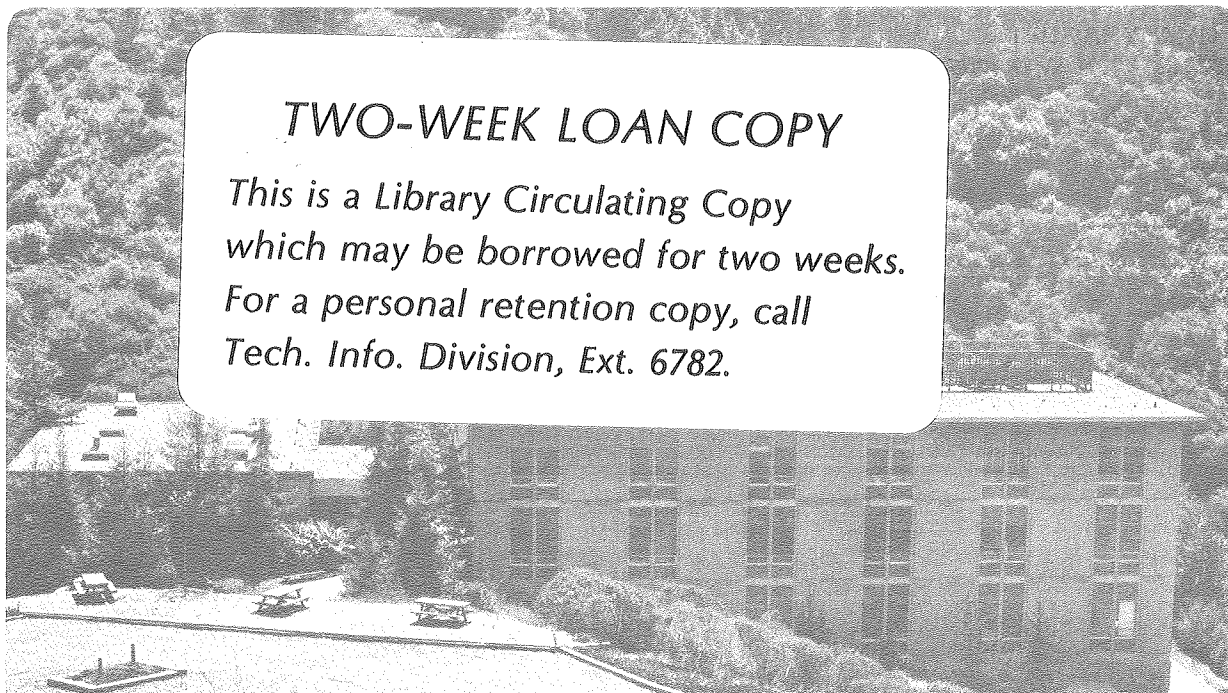M. Baluka[†], N. Edelstein and T.A. O'Donnell[††]

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ABSTRACT

Spectra have been recorded for solutions in anhydrous hydrogen fluoride (AHF) of uranium and neptunium in oxidation states (III) to (VI). The spectra for U(III), Np(III) and Np(IV) in AHF are very similar to those in acidified aqueous solution, but that for U(IV) suggests that the cationic species is UF_2^{2+}. The AHF spectra for the elements in oxidation states (V) and (VI) are not comparable with those of the formally analogous aqueous solutions, where the elements exist as well-defined dioxo-cations. However, the AHF spectra can be related to spectra in the gas phase, in the solid state or in non-aqueous solvents for each element in its appropriate oxidation state.

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INTRODUCTION

Gillespie[1] and others have shown that superacid media are particularly effective in producing stable solutions of relatively simple cationic species, frequently with charges much higher than those which can exist in water. Thus entities such as S_8^{2+}, Se_4^{2+} and I_2^+ exist in superacid media, whereas related species in aqueous solution are oxo- or hydroxo-acids or anions. Anhydrous hydrogen fluoride (AHF), as a solvent, is extremely acidic and its acidity is increased markedly by addition of simple Lewis acids such as BF_3, AsF_5, or SbF_5. In this solvent, solvation of cations and fluoro-complexation can occur but there is no possible process which corresponds with oxo-complexation which accounts for much of the complexity in speciation in aqueous solutions. Furthermore, most anions are solvolysed or protonated in AHF. The only anions other than fluoride which do exist in AHF are those derived from the Lewis acids of the systems, e.g. BF_4^-, AsF_6^- and SbF_6^-, and it is shown on spectroscopic grounds in this work that they appear to have no observable complexing effect on cations in AHF solution. There is some experimental evidence that fluoro-complexation of cations in AHF is not as strong as hydroxo-complexation in water and the summation of all of these considerations has led to the postulation that intrinsically AHF should provide simpler cationic speciation than does water.[2]

There are some difficulties in making valid comparisons of spectra in aqueous solution of uranium and neptunium in oxidation states (III) to (VI). U(III) is relatively unstable in aqueous

solution, reducing water. Spectra of U(IV) have been recorded
in solutions strongly acidified with $HClO_4$, so that hydrolysis is
minimized and there is no complexation by species such as halides
or the common oxo-anions. U(V), formally present as UO_2^+, dis-
proportionates very easily to U(IV) and U(VI), the latter being
hydrolyzed to UO_2^{2+}, the spectrum of which is due to a charge
transfer band in the near ultra violet. Np(III) and Np(IV)
spectra can be recorded reliably in acidified non-complexing solution.
Np(V), existing as NpO_2^+, has been regarded as surprisingly stable
in aqueous solution. This stability will be discussed later in
this paper. Np(VI) is usually in solution as NpO_2^{2+}. The spectra
of these di-oxo species of U and Np cannot be related to a simple
aquated cationic species as is done for the lower oxidation states
of these elements.

Until fairly recently, it has not been possible to investigate
spectral or other properties in AHF solution of d- or f-transition
elements over a wide range of oxidation states. As indicated above,
most anions are solvolysed to fluoride and, further, fluorides of
transition metals in low oxidation states are sparingly soluble
in AHF. It is now possible to circumvent the problem of the
insolubility of low-oxidation state fluorides of heavy metals and
to study their cations in solution. The difluorides, NiF_2 and
CoF_2, when suspended in AHF and exposed to a pressure of about 2
atmospheres of BF_3, a relatively weak Lewis acid in HF, dissolved
within minutes to give concentrated solutions (up to 1M) and
electronic spectra were recorded.[3] These spectra indicate that

the solutions contain cations, solvated by HF molecules with the same coordination as in water. It appears that fluoride ions in the insoluble fluorine-bridged polymeric binary fluorides have been converted to BF_4^- anions which are then in solution as the counter-ions to the solvated cations.

Similar treatment of PrF_3 and NdF_3 with HF and BF_3 gave much less concentrated solutions (about 5×10^{-2}M) after many hours. Presumably, as the charge on the cation increases, the polymeric fluoride lattice, now more favoured energetically, is harder to disrupt to produce solvated ions. However, again the spectra[3] indicated formation of simple HF solvated cations, with BF_4^- counter-ions.

In the preliminary stages of the present work, application of BF_3 at 2 atmospheres pressure to a suspension of UF_4 in HF produced no discernible amounts of uranium(IV) in solution. These interactions of BF_3 in HF with di-, tri- and tetra-fluorides are consistent with the action of a relatively weak Lewis acid. Obviously, stronger Lewis acids such as SbF_5 and AsF_5 would be more likely to produce HF solutions of U(IV). These acids had not been used in the initial study[3] because they, unlike BF_3, are potential oxidants in HF and it was not known at that time whether they might oxidize Ni(II) or Co(II).

For dissolution of UF_4, AsF_5 was used initially as the Lewis acid and was maintained at a pressure of about 2 atmospheres over a stirred suspension of UF_4 in HF to provide over several days a green solution, the spectrum of which was recorded and is shown in Figure 1b. SbF_5 was also used subsequently as a Lewis acid to produce U(IV) solutions in

AHF and identical spectra were recorded.

Since UF_4 dissolved very slowly in HF-AsF_5 to give a solution only about 5×10^{-2}M in U(IV), it was decided to treat metallic uranium in the form of turnings with HF-AsF_5 in an attempt to achieve more rapid solution. This solution did become colored quite rapidly, being green in reflected light and red in transmitted light, the latter color indicating the possible presence of some U(III) in solution. This observation is in contrast to the situation in H_2O since aqueous solutions of U(III) require complexation by ligands such as chloride for reasonable stability and even those solutions gradually reduce water and form U(IV). The next step was to treat metallic uranium in HF with BF_3 at 2 atmospheres pressure. Within minutes the solution became pink and, after overnight stirring, was a strong magenta color and was about 0.1M in uranium. The UV-visible spectrum of this solution is shown in Figure 1a.

UF_5 suspended in AHF was treated with the two Lewis acids AsF_5 and SbF_5, to produce U(V) solutions. UF_6 is relatively soluble in AHF and spectra were recorded on the simple solution and on solutions containing AsF_5 and SbF_5. (See Figure 1c).

Solutions containing neptunium in oxidation states (III) to (VI) in the presence of the different Lewis acids were prepared essentially as described above for the uranium systems. As the acidity of the HF solutions was increased by addition of Lewis acids of increasing strength, the stability of solutions of the two hexafluorides decreased. The spectrum for a solution of Np(VI) in

$HF-SbF_5$ on standing for many hours changed progressively to that for
Np(V) and similar but less extensive reduction occurred to the U(VI)
system. There is now evidence[4] to suggest that strongly protonating
media leach unsaturated low molecular weight fractions from Kel-F to
provide reducing species in AHF solutions.

The work reported here allows a more comprehensive and valid
comparison of spectra in AHF of uranium and neptunium in oxidation
states (III) to (VI) than is possible in aqueous solutions. Spectro-
scopic evidence has been obtained to show that complexation of cations
in AHF by the fluoro-anions BF_4^-, AsF_6^- and SbF_6^- is insignificant.

EXPERIMENTAL SECTION

Preparation of Uranium and Neptunium Solutions

Oxidation State (III)

Treatment with $HF-BF_3$ of metallic uranium in the form of turnings,
which had extensive surface oxidation led to the formation of large
amounts of U(IV) as insoluble UF_4. Consequently a small cube (about
0.5g) of the metal and triply distilled HF (10 to 15 ml) were added
to a Kel-F trap fitted with a Kel-F valve and provided with a Teflon-
coated magnetic stirrer. BF_3, which has only small solubility in HF
at room temperature was applied until the total pressure in the trap
was 3 atmospheres, i.e. the vapor pressures of HF and BF_3 above the
liquid were approximately 1 atm. and 2 atm. respectively. Within
minutes, a pink color developed in the solution and this became a strong

magenta color overnight. There was some apparent formation of UF_4.
This is consistent with surface oxide on the metal providing a source
of U(IV), which cannot be held in solution by the weak Lewis acidity
of BF_3 and yields a precipitate of UF_4. Therefore, metallic uranium
was treated for a short time with HF and BF_3 or AsF_5. This procedure
removed the surface contaminants and some metal, and the resulting
solution was poured off. There was evidence in these preliminary steps
that U(III) solutions in HF reacted with the surface of relatively
new Kel-F traps. The remaining clean metal was treated with HF
and BF_3 and the solution filtered into a Kel-F trap, which had been
treated previously first with ClF_3 and, after careful removal of ClF_3,
with HF and H_2. Under these conditions magenta solutions of U(III)
in HF were obtained which were stable indefinitely. Weighing of the
trap and residue after removal of the HF and BF_3 indicated that the
solution was approximately 0.1M in U(III). AsF_5 at a partial pressure
of 2 atmospheres also gave a solution containing U(III).

Similar procedures produced stable solutions of neptunium(III).
In order to investigate spectroscopically the possible complexing
effects of BF_4^-, AsF_6^- and SbF_6^- in HF solution, the Lewis acids AsF_5
and SbF_5 were used to produce solutions of Np(III). AsF_5 was added
progressively until the partial pressure of AsF_5 in the system was
2 atmos., i.e. a solution approximately 5M in AsF_6 was formed (see
below). A concentrated solution (10M) of SbF_5 in HF was also used to
give a Np(III) solution.

Oxidation State (IV)

AsF$_5$ was applied to a suspension of UF$_4$ in a Kel-F tube, as above, until the total pressure became steady at 3 atmospheres. The Kel-F trap was weighed evacuated initially, and then after each addition of HF and AsF$_5$. Weight increments indicated that the solution was approximately 5M in AsF$_5$ (mostly as AsF$_6^-$) on equilibration.

After stirring for several days much green solid remained but the pale green supernatant solution was filtered through Teflon filter paper (Millipore Corporation) held in a Kel-F filter cartridge into another Kel-F trap. Weighing of the residue in this second trap after removal of HF and AsF$_5$ indicated that the solution was about 5×10^{-2}M in U(IV).

A green solution containing U(IV) was also produced with SbF$_5$ at a concentration of 3M.

Np(IV) solutions were prepared from NpF$_4$ using AsF$_5$ at a partial pressure of 2 atmos. and SbF$_5$ (10M in solution).

Oxidation State V.

UF$_5$ and NpF$_5$ was prepared by reduction of UF$_6$ and NpF$_6$ with PF$_3$ at -78°C[5,6]. The solids, suspended in stirred HF, were treated with AsF$_5$ at a partial pressure of 1.5 atmos. and with SbF$_5$ at concentrations of 0.4M, 1M and 10M.

Oxidation State VI

The hexafluorides are readily soluble in AHF at room temperature.[7] In order to make comparisons with those uranium fluorides which needed

Lewis acids to cause dissolution, the UF_6 solution was treated with AsF_5 (1.5 atmos.) and SbF_5 (10M).

NpF_6 was prepared by the simplified method reported for the preparation of RuF_6 and PuF_6.[8] A solution about 0.15M in the hexafluoride was prepared and treated with BF_3 (2 atmos.), AsF_5 (2 atmos.) and SbF_5 (10M).

Measurements

The cells and procedures were essentially as reported earlier,[3] and a Cary 17 spectrophotometer was used for recording spectra.

RESULTS AND DISCUSSION

Aqueous spectra are available for comparison with the corresponding ones in AHF for the simple aquo-cations of U(III) and U(IV)[9] and for Np(III) and Np(IV)[10] in strongly acid non-complexing solutions and these have been compared with the AHF spectra (Figs. 1 and 2) of the same elements in oxidation states (III) and (IV).

Cohen and Carnall[9] recorded the aqueous spectrum for U(III) after reduction of U(VI) to U(III) in 1.0M $DClO_4$ in a spectral cell. As had been found with the spectra of tripositive lanthanides in AHF,[3] similarities between the aqueous and AHF spectra for U(III) are very marked. The major difference in this case is that the relative intensities of the two principal bands in each solvent are reversed. The positions of the bands for each solvent are given in Table I. Peak positions are shifted by about 20 - 40 nm to higher

energies in passing from H_2O to AHF. The shifts to higher energies in moving from aqueous to AHF solutions are smaller for lanthanides (3-5 nm) but that for d-transition elements are very much larger (50-100 nm) and to lower energies.[3] The aqueous and AHF spectra are very similar to that recorded for U(III) in formic acid.[11,12]

The spectra for Np(III) and Np(IV) in AHF (Fig. 2) are very similar to those for Np(III) and Np(IV) in H_2O.[10] Again, there are relatively small shifts in peak positions to higher energies in AHF (see Table 2), although these are smaller for Np(IV) than for Np(III).

Although the AHF spectra for U(III), Np(III) and Np(IV) are very similar to the aqueous counterparts, the U(IV) spectrum in $HF-AsF_5$ is different than the spectrum recorded for U(IV) in 1M $DClO_4-D_2O$ by Cohen and Carnall,[9] the shifts in positions of major peaks being 100 nm or greater. Their spectrum was reproduced in $HClO_4$ medium by Stein and co-workers,[13] who then added aqueous HF progressively to their 0.03M U(IV) solution until the HF concentration was 0.080M, observing progressive changes in the spectra. They postulated the very marked shifts in peak positions and the development of vibrational fine structure in the range 400 - 650 nm indicated the formation of UF_2^{2+} as fluoride was added. They also showed that, as fluoride was added progressively to a 1M H_2SO_4 solution containing U(IV), similar spectral characteristics developed before the precipitation of a compound which was amorphous but which had a composition close to $UF_2SO_4 \cdot 2H_2O$. They ultimately crystallized $UF_2SO_4 \cdot 2H_2O$ from a solution initially 6M in H_2SO_4 and 0.9M in HF.

Figure 1b shows the spectrum for U(IV) in HF/AsF_5. It is remarkably similar to the spectrum marked E in Fig. 2 of the paper by Stein et al., i.e. the one postulated as being due to UF_2^{2+}; suggesting that the species UF_2^{2+}, which Stein et al. compare spectrally and in stability with NpO_2^+ and PuO_2^{2+}, is the dominant uranium-containing species in these HF solutions. A comparison of the vibrational fine structure for the two solutions is given in Table 3. Supporting evidence for this proposal is that the involatile green residue, obtained after evaporation of free HF and AsF_5 from the U(IV) solution and pumping at room temperature, showed a weight increase over the original weight of UF_4 which corresponded with the formation of a compound having the formula $UF_2(AsF_6)_2$.

It is interesting to speculate that the stability of the iso-electronic species UF_2^{2+}, NpO_2^+ and PuO_2^{2+} could provide a rationalization of an apparent paradox in the aqueous chemistry of U, Np and Pu in high oxidation states. It has long been recognized that Np(V), present as NpO_2^+, is very much more stable towards disproportionation than the corresponding dioxo-species for U and Pu. Assuming that two favoured species for U are UO_2^{2+} and UF_2^{2+} (in aqueous solutions containing fluoride), the inclusion of NpO_2^+ in the isoelectronic series could be used as a basis for consideration of the apparently anomalous stability of Np(V) in solution. On the other hand, there is nothing in the known solution chemistry of U(IV) and Np(IV) to suggest that the speciation of the two elements in the same oxidation state should be so different in AHF.

Figures 1 and 2 also give spectra for U(V), U(VI), Np(V) and Np(VI) in AHF in the presence of appropriate Lewis acids. Not surprisingly, these spectra are quite different from the formally analogous ones reported for aqueous solutions of these elements in oxidation states (V) and (VI) in which dioxo-cations are formed. The UO_2^{2+} entity is stable in AHF. When UO_2F_2 is dissolved in $HF-AsF_5$, the spectrum in the 340 - 350 nm region, although much better resolved, is very similar to that for UO_2^{2+} in aqueous $HClO_4$ solution and a strong Raman signal, characteristic of UO_2^{2+}, is obtained for the $HF-AsF_5$ solution.[14] Qualitatively, the present spectra resemble appropriate spectra of related solids or spectra in the gas phase or in those non-aqueous solvents in which the dioxo-cations are not formed. The spectrum of U(V) in acidic AHF is similar to those reported by Ryan[15] for U(V) in halo-complexes of U(V). As expected, there is no absorbance in the visible region or the near-UV by solutions of UF_6, the only spectral feature in the UV resulting from charge transfer. Earlier conductance and Raman spectroscopic studies have shown that UF_6 dissolves in AHF as the molecular entity.[7] The AHF solution spectrum for NpF_5 resembles that for a fluorocarbon mull of solid $CsNpF_6$[16] and that for NpF_6 in neutral HF or in HF containing the Lewis acid BF_3 is closely related to the gas phase spectrum.[17] AsF_5, a stronger Lewis acid than BF_3, could not be used reliably in AHF solutions of NpF_6 for the reasons given below.

UF_6 and NpF_6 both have reasonable solubility in neutral HF, whereas

the pentafluorides required the presence of a Lewis acid for dissolution. In order to make the spectra for both elements strictly comparable in all oxidation states, the three Lewis acids used in this study were added to both hexafluoride solutions. BF_3 had no effect on either spectrum. The UF_6 spectrum was unchanged by the addition of AsF_5 but the NpF_6 spectrum was made more complex. The addition of SbF_5, particularly in high concentration (10M) and on standing, caused the observed spectra to be very different from those for both hexafluorides. After about 1 day the spectrum for NpF_6-SbF_5-HF had changed to being almost identical with that for NpF_5-SbF_5-HF. As mentioned earlier, strongly acidic HF can protonate unsaturated material in Kel-F (presumably low molecular weight fractions of the polymer) and leach these from the Kel-F container into solution.[4] This material could then reduce Np(VI) to Np(V). This proposed behaviour is consistent with the spectroscopic observation in the present work that NpF_6 solutions were reduced more readily than UF_6 in SbF_5-HF solutions and that AsF_5-HF reduced Np(VI) but not U(VI). The known chemistry of actinide hexafluorides shows that NpF_6 is a stronger oxidant than UF_6.[18]

In the "Experimental Section" of this paper it was reported that solutions were prepared for both metals in a wide range of oxidation states using the three Lewis acids, BF_3, AsF_5 and SbF_5 with each system where possible, i.e. each of the solutions was prepared, whenever possible, containing the anions BF_4^-, AsF_6^- or SbF_6^- or the appropriate polymeric anions. Except for the specific chemical reduction referred to above for U(VI) and Np(VI) in highly acidic solutions, no significant spectroscopic differences were observed that could be attributed to the

counter anions in any series of spectra, i.e. complexation by fluoro-anions is not significant, nor is there any detectable fluoro-complexation of the actinide ions in moving from the fairly acidic $HF-AsF_5$ solutions to the weakly acidic $HF-BF_3$ solutions. Such effects, although small, have been observed for spectra in AHF solution of differing acidity for cations of d-transition metals.[4]

In order to make the actinide spectra as strictly comparable as possible and to eliminate effects due to introduction of impurities into $HF-SbF_5$ solutions, all spectra given in Figs. 1 and 2 are in $HF-AsF_5$, except for Np(VI) which is susceptible to reaction with the impurities leached from the Kel-F by $HF-AsF_5$. In this case the $HF-BF_3$ is given.

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Table 1

Positions of Major Peaks in Spectra of U(III) in
H_2O and AHF (nm)

U^{3+} in 1M DCl_4-D_2O	U^{3+} in AsF_5-HF
1219	1198
1064	1010
	967
967	942
898	876
876	844
	820
	700
636	591
615	558
	520
522	503
507	482
	477
	442
451	429
	411

Table 2

Positions of Major Peaks in Spectra of
Np(III) in H_2O and AHF (nm)

Np^{3+} in 2M $HClO_4$-H_2O	Np^{3+} in AsF_5-HF
1363	1338
991	966
849	829
786	760
660	643
600	586
552	544

Table 3

Positions of Vibrational Fine Structure in U(IV) Solutions (nm)

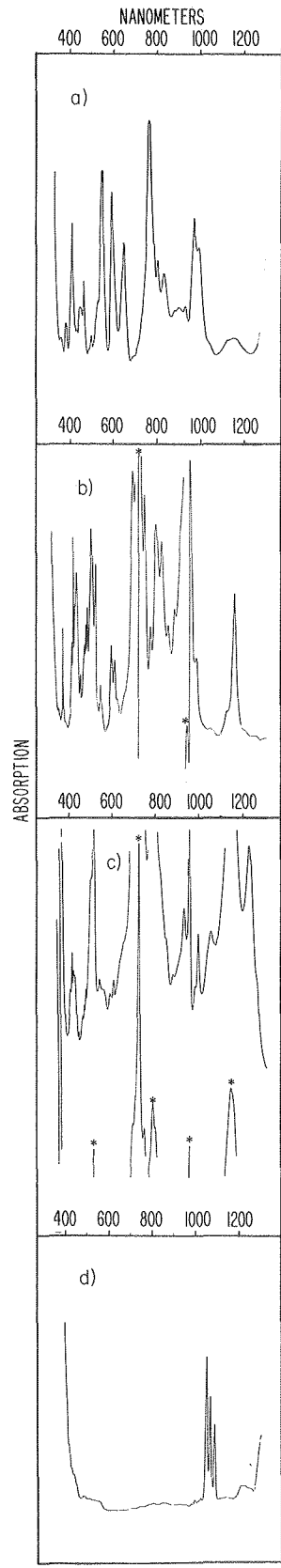| U^{4+} in AsF_5-HF	.03MU^{4+} in 1M $HClO_4$ and .08 M HF*
390	405
420	426
439	452
458	469
478	486
	495
506	525
560	590
600	610
650	626
	642

*From Reference 14

Figure Captions

Figure 1. Optical spectra of a) U(III)/AHF and AsF_5 (2 atmos.)

b) U(IV)/AHF and AsF_5 (2 atmos.) c) UF_5/AHF and AsF_5

(1.5 atmos.) d) UF_6/AHF and AsF_5 (1.5 atmos.).

Figure 2. Optical spectra of a) Np(III)/AHF and AsF_5 (2 atmos.)

b) Np(IV)/AHF and AsF_5 (2 atmos.) c) NpF_5/AHF and AsF_5

(2 atmos.) d) NpF_6/AHF and BF_3 (2 atmos.) . The *

above certain peaks represent absorption occurring on

the second absorption scale (OD between 1 and 2) of the

Cary 17.

Figure 1

Figure 2