



RESEARCH ARTICLE

Gas-Phase Coordination Complexes of $\text{U}^{\text{VI}}\text{O}_2^{2+}$, $\text{Np}^{\text{VI}}\text{O}_2^{2+}$, and $\text{Pu}^{\text{VI}}\text{O}_2^{2+}$ with Dimethylformamide

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Electrospray ionization of actinyl perchlorate solutions in H_2O with 5% by volume of dimethylformamide (DMF) produced the isolatable gas-phase complexes, $[\text{An}^{\text{VI}}\text{O}_2(\text{DMF})_3(\text{H}_2\text{O})]^{2+}$ and $[\text{An}^{\text{VI}}\text{O}_2(\text{DMF})_4]^{2+}$, where An = U, Np, and Pu. Collision-induced dissociation confirmed the composition of the dipositive coordination complexes, and produced doubly- and singly-charged fragment ions. The fragmentation products reveal differences in underlying chemistries of uranyl, neptunyl, and plutonyl, including the lower stability of Np(VI) and Pu(VI) compared with U(VI).

Key words: Neptunyl, Plutonyl, Uranyl, Actinide, Neptunium, Plutonium, Uranium, Inorganic, Electrospray, Collision induced dissociation

Introduction

The chemistry of the early actinides, from thorium to americium, is of particular technological and scientific significance [1]. The linear, hexavalent actinyl ions, $\{\text{O}=\text{An}^{\text{VI}}=\text{O}\}^{2+}$, are important in solution chemistry of U [2], Np [3] and Pu [4]. The americyl ion, $\text{Am}^{\text{VI}}\text{O}_2^{2+}$, is a stable species in solution but is not predominant under most conditions [5]. The uranyl ion is particularly prevalent and has been extensively studied by both experiment and theory [6]. The transfer of monovalent pentavalent $\text{U}^{\text{V}}\text{O}_2^+$ from solution to the gas phase using electrospray ionization (ESI) was first reported in 1992 [7]. Since then, use of ESI has been expanded to allow generation of a wide range of pentavalent and hexavalent uranyl ions, monovalent and dipositive, by ESI [8–12] and, in turn, has allowed

investigation of intrinsic uranyl coordination chemistry. Of particular relevance to the present work, ESI of solutions of uranyl in water/acetone and water/acetonitrile have revealed the affinity of gas-phase uranyl for more basic organic ligands and penta-coordination, as in $[\text{U}^{\text{VI}}\text{O}_2(\text{CH}_3\text{COCH}_3)_5]^{2+}$ and $[\text{U}^{\text{VI}}\text{O}_2(\text{CH}_3\text{CN})_5]^{2+}$ [12, 13].

Stability of the dipositive actinyl ions in solution decreases following the trend [14]: $\text{U}^{\text{VI}}\text{O}_2^{2+} \gg \text{Pu}^{\text{VI}}\text{O}_2^{2+} > \text{Np}^{\text{VI}}\text{O}_2^{2+} > \text{Am}^{\text{VI}}\text{O}_2^{2+}$. Although $\text{U}^{\text{VI}}\text{O}_2^{2+}$ ligated by basic electron-donating ligands has been sufficiently stabilized to enable its transfer from solution to the gas phase, it does not necessarily follow that the less stable dipositive actinyl ions can be similarly transferred from solution to gas. The standard reduction potentials for $\text{An}^{\text{VI}}\text{O}_2^{2+} \rightarrow \text{An}^{\text{V}}\text{O}_2^+$ are: 0.09 V for $\text{U}^{\text{VI}}\text{O}_2^{2+}$; 0.95 V for $\text{Pu}^{\text{VI}}\text{O}_2^{2+}$; 1.16 V for $\text{Np}^{\text{VI}}\text{O}_2^{2+}$; and 1.60 V for $\text{Am}^{\text{VI}}\text{O}_2^{2+}$ [15]. It is evident that relative to $\text{U}^{\text{VI}}\text{O}_2^{2+}$, the other three $\text{An}^{\text{VI}}\text{O}_2^{2+}$ should be prone to reduction during ESI.

Early plutonium ESI/MS work focused on the speciation of Pu(IV) in the gas phase [16, 17]. The first report appeared in 2003, where ESI/MS was used to identify the molecular

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structure of radiolytic products of irradiated TRPO-kerosene systems [16]. More recently, Walther et al. employed ESI/MS to characterize tetravalent plutonium polymer growth [18].

Recently, we reported transfer of solvent-coordinated $\text{Pu}^{\text{VI}}\text{O}_2^{2+}$ ions from solution to the gas phase by ESI of plutonyl in acetone/water and acetonitrile/water [19]. Ion complexes were isolated in an ion trap for mass analysis and collision-induced dissociation (CID). Parallel studies of

uranyl revealed inherent differences between the coordination and redox chemistries of Pu and U in the gas phase. In the initial study, attempts to transfer $\text{Np}^{\text{VI}}\text{O}_2^{2+}$ from solution to the gas phase, using acetonitrile or acetone as co-solvent (and as basic ligands to stabilize dipositive gas-phase complex ions), were unsuccessful. As we report here, use of the more basic ligand dimethylformamide (DMF) allows for transfer of divalent $\text{Np}^{\text{VI}}\text{O}_2^{2+}$ complexes to the gas phase. This has enabled the first comparison of the gas-

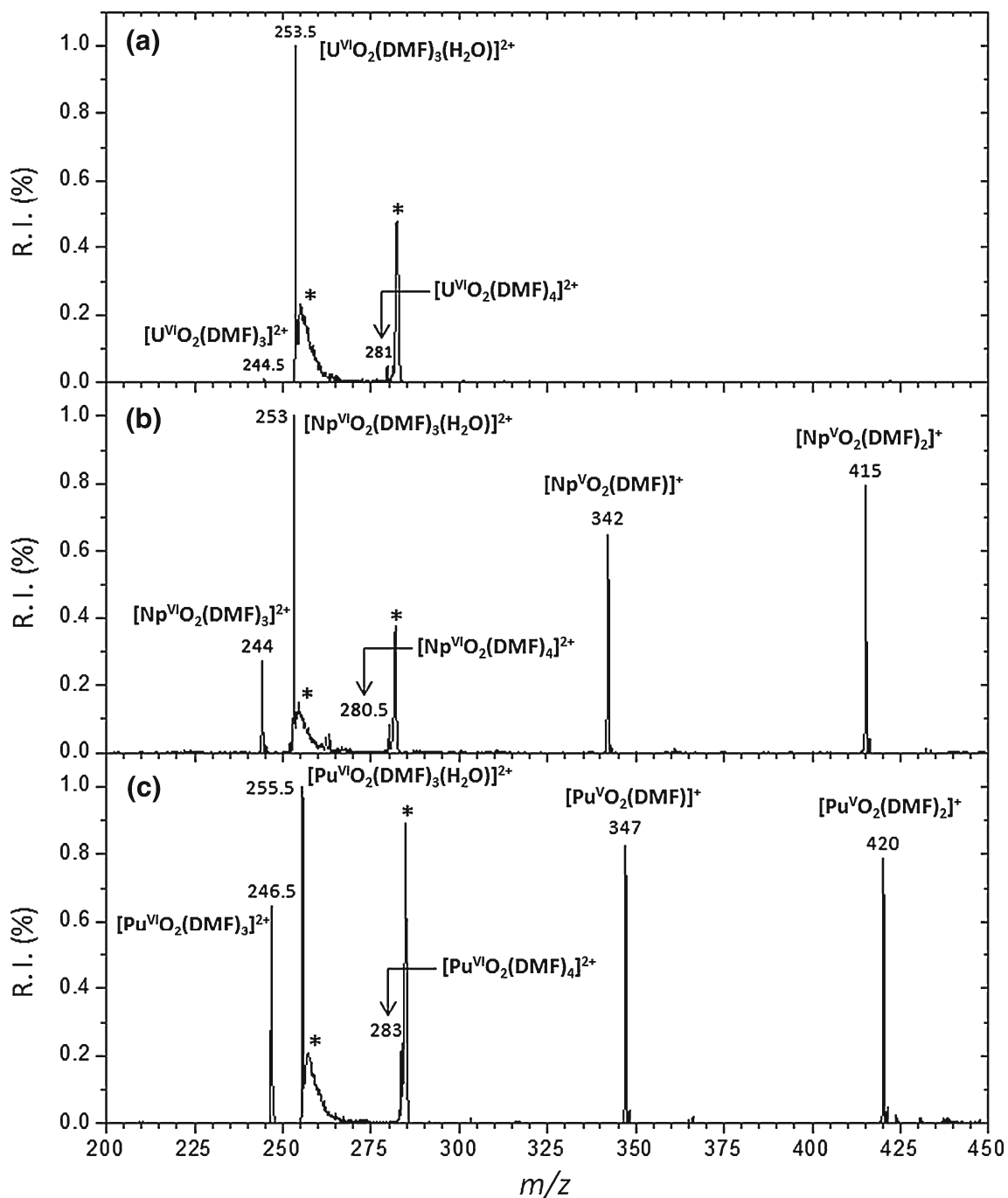


Figure 1. CID (MS/MS stage) of (a) $[\text{UO}_2(\text{DMF})_4]^{2+}$, (b) $[\text{NpO}_2(\text{DMF})_4]^{2+}$, and (c) $[\text{PuO}_2(\text{DMF})_4]^{2+}$. Asterisked features are artifacts (see Figure S1). Species containing water were produced by hydration of primary CID products in the ion trap

phase behavior of uranyl, neptunyl, and plutonyl complexes with identical ligand composition and coordination number.

Experimental Methods

Uranyl, neptunyl, and plutonyl solutions in DMF/water were prepared at a concentration of 80 μM in an organic solvent/water ratio of 5/95 from actinyl perchlorate stock solutions in water. The actinide isotopes employed were

U-238, Np-237, and Pu-242. All handling of these hazardous radionuclides was in a containment glove box in a radiological laboratory. The ESI/MS and CID experiments were performed with an Agilent 6340 Quadrupole Ion Trap (QIT) mass spectrometer, with the ESI source housed within a radiological-containment glove box. In high resolution mode, the instrument has a detection range of m/z 50–2200 and a resolution of m/z \sim 0.25 (full width half maximum). Mass spectra were

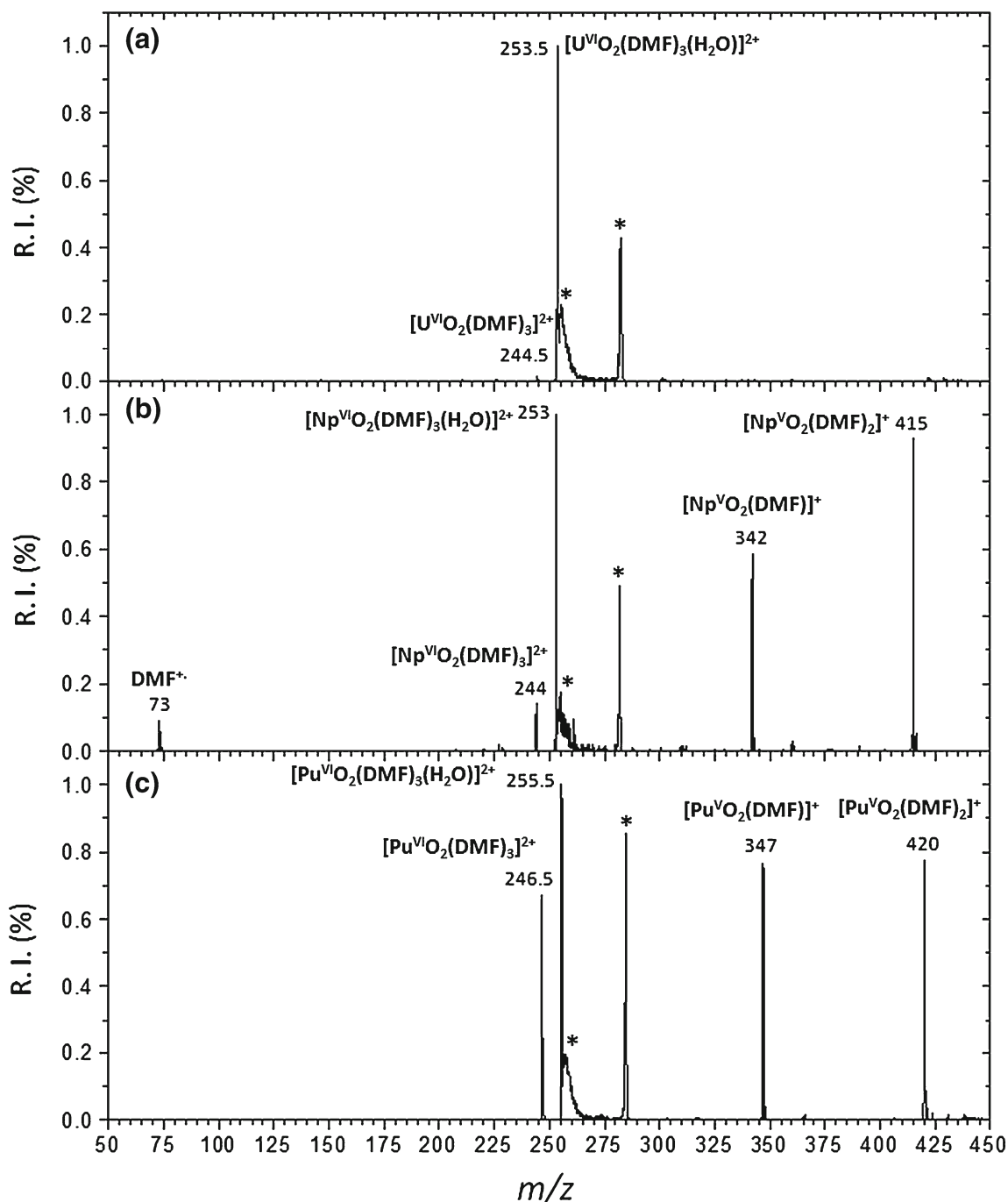


Figure 2. CID (MS³ stage) of (a) $[\text{UO}_2(\text{DMF})_3]^{2+}$, (b) $[\text{NpO}_2(\text{DMF})_3]^{2+}$, and (c) $[\text{PuO}_2(\text{DMF})_3]^{2+}$ generated from CID of $[\text{AnO}_2(\text{DMF})_4]^{2+}$. Asterisked features are artifacts (see Figure S1). Species containing water were produced by hydration in the ion trap

recorded in the positive ion accumulation and detection mode using instrumental parameters similar to those employed in our earlier study of $\text{Pu}^{\text{VI}}\text{O}_2^{2+}$ species [19].

Solutions were injected into the electrospray capillary via a syringe pump at a rate of 60 $\mu\text{L}/\text{h}$. Nitrogen gas was used for nebulization and drying in the ion transfer capillary. CID experiments were performed using the He trapping gas at a pressure of $\sim 10^{-4}$ Torr; tickle voltages ranged between 0.1 V

and 1.0 V applied for 40 ms. The background water pressure in the ion trap was $\sim 10^{-6}$ Torr.

Results and Discussion

Our hypothesis was that DMF as the co-solvent, with a gas-phase basicity of 857 kJ/mol, compared to basicities of 660, 748, and 782 kJ/mol, for water, acetonitrile, and

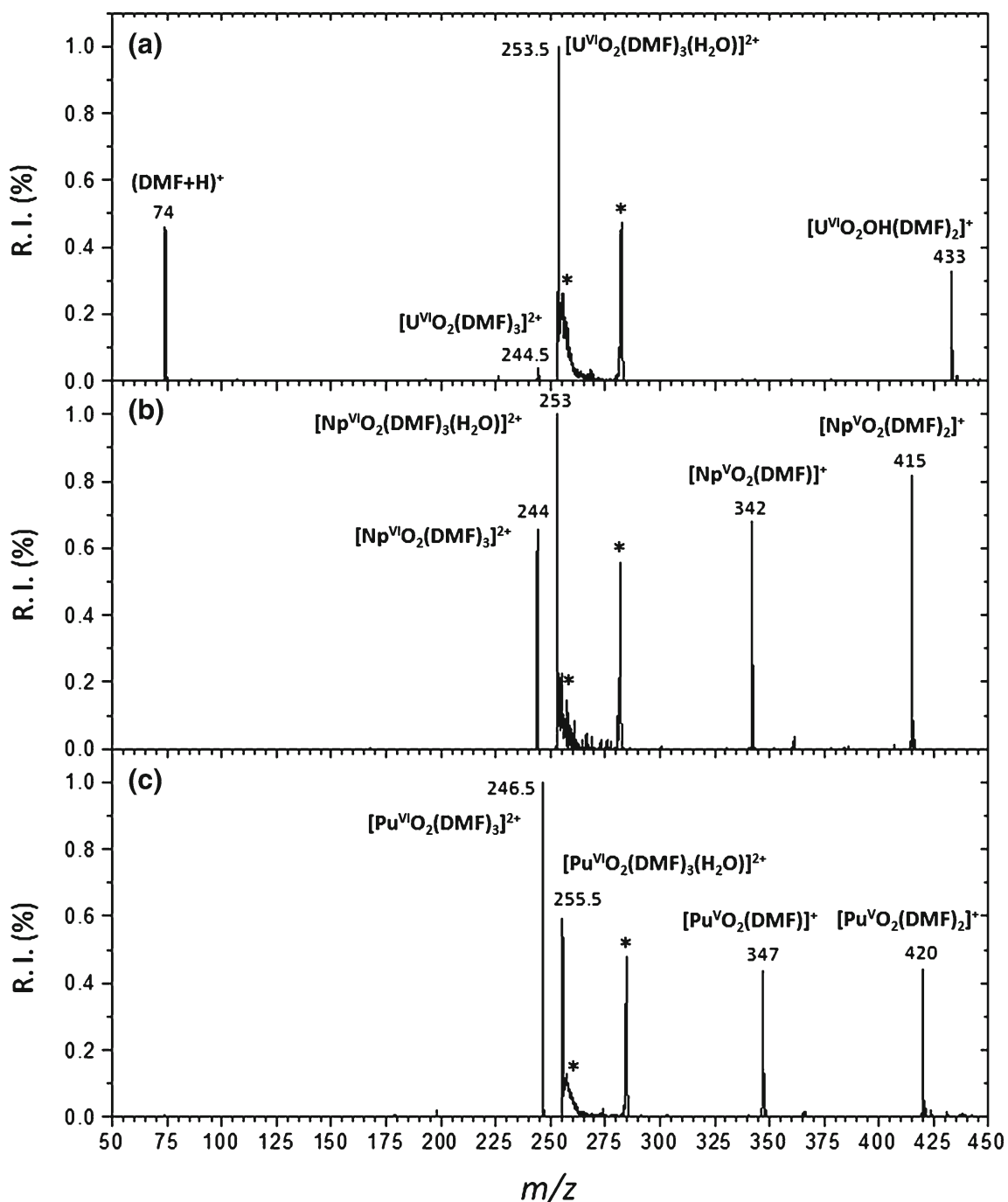


Figure 3. CID (MS³ stage) of (a) $[\text{UO}_2(\text{DMF})_3(\text{H}_2\text{O})]^{2+}$, (b) $[\text{NpO}_2(\text{DMF})_3(\text{H}_2\text{O})]^{2+}$, and (c) $[\text{PuO}_2(\text{DMF})_3(\text{H}_2\text{O})]^{2+}$. These ions were generated from CID of $[\text{AnO}_2(\text{DMF})_4]^{2+}$ and hydration of the $[\text{AnO}_2(\text{DMF})_3]^{2+}$ products. Asterisked features are artifacts (see Figure S1)

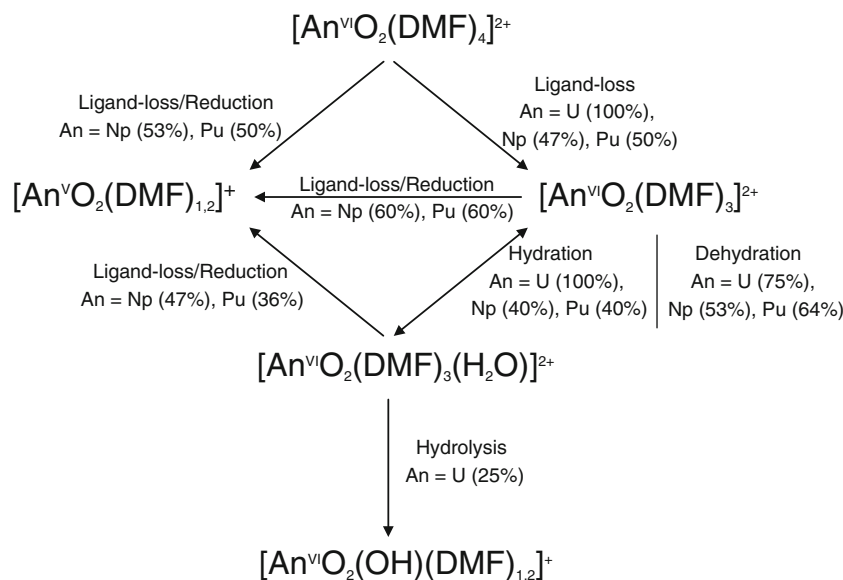
acetone, respectively [20], would facilitate transfer of dipositive $\text{Np}^{\text{VI}}\text{O}_2^{2+}$ complexes to the gas phase. Indeed, ESI generated a range of monopositive and dipositive complexes containing $^{238}\text{U}^{\text{VI}}\text{O}_2^{2+}$, $^{237}\text{Np}^{\text{VI}}\text{O}_2^{2+}$ or $^{242}\text{Pu}^{\text{VI}}\text{O}_2^{2+}$ (spectra not shown). The monopositive complexes included DMF-, or DMF- and H_2O -coordinated $\text{An}^{\text{V}}\text{O}_2^+$ ($\text{An} = \text{U}, \text{Np}, \text{or Pu}$) complexes with between 1 and 3 ligands, or for the case of U, solvent-coordinated $\text{U}^{\text{VI}}\text{O}_2\text{OH}^+$ species. The compositions of all of the actinyl ion complexes, some of which were of low intensity, were definitively confirmed by CID fragmentation as described below. Of particular interest in this study were the dipositive species, of which the most abundant were those with compositions $[\text{An}^{\text{VI}}\text{O}_2(\text{DMF})_4]^{2+}$ and $[\text{An}^{\text{VI}}\text{O}_2(\text{DMF})_3(\text{H}_2\text{O})]^{2+}$. The abundances of the uranyl complexes were much greater than those of the neptunyl and plutonyl complexes, typically by about an order of magnitude. Unlike earlier experiments focusing on uranyl and plutonyl complexes with acetonitrile or acetone ligands, formation of gas-phase species containing $^{238}\text{U}^{\text{VI}}\text{O}_2^{2+}$, $^{237}\text{Np}^{\text{VI}}\text{O}_2^{2+}$, or $^{242}\text{Pu}^{\text{VI}}\text{O}_2^{2+}$ coordinated by five DMF ligands was not observed. The bond energy should decrease with increasing ligand number [21], and the high basicity of DMF relative to acetonitrile or acetone should result in greater electron donation to the metal center by the first four ligands, which may render addition of a fifth DMF ligand energetically unfavorable. Similar shifts to higher stability of complexes with four ligands relative to those with five have been observed previously with gas-phase uranyl-nitrile complexes [12].

Figure 1 shows the CID spectrum produced from $[\text{An}^{\text{VI}}\text{O}_2(\text{DMF})_4]^{2+}$, $\text{An} = \text{U}, \text{Np}, \text{and Pu}$, precursor ions. In each spectrum, abnormal artifact peaks, the origins of which are unknown, were observed in the region of the precursor and

doubly-charged product ions. These are marked in Figures 1, 2 and 3 by asterisks, and a version of the spectra with expanded m/z axis is shown in Figure S1 to demonstrate that precursor and product ion peaks can be distinguished from the artifact peaks. For $[\text{U}^{\text{VI}}\text{O}_2(\text{DMF})_4]^{2+}$ (Figure 1a), fragmentation was dominated by formation of (doubly-charged) $[\text{U}^{\text{VI}}\text{O}_2(\text{DMF})_3]^{2+}$ and $[\text{U}^{\text{VI}}\text{O}_2(\text{DMF})_3(\text{H}_2\text{O})]^{2+}$ at m/z 244.5 and 253.5, respectively. Water-containing species such as $[\text{U}^{\text{VI}}\text{O}_2(\text{DMF})_3(\text{H}_2\text{O})]^{2+}$ were produced by hydration of an under-coordinated CID product, in this case $[\text{U}^{\text{VI}}\text{O}_2(\text{DMF})_3]^{2+}$. Singly-charged product ions such as $[\text{U}^{\text{VI}}\text{O}_2\text{OH}(\text{DMF})_2]^+$ (m/z 364) were generated at less than 1% relative intensity.

CID spectra of $[\text{An}^{\text{VI}}\text{O}_2(\text{DMF})_4]^{2+}$ for $\text{An} = \text{Np}$ and Pu are shown in Figure 1b and c, respectively. Doubly-charged product ions included $[\text{An}^{\text{VI}}\text{O}_2(\text{DMF})_3]^{2+}$ and $[\text{An}^{\text{VI}}\text{O}_2(\text{DMF})_3(\text{H}_2\text{O})]^{2+}$ at m/z 244 and 253 for $^{237}\text{Np}^{\text{VI}}\text{O}_2^{2+}$ and m/z 246.5 and 255.5 for $^{242}\text{Pu}^{\text{VI}}\text{O}_2^{2+}$. Unlike the case for the uranyl complexes with DMF, CID of the neptunyl and plutonyl complexes generated abundant monopositive product ions. For both, prominent $[\text{An}^{\text{V}}\text{O}_2(\text{DMF})]^+$ and $[\text{An}^{\text{V}}\text{O}_2(\text{DMF})_2]^+$ species appeared at m/z 342 and 415 for neptunium, and m/z 347 and 420 for plutonium. The singly-charged product ions for the neptunyl and plutonyl precursors were ca. two orders of magnitude more abundant than those for the corresponding uranyl precursor; these results reflect the greater propensity of Np^{VI} and Pu^{VI} to reduce to the pentavalent oxidation state as compared with more stable U^{VI} .

The $[\text{An}^{\text{VI}}\text{O}_2(\text{DMF})_3]^{2+}$ product species from dissociation of each actinyl complex was isolated and subjected to a subsequent CID stage (Figure 2). Each of these species, during isolation for CID, formed the hydrated, doubly



Scheme 1. Primary fragmentation (ligand-loss and dehydration), hydration, and hydrolysis pathways, which were observed during CID. The distributions among pathways are given as percentages. Retention of the U^{VI} oxidation state throughout is evident

charged $[\text{An}^{\text{VI}}\text{O}_2(\text{DMF})_3(\text{H}_2\text{O})]^{2+}$ ion (m/z 253.5, 253, and 255.5 for An = U, Np, and Pu, respectively). In addition, the singly-charged $[\text{An}^{\text{V}}\text{O}_2(\text{DMF})]^{+}$ and $[\text{An}^{\text{V}}\text{O}_2(\text{DMF})_2]^{+}$ CID products were also generated for An = Np and Pu. For $[\text{Np}^{\text{VI}}\text{O}_2(\text{DMF})_3]^{2+}$, a peak at m/z 73 was also observed in the CID spectrum, which corresponds to the radical cation DMF^+ . This species in particular is consistent with oxidative elimination of a ligand during the formation of the monovalent $[\text{An}^{\text{V}}\text{O}_2(\text{DMF})]^{+}$ and $[\text{An}^{\text{V}}\text{O}_2(\text{DMF})_2]^{+}$ product ions.

Sufficient intensities of the $[\text{An}^{\text{VI}}\text{O}_2(\text{DMF})_3(\text{H}_2\text{O})]^{2+}$ ions were generated by CID (and hydration) to allow investigation of secondary CID (Figure 3). For $[\text{U}^{\text{VI}}\text{O}_2(\text{DMF})_3(\text{H}_2\text{O})]^{2+}$ (Figure 3a), elimination of H_2O followed by rapid re-addition of indigenous H_2O was observed: this leads to re-generation of the precursor, which manifests as an apparent “steady state” of precursor ion with increasing applied collision voltage or CID duration. This same phenomenon was observed for each $[\text{An}^{\text{VI}}\text{O}_2(\text{DMF})_3(\text{H}_2\text{O})]^{2+}$ precursor and reflects the rapid ligand addition rates for the hypo-coordinated dipositive complexes with only three coordinating ligands [5e, 6]. The dominant singly-charged product ions observed for $[\text{U}^{\text{VI}}\text{O}_2(\text{DMF})_3(\text{H}_2\text{O})]^{2+}$ were protonated DMF, $(\text{DMF}+\text{H})^{+}$, at m/z 74 and $[\text{U}^{\text{VI}}\text{O}_2\text{OH}(\text{DMF})_2]^{+}$ at m/z 433. The reduced species $[\text{U}^{\text{V}}\text{O}_2(\text{DMF})]^{+}$ and the species $[\text{U}^{\text{VI}}\text{O}_2\text{OH}(\text{DMF})]^{+}$ were observed at less than 1% relative intensity. The prominent peaks at m/z 74 and 433 in the CID spectrum of $[\text{U}^{\text{VI}}\text{O}_2(\text{DMF})_3(\text{H}_2\text{O})]^{2+}$ are consistent with a hydrolysis reaction activated by CID in which the bound H_2O ligand is split, with elimination of a DMF ligand in protonated form, and retention of hydroxide anion by the uranyl dication.

The CID spectrum of $[\text{U}^{\text{VI}}\text{O}_2(\text{DMF})_3(\text{H}_2\text{O})]^{2+}$ contrasts sharply with the product ion spectra for $[\text{Np}^{\text{VI}}\text{O}_2(\text{DMF})_3(\text{H}_2\text{O})]^{2+}$ and $[\text{Pu}^{\text{VI}}\text{O}_2(\text{DMF})_3(\text{H}_2\text{O})]^{2+}$ (Figure 3b and c, respectively), for which the reduced $[\text{An}^{\text{V}}\text{O}_2(\text{DMF})]^{+}$ and $[\text{An}^{\text{V}}\text{O}_2(\text{DMF})_2]^{+}$ were dominant. Instead of ligated hydroxides, H_2O adducts of the reduced $[\text{An}^{\text{V}}\text{O}_2(\text{DMF})]^{+}$ and $[\text{An}^{\text{V}}\text{O}_2(\text{DMF})_2]^{+}$ products were observed at m/z 360 and 365 for Np and Pu, respectively.

The CID results are summarized in Scheme 1, where gas-phase hydration and hydrolysis processes are included along with CID fragmentation processes. A striking aspect of these results is that the uranyl(VI) oxidation state is retained to a greater extent than either neptunyl(VI) or plutonyl(VI), which is in accord with condensed phase actinyl oxidation/reduction behavior [14, 15].

Overall, the ESI mass spectrometry and CID results confirm the transfer of dipositive, hexavalent actinyl complexes of $^{238}\text{U}^{\text{VI}}\text{O}_2^{2+}$, $^{237}\text{Np}^{\text{VI}}\text{O}_2^{2+}$, or $^{242}\text{Pu}^{\text{VI}}\text{O}_2^{2+}$ with DMF to the gas phase. This is the first report of such transfer of dipositive neptunyl complexes to the gas phase. As the electron affinities of $\text{Np}^{\text{VI}}\text{O}_2^{2+}$ and $\text{Pu}^{\text{VI}}\text{O}_2^{2+}$ are comparable (15.1 ± 0.4 eV) [22] and are at least 2 eV greater than the ionization energies (IEs) of water (12.6 eV) and DMF (9.12 eV) [20], stabilization of dipositive actinyl ions against

electron transfer from these neutrals requires charge donation by coordinating ligands. Coordination of the actinyl by electron-donating ligands reduces the effective electron affinity of the complexed dipositive ion such that charge exchange is not energetically favorable. The results suggest that four basic ligands are needed to stabilize dipositive actinyl ions in the gas phase, and that more nucleophilic DMF ligands are more effective than water at stabilizing dipositive ions, in general, in the gas phase. At least three DMF ligands, along with either a fourth DMF or a water, were necessary for the generation of sufficient neptunyl complexes for CID study.

Acknowledgments

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