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Molecular Uranates: Laser Synthesis of Uranium Oxide Anions in the Gas Phase

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Laser ablation of solid UO_3 or $(NH_4)_2U_2O_7$ yielded in the gas phase molecular uranium oxide anions with compositions ranging from $[UO_n]^-$ ($n = 2-4$) to $[U_{14}O_n]^-$ ($n = 32-35$), as detected by Fourier transform ion cyclotron resonance mass spectrometry. The cluster series $[U_xO_{3x}]^-$ for $x \leq 6$ and various $[U_xO_{3x-y}]^-$, in which y increased with increasing x, could be identified. A few anions with H atoms were also present, and their abundance increased when hydrated UO_3 was used in place of anhydrous UO_3. Collision-induced dissociation experiments with some of the lower m/z cluster anions supported extended structures in which neutral UO_3 constitutes the building block. Cationic uranium oxide clusters $[U_xO_n]^+$ ($x = 2-9$; $n = 3-24$) could also be produced and are briefly discussed. Common trends in the O/U ratios for both negative and positive clusters could be unveiled.

The uranates are an important class of uranium compounds.[1] Ammonium diuranate (ADU), $(NH_4)_2U_2O_7$, in particular has played a historical role[2] and is still a technologically important compound.[3] 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] The more common uranates are U^{VI} compounds, with compositions $M_mU_nO_{3n+1}$, where $m = 2$ when M = alkali metal and $m = 1$ when M = alkaline earth; uranates involving U^V and U^{IV} are also known, and the more common have compositions MUO_3 with M = alkali metal for U^V and M = alkaline earth for U^{IV}.[1] The solid-state structures of the uranates reveal that they possess extended arrangements, layered or pillared, in which, depending on the oxidation state of the U atom, a uranyl moiety may or may not be present.[1,4]

Laser desorption/ionization (LDI) or laser ablation (LA) coupled with mass spectrometry is a technique that has produced numerous examples of novel molecular species.[5] Several negatively charged metal chalcogenide clusters, namely, sulfides[6] and oxides,[5c,7] have been previously generated by LDI/LA and studied by Fourier transform ion cyclotron resonance mass spectrometry (FTICR/MS).

Here we report that LA of UO_3 (anhydrous/orange or hydrated/yellow) or ADU, as powders or pellets, readily yields in the gas phase molecular uranium oxide anions with compositions ranging from $[UO_n]^-$, with $n = 2-4$, to $[U_{14}O_n]^-$, with a tentatively assigned range $n = 32-35$. A Spectra-Physics GCR-11 Nd:YAG laser (1064 nm) with an average focused power density of ca. 200 MW cm^{-2} was used. Single or multiple pulses on the same or on fresh spots yielded similar results. The ions were detected by FTICR/MS in an Extrel/Finnigan FTMS 2001-DT 3 T spectrometer, with an "internal" source design in which the sample sets close to the ICR cell. The potential of the front trap plate was set to 0 V for 100 μs immediately after the laser pulse. Similar results were obtained with operating pressures of $(2-5) \times 10^{-8}$ Torr of background gases (water and air) or ca. 10^{-6} Torr of argon.

Figure 1 displays a representative, average resolution (resolving power of ca. 1500 at m/z 300 and ca. 200 at m/z 2000) mass spectrum obtained from a powdered anhydrous UO_3 sample. Figure 1a shows the entire spectrum where clusters up to $U_{14}O_n^-$ 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.

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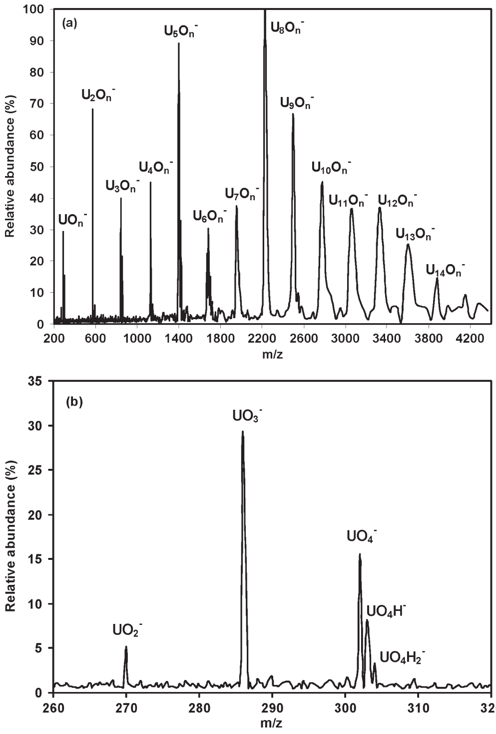

Figure 1. (a) LDI(−) mass spectrum of a powdered anhydrous UO_3 sample. (b) Low *m*/*z* region of the spectrum.

Typically, the anhydrous UO_3 and the ADU samples gave rise to low amounts of anions containing H atoms, but these were enhanced in the case of the hydrated UO_3 samples. These results suggest that the H atoms 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 of the same sample; within each group, relative intensities were more constant. Surface variations as probed by the laser (ca. 100 μm spot) may dictate the differences in the relative abundances of each group of clusters. The mechanism of formation of the cluster anions is uncertain; they may eventually be formed in the laser plume by interaction of electrons with neutral gas-phase species.[7e] The electron affinities of neutral U_xO_y species are virtually unkown, including the case of UO_3, for which only an upper limit of 2.1 eV has been proposed.[8]

In Figure 2, we present a map of the $[U_xO_n]^-$ ions observed up to $x = 11$, with the solid line marking the $[U_xO_{3x}]^-$ stoichiometry that trends toward an average oxidation state of VI for the U atom; the dashed line indicates the $[U_xO_{2.5x}]^-$ stoichiometry that trends toward an average oxidation state of V. The exact compositions were confirmed in high-resolution (resolving power of ca. 10 000 at *m*/*z* 300 and ca. 1000 at *m*/*z* 2000) mass spectra up to clusters with six U atoms; for $x = 7-11$, the compositions are somewhat less definitive. A deviation from the $[U_xO_{3x}]^-$ line for $x > 5$ can be discerned, revealing enhancements of compositions $[U_xO_{3x-y}]^-$ in which y increases with increasing x, converging toward the line corresponding to $[U_xO_{2.5x}]^-$.

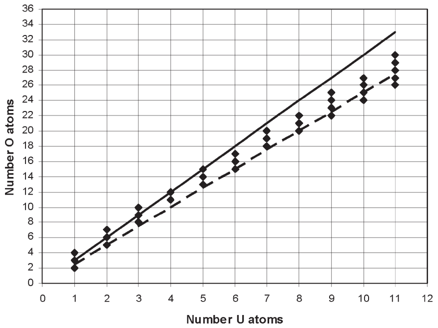

Figure 2. Map of compositions of the $[U_xO_n]^-$ ions observed up to $x = 11$. The solid line indicates the $[U_xO_{3x}]^-$ composition, and the dashed line indicates the $[U_xO_{2.5x}]^-$ composition.

UO_2^- was previously identified by Andrews and co-workers in reactions of laser-ablated U with O_2 in a neon matrix.[9] UO_3^- was reported in early secondary ion mass spectrometry studies of uranium oxides;[10] later high-temperature studies with U_3O_8 failed to identify UO_3^-.[8] Recent electrospray ionization mass spectrometry studies of uranyl solutions[11] have identified several $U_xO_y^-$ and $U_xO_yH_z^-$ species that bear noticeable resemblances with the uranium oxide anions reported here. The observed uranium oxide anions also show similarities to the ones produced from group 6 metal oxides by LDI/LA.[7a,7d−7g]

The different uranium oxide anions obtained reflect the availability of different oxidation states for $U^{III}-U^{VI}$. Of note are the anions UO_4^-, $U_2O_7^-$, and $U_3O_{10}^-$, in which the U atoms would have formal valences 7, 6.5, and 6.3, respectively, if all of the O atoms were present as O^{2-}. $U_2O_7^-$ and $U_3O_{10}^-$ were always obtained in very low abundances and were in all cases accompanied by $U_2O_7H^-$ and $U_3O_{10}H^-$ anions ($U_2O_7H_2^-$ and $U_3O_{10}H_2^-$ were not observed), in both of which U is in the more common formal oxidation state VI, assuming that the H atom is present in a hydroxide ligand. 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 atom is present in a hydroxide. The remaining anions all have the U atom in formal valences of 3−5, with the low-abundance UO_2^- being the only U^{III} species.

The abundant UO_4^- species is a remarkable result. If all of the O atoms are present as terminal O^{2-}, the U atom will be in an awkward formal oxidation state VII. More reasonable possibilities comprise the presence of bidentate or monodentate O_2^{2-} moieties, which would lead to U^V species, or of an oxidized O^- corresponding to U^{VI}; these have been previously invoked to account for observed gas-phase uranium oxide anions.[11] Another possibility would be the presence of a superoxo O_2^- ligand, as was recently identified in gas-phase studies of cationic uranium oxide species.[12] The same reasoning can be applied to the $U_2O_7^-$ and $U_3O_{10}^-$ anions,

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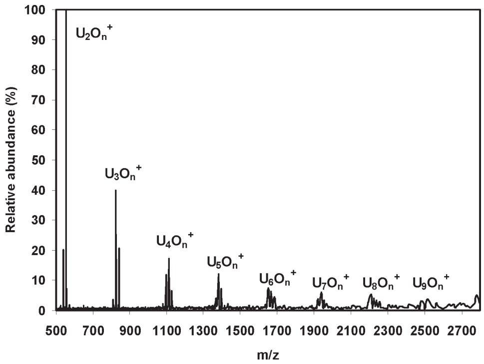

Figure 3. (a) LDI(+) mass spectrum of a powdered anhydrous UO_3 sample. The highly abundant UO^+ and UO_2^+ ions were ejected prior to detection.

which can be described as $(UO_3)UO_4^-$ and $(UO_3)_2UO_4^-$, respectively. Interestingly, UO_4^- could also be formed, under thermal conditions, in the gas-phase oxidation reaction $UO_3^- + N_2O \rightarrow UO_4^- + N_2$ and was inert in collision-induced dissociation (CID) experiments using argon as a collision gas. CID was also performed for other lower *m*/*z* anions, using collision energies (laboratory frame) of 5−30 eV in a presumed multiple-collision environment. Loss of UO_3 was observed in the cases of $U_3O_9^-$ and $U_4O_{12}^-$, while for $U_3O_8^-$ and $U_4O_{11}^-$ no products were detected; UO_3^- and $U_2O_6^-$ were also inert. Electron detachment has been previously invoked to explain the nonobservation of CID products for some transition-metal oxide anions.[7a,7b] 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 uranates, including the intriguing UO_4^- species, are being investigated via gas-phase reactivity studies and density functional theory calculations.[13]

Cationic uranium oxide clusters $[U_xO_n]^+$ (x = 2−9; n = 3−24) could also be produced from the same samples as those used in the generation of uranates. Cationic clusters have been previously obtained in several studies using either fast atom bombardment[14] or LDI/LA.[15] 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 H atoms was increased when hydrated UO_3 was used. In Figure 4, we present a map of the $[U_xO_n]^+$ ions observed up to x = 9, with the solid and dashed lines indicating the $[U_xO_{2x}]^+$ and $[U_xO_{2.5x}]^+$ compositions, respectively. Intriguingly, as in the case of the anions, the formal valence on the U atom appears to tend to V while the O/U ratio approaches ca. 2.5, as the size of the clusters increases.

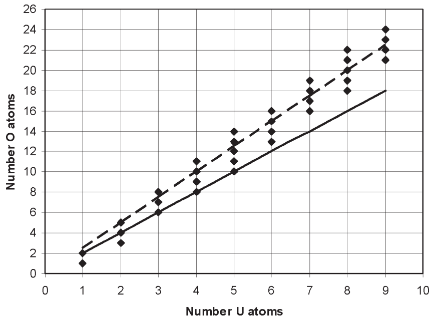

Figure 4. Map of compositions of the $[U_xO_n]^+$ ions observed up to $x = 9$. The solid line indicates the $[U_xO_{2x}]^+$ composition, and the dashed line indicates the $[U_xO_{2.5x}]^+$ composition.

The 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 toward $[U_xO_{2.5x}]^{\pm}$, in which the average formal U atom valence state is close to V, as in the bulk uranium compound, U_2O_5.[1a] For the smaller species, the formal U atom valence is higher in the negative ions and lower in the positive ions; while it was found that UO_4^- is a dominant species, UO_3^+ was never observed. For smaller molecular species, the presence of the negative charge 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.

The uranium oxide clusters obtained in this work and in other gas-phase studies,[11,12] with their structures elucidated via chemical and theoretical studies,[12,13] may constitute a new class of U/O systems to compare with structures found in the solid state, particularly the novel and exciting uranium polyoxometalates recently described.[16]

In summary, we have produced molecular uranium oxide anions (uranates) in the gas phase by LA of uranium oxides. Compositions ranging from $[UO_n]^-$ (n = 2−4) to $[U_xO_n]^-$ (x = 1−14; n = 2−35) were identified. Cationic uranium oxide clusters $[U_xO_n]^+$ (x = 2−9; n = 3−24) were also obtained with the same samples. Common trends in O/U ratios for both negative and positive clusters were unveiled.

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