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

Permalink
https://escholarship.org/uc/item/95m7p211

Author
Baluka, M.

Publication Date
2013-09-09
ELECTRONIC SOLUTION SPECTRA FOR URANIUM AND NEPTUNIUM IN OXIDATION STATES (III) TO (VI) IN ANHYDROUS HYDROGEN FLUORIDE

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

October 1980
DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.
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.

---

†Present address: Institute for Low Temperature Research, Polish Academy of Sciences, Wroclaw, Poland

‡‡Present address: University of Melbourne, Victoria, Australia
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 HClO₄, 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 UO₂⁺, disproportionates very easily to U(IV) and U(VI), the latter being hydrolyzed to UO₂²⁺, 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 NpO₂⁺, 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 NpO₂²⁺. 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, NiF₂ and CoF₂, when suspended in AHF and exposed to a pressure of about 2 atmospheres of BF₃, a relatively weak Lewis acid in HF, dissolved within minutes to give concentrated solutions (up to 1M) and electronic spectra were recorded. 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 $5 \times 10^{-2}$ 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 x $10^{-2}$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$_2$O 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\textsubscript{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\textsuperscript{(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. Spectroscopic evidence has been obtained to show that complexation of cations in AHF by the fluoro-anions BF\textsubscript{4}\textsuperscript{-}, AsF\textsubscript{6}\textsuperscript{-} and SbF\textsubscript{6}\textsuperscript{-} is insignificant.

EXPERIMENTAL SECTION

Preparation of Uranium and Neptunium Solutions

Oxidation State (III)

Treatment with HF-BF\textsubscript{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\textsubscript{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\textsubscript{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\textsubscript{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 x 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 UF₆ solution was treated with AsF₅ (1.5 atmos.) and SbF₅ (10M).

NpF₆ was prepared by the simplified method reported for the preparation of RuF₆ and PuF₆.(8) A solution about 0.15M in the hexafluoride was prepared and treated with BF₃ (2 atmos.), AsF₅ (2 atmos.) and SbF₅ (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 DCI0₄ in a spectral cell. As had been found with the spectra of tripotent 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 H₂O 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. The aqueous and AHF spectra are very similar to that recorded for U(III) in formic acid.

The spectra for Np(III) and Np(IV) in AHF (Fig. 2) are very similar to those for Np(III) and Np(IV) in H₂O. 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-AsF₅ is different than the spectrum recorded for U(IV) in 1M DCl0₄-D₂O by Cohen and Carnall, the shifts in positions of major peaks being 100 nm or greater. Their spectrum was reproduced in HCl0₄ medium by Stein and co-workers, 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 UF₂²⁺ as fluoride was added. They also showed that, as fluoride was added progressively to a 1M H₂SO₄ solution containing U(IV), similar spectral characteristics developed before the precipitation of a compound which was amorphous but which had a composition close to UF₂SO₄.2H₂O. They ultimately crystallized UF₂SO₄.2H₂O from a solution initially 6M in H₂SO₄ 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 isoelectronic 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 $\text{UO}_2^{2+}$ entity is stable in AHF. When $\text{UO}_2\text{F}_2$ is dissolved in HF-AsF$_5$, the spectrum in the 340 - 350 nm region, although much better resolved, is very similar to that for $\text{UO}_2^{2+}$ in aqueous HClO$_4$ solution and a strong Raman signal, characteristic of $\text{UO}_2^{2+}$, 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. BF₃ had no effect on either spectrum. The UF₆ spectrum was unchanged by the addition of AsF₅ but the NpF₆ spectrum was made more complex. The addition of SbF₅, 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 NpF₆-SbF₅-HF had changed to being almost identical with that for NpF₅-SbF₅-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. This material could then reduce Np(VI) to Np(V). This proposed behaviour is consistent with the spectroscopic observation in the present work that NpF₆ solutions were reduced more readily than UF₆ in SbF₅-HF solutions and that AsF₅-HF reduced Np(VI) but not U(VI). The known chemistry of actinide hexafluorides shows that NpF₆ is a stronger oxidant than UF₆.

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, BF₃, AsF₅ and SbF₅ with each system where possible, i.e. each of the solutions was prepared, whenever possible, containing the anions BF₄⁻, AsF₆⁻ or SbF₆⁻ 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.

**ACKNOWLEDGEMENTS**

We are grateful for financial support from the American Educational
Foundation Fulbright Program (M.B.) and to the Council of the University
of Melbourne for granting sabbatical leave (T.A.O'D.). We wish to
thank R.N.R. Mulford of Los Alamos National Laboratory for providing
the samples of Np metal used in this work.

This work was supported by the Division of Chemical Sciences,
Office of Basic Energy Sciences, U.S. Department of Energy under
REFERENCES

(5) O'Donnell, T.A., Rietz, R., Yeh, S., unpublished observations.
(12) After this work was completed the following report was found which states that treatment of U metal with HF and SbF₅ yielded a solid residual which was U(SbF₆)₃. Tarvero, M., Rapport CEA-R3205, 1967, 51.
Table 1

Positions of Major Peaks in Spectra of U(III) in H₂O and A HF (nm)

<table>
<thead>
<tr>
<th>U³⁺ in 1M DCI₄-D₂O</th>
<th>U³⁺ in AsF₅-HF</th>
</tr>
</thead>
<tbody>
<tr>
<td>1219</td>
<td>1198</td>
</tr>
<tr>
<td>1064</td>
<td>1010</td>
</tr>
<tr>
<td></td>
<td>967</td>
</tr>
<tr>
<td>967</td>
<td>942</td>
</tr>
<tr>
<td>898</td>
<td>876</td>
</tr>
<tr>
<td>876</td>
<td>844</td>
</tr>
<tr>
<td></td>
<td>820</td>
</tr>
<tr>
<td></td>
<td>700</td>
</tr>
<tr>
<td>636</td>
<td>591</td>
</tr>
<tr>
<td>615</td>
<td>558</td>
</tr>
<tr>
<td></td>
<td>520</td>
</tr>
<tr>
<td>522</td>
<td>503</td>
</tr>
<tr>
<td>507</td>
<td>482</td>
</tr>
<tr>
<td></td>
<td>477</td>
</tr>
<tr>
<td></td>
<td>442</td>
</tr>
<tr>
<td>451</td>
<td>429</td>
</tr>
<tr>
<td></td>
<td>411</td>
</tr>
</tbody>
</table>
Table 2

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

<table>
<thead>
<tr>
<th>Np(^{3+}) in 2M HClO(_4)-H(_2)O</th>
<th>Np(^{3+}) in AsF(_5)-HF</th>
</tr>
</thead>
<tbody>
<tr>
<td>1363</td>
<td>1338</td>
</tr>
<tr>
<td>991</td>
<td>966</td>
</tr>
<tr>
<td>849</td>
<td>829</td>
</tr>
<tr>
<td>786</td>
<td>760</td>
</tr>
<tr>
<td>660</td>
<td>643</td>
</tr>
<tr>
<td>600</td>
<td>586</td>
</tr>
<tr>
<td>552</td>
<td>544</td>
</tr>
</tbody>
</table>
Table 3

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

<table>
<thead>
<tr>
<th>U⁴⁺ in AsF₅-HF</th>
<th>0.03M U⁴⁺ in 1M HClO₄ and 0.08 M HF*</th>
</tr>
</thead>
<tbody>
<tr>
<td>390</td>
<td>405</td>
</tr>
<tr>
<td>420</td>
<td>426</td>
</tr>
<tr>
<td>439</td>
<td>452</td>
</tr>
<tr>
<td>458</td>
<td>469</td>
</tr>
<tr>
<td>478</td>
<td>486</td>
</tr>
<tr>
<td></td>
<td>495</td>
</tr>
<tr>
<td>506</td>
<td>525</td>
</tr>
<tr>
<td>560</td>
<td>590</td>
</tr>
<tr>
<td>600</td>
<td>610</td>
</tr>
<tr>
<td>650</td>
<td>626</td>
</tr>
<tr>
<td></td>
<td>642</td>
</tr>
</tbody>
</table>

*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