Molecular uranates - laser synthesis of uranium oxide anions in the gas phase

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Abstract

Laser desorption/ionization of solid uranium trioxide or ammonium diuranate yielded in the gas phase molecular uranium oxide anions with compositions ranging from $[\text{UO}_n]^-$ ($n = 2-4$) to $[\text{U}_{14}\text{O}_n]^-$ ($n = 32-35$), as detected by Fourier transform ion cyclotron resonance mass spectrometry. Several cluster series could be identified, namely $[\text{U}_x\text{O}_{3x}]^-$ for $x \leq 6$, and various $[\text{U}_x\text{O}_{3x-y}]^-$ series in which y increased with increasing x . The different cluster series obtained reflect the availability of different oxidation states for uranium (mainly IV-VI). In a few anions hydrogen was also present, namely in $[\text{UO}_4\text{H}]^-$, $[\text{UO}_4\text{H}_2]^-$, and $[\text{U}_2\text{O}_7\text{H}]^-$, and their abundance increased when hydrated (yellow) UO_3 was used in place of anhydrous (orange) UO_3 . No major discontinuities in the abundances of the clusters could be detected, suggesting that there are no “magic number” compositions with special stability. Collision-induced dissociation experiments performed with some of the lower-mass cluster anions supported extended structures in which neutral UO_3 constitutes the main building block. Previously described cationic uranium oxide clusters $[\text{U}_x\text{O}_n]^+$ ($x = 2-9$; $n = 3-24$) could also be produced and are briefly discussed.

Communication

The uranates are an important class of uranium compounds [1,2]. Ammonium diuranate (ADU), $(\text{NH}_4)_2\text{U}_2\text{O}_7$, in particular has played a historical role [3] and is a technological important compound until this day [4]. Uranates precipitate readily from solutions of uranyl salts by reaction with alkaline, alkaline-earth, or ammonium hydroxides; more generally, they are produced by high temperature reactions of alkaline, alkaline-earth, or other metal salts with the proper amounts of uranium oxides in the solid state or in molten salts [1,2]. The more common uranates are U(VI) compounds, with the compositions $\text{M}_m\text{U}_n\text{O}_{3n+1}$, where $m = 2$ when $\text{M} = \text{alkali metal}$, and $m = 1$ when $\text{M} = \text{alkaline-earth}$; uranates involving U(V) and U(IV) are also known and the more common have compositions MUO_3 with $\text{M} = \text{alkali metal}$ for U(V) and $\text{M} = \text{alkaline-earth}$ for U(VI) [1,2]. The solid state structures of the uranates, when completely determined, reveal that they possess extended arrangements, layered or pillared, in which, depending on the oxidation state of the uranium, a uranyl moiety may or may not be present [1,2,5].

Laser desorption/ionization (LDI), or laser ablation, coupled to mass spectrometry is a technique that has

produced numerous examples of novel molecular species [6-8]. Several negatively charged metal chalcogenide clusters, namely sulfides [9-11] and oxides [8,12-22] have been previously generated by LDI and studied by Fourier transform ion cyclotron resonance mass spectrometry (FTICR/MS).

Here we report that LDI of uranium trioxide (anhydrous/orange and hydrated/yellow) and ammonium diuranate, as powders or pellets, readily yields in the gas phase molecular uranium oxide anions with compositions ranging from $[\text{UO}_n]^-$, with $n = 2-4$, to $[\text{U}_{14}\text{O}_n]^-$, with a tentatively assigned range $n = 32-35$. Single or multiple pulses from a Spectra-Physics GCR-11 Nd:YAG laser at the fundamental wavelength (1064 nm) and with an average focused power density of ca. 200 MW cm^{-2} were used, and the ions were detected by FTICR/MS in a Extrel/Finnigan FTMS 2001-DT 3 Tesla spectrometer.

Figure 1 displays a representative, average resolution mass spectrum obtained from a powdered anhydrous UO_3 sample. Figure 1a shows the entire spectrum where clusters up to $\text{U}_{14}\text{O}_n^-$ can be observed, while Figure 1b shows the low m/z region of the spectrum where the species UO_2^- , UO_3^- , UO_4^- , UO_4H^- , and UO_4H_2^- can be recognized. Typically, the anhydrous UO_3 and the ADU samples gave rise to low amounts of anions containing hydrogen, but these were enhanced in the case of the hydrated UO_3 sample. These results suggest that the hydrogens in the product ions originate primarily from water or hydroxyl groups in the samples. The relative intensities of each group of clusters with the same number of U atoms showed a wide variation, even from spot to spot the same sample; within each group relative intensities were more constant. There was no attempt to systematically study these variations in intensity, for instance in relation to the laser power density. Accordingly, the irreproducible appearance of high-abundance cluster groups such as U_5O_n^- in Figure 1a should not necessarily be considered to indicate special stability.

In Figure 2 we present a map of the $[\text{U}_x\text{O}_n]^-$ ions observed up to $x = 11$, with the solid line on the map marking the $[\text{U}_x\text{O}_{3x}]^-$ stoichiometry; the dashed line indicates the $[\text{U}_x\text{O}_{2.5x}]^-$ stoichiometry. The exact compositions were confirmed in high resolution mass spectra up to clusters with six U atoms; for $x = 7-11$ the compositions are somewhat less definitive. A deviation from the $[\text{U}_x\text{O}_{3x}]^-$ line for $x > 5$ can be discerned, revealing enhancements of compositions $[\text{U}_x\text{O}_{3x-y}]^-$ in which y increases with increasing x . The observed compositions show similarities to those of the Group 6 metal oxide anions that have been the object of several LDI-FTICR/MS studies [12,16-22].

UO_2^- was previously identified by Andrews and co-workers in reactions of laser-ablated uranium with O_2 in a neon matrix [23]. UO_3^- was reported in early secondary-ion mass spectrometry (SIMS) studies of uranium oxides [24,25]; later high-temperature studies with U_3O_8 , aiming at the determination of the electron affinity of UO_3 , failed to identify UO_3^- [26].

The different uranium oxide anions obtained reflect the availability of different oxidation states for uranium (III-VI). Of note are the anions UO_4^- , U_2O_7^- , and $\text{U}_3\text{O}_{10}^-$ in which the U atoms have formal average oxidation states 7, 6.5, and 6.3, respectively. U_2O_7^- and $\text{U}_3\text{O}_{10}^-$ were present in very low abundances in all mass spectra and were in all cases accompanied by $\text{U}_2\text{O}_7\text{H}^-$ and $\text{U}_3\text{O}_{10}\text{H}^-$ anions, in both of which U is in the more common formal oxidation state VI, assuming that the H is present in a hydroxide ligand and not directly bonded to the U metal center. Conversely, UO_4^- was always one of the major peaks in the spectra, as was

UO_4H^- , again a U(VI) species if the H is present in a hydroxide. The remaining anions all have the U in formal valences III to VI, with the low abundance UO_2^- being the only U(III) species. An analysis of the formal valence on U for all the anions identified indicates that it tends to 5 as the size of the clusters increases, as is seen in Figure 1a by the convergence towards the line corresponding to $[\text{U}_x\text{O}_{2.5x}]^-$; the O/U ratio clearly tends to 2.5 as the size of the clusters increases.

The abundant UO_4^- species, which formally comprises U(VII), is a remarkable result. To probe the stability of this species, the following gas-phase oxidation reaction was studied:

The reaction given by Equation (1) proceeds under thermal conditions, demonstrating that UO_4^- is indeed an inherently stable species, and not merely a consequence of the LDI conditions. DFT calculations are being performed to illuminate the nature of the intriguing UO_4^- species [27].

Collision induced dissociation (CID) experiments using Ar as a collision gas were performed for some of the lower mass anions. Loss of UO_3 was observed in the cases of U_3O_9^- and $\text{U}_4\text{O}_{12}^-$, while for U_3O_8^- and $\text{U}_4\text{O}_{11}^-$ no ionic products were detected; the latter occurred also for UO_3^- , UO_4^- , and U_2O_6^- . Electron detachment is a possible process and has been previously invoked to explain the non-observation of ionic CID products for some transition metal oxide anions [12,13]. The observation of UO_3 loss indicates that the clusters may have extended structures in which neutral UO_3 constitutes the main building block.

The structures and chemical properties of some of the lower mass uranates are being investigated via gas-phase reactivity studies and theoretical calculations [27].

Cationic uranium oxide clusters $[\text{U}_x\text{O}_n]^+$ ($x = 2-9$; $n = 3-24$) could also be produced from the same samples used in the generation of the uranates. This type of clusters has been previously obtained in several studies using either fast-atom bombardment (FAB) [28,29] or LDI [30-35]. Figure 3 shows a representative mass spectrum obtained from a powdered anhydrous UO_3 sample, in which the highly abundant UO^+ and UO_2^+ ions were ejected prior to detection; no UO_3^+ was ever detected. As with the anions, the formation of cations containing hydrogen was increased when hydrated UO_3 was used. In Figure 4 we present a map of the $[\text{U}_x\text{O}_n]^+$ ions observed up to $x = 9$, with the solid and dashed lines indicating the $[\text{U}_x\text{O}_{2x}]^+$ and $[\text{U}_x\text{O}_{2.5x}]^+$ compositions, respectively. Contrary to the anions, no “hypervalent” U species were observed but, intriguingly, as in the case of the anions, the formal valence on U appears to tend to 5 while the O/U ratio approaches ca. 2.5, as the size of the clusters increases.

The disparate results for the negative and positive uranium oxide speciation are noteworthy. As is seen in Figures 2 and 4, as the cluster sizes increase to > 5 U atoms, the compositions of the negative and positive clusters generally converge towards $[\text{U}_x\text{O}_{2.5x}]^{+/-}$, in which the average formal uranium valence state is close to V, as in the bulk uranium compound, U_2O_5 [1]. For the smaller species, the formal uranium valence state is higher in the negative ions, and lower in the positive ions. It was found that UO_4^- , “U(VII)”, and UO_2^+ , “U(V)”, are the dominant species; UO_3^+ , “U(VII)”, was never observed. For the small molecular species the presence of the negative charge evidently enhances the stability of higher formal valence states. As the size of the cluster increases, the presence of a single charge, positive or negative, does not appear to appreciably

affect the average valence states or stoichiometries; in the extreme of an extended solid lattice, an additional single charge does not affect the bulk properties.

In summary, we have produced molecular uranium oxide anions (uranates) in the gas phase by LDI of uranium oxides. Compositions ranging from $[\text{UO}_n]^-$ ($n = 2-4$) to $[\text{U}_x\text{O}_n]^-$ ($x = 1-14$; $n = 2-35$) could be identified, constituting the first observation of anionic uranium oxide clusters. Previously described cationic uranium oxide clusters $[\text{U}_x\text{O}_n]^+$ ($x = 2-9$; $n = 3-24$) were also obtained with the same samples.

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Figure 1. (a) LDI(-) mass spectrum of a powdered anhydrous UO_3 sample. (b) Low m/z region of the spectrum.

Figure 2. Map of the compositions of the $[U_xO_n]^-$ ions observed up to $x = 11$; the solid line indicates the $[U_xO_{3x}]^-$ composition and the dashed line indicates the $[U_xO_{2.5x}]^-$ composition.

Figure 3. (a) LDI(+) mass spectrum of a powdered anhydrous UO_3 sample; the highly abundant low mass UO^+ and UO_2^+ ions were ejected prior to detection.

Figure 4. Map of the compositions of the $[U_xO_n]^+$ ions observed up to $x = 9$; the solid line indicates the $[U_xO_{2x}]^+$ composition and the dashed line indicates the $[U_xO_{2.5x}]^+$ composition.