Dissociation of Gas-Phase, Doubly-Charged Uranyl-Acetone Complexes by Collisional Activation and Infrared Photodissociation

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ABSTRACT

Past studies of fragmentation reactions of doubly-charged uranyl (UO_2^{2+}) complexes have been impeded by very rapid water addition reactions that cause H_2O adducts to dominate product ion spectra. The fragmentation of uranyl-acetone (aco) complexes ($[\text{UO}_2(\text{aco})_n]^{2+}$, $n=1-5$), generated by electrospray ionization, is revisited here using: (a) collisional activation in a linear ion trap (LIT) mass spectrometer in which the level of background H_2O is significantly lower, and (b) infrared photodissociation (IRMPD, $10.6\ \mu\text{m}$) in the LIT and a Fourier-transform ion cyclotron resonance (FT-ICR) mass spectrometer. Lower levels of adventitious H_2O in the LIT provided access to fragmentation of $[\text{UO}_2(\text{aco})_n]^{2+}$, $n=1-5$. For $n=3-5$, direct elimination of aco ligands is the favored fragmentation pathway. For $n=1$ and 2, charge reduction reactions are dominant. For $[\text{UO}_2(\text{aco})_2]^{2+}$, the most abundant product ion is $[\text{UO}_2(\text{aco})]^+$, while UO_2^+ is observed following collision-induced dissociation (CID) of $[\text{UO}_2(\text{aco})]^{2+}$. Minor peaks corresponding to ligated $[\text{UO}_2\text{OH}]^+$ are also observed. The IRMPD experiments in the FT-ICR yielded highly accurate mass measurements that confirm composition assignments, and shed light on dissociation reactions in a gas-phase environment that is entirely free of adventitious H_2O . For $[\text{UO}_2(\text{aco})_n]^{2+}$, $n=3-5$, the primary photodissociation channel is direct aco elimination, along with charge-reduction pathways that involve intra-complex proton transfer and formation of species that contain enolate ligands. Similar pathways are observed for IRMPD measurements in the LIT.

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1.0 INTRODUCTION

Exploration of intrinsic (i.e. gas-phase) uranyl ion (UO_2^{2+}) chemistry in the past was difficult because of the lack of effective methods for generating doubly-charged complexes containing UO_2^{2+} . Schwarz and coworkers reported the formation of the “bare” uranyl dication by gas-phase oxidation and charge exchange reactions¹, which yielded a value for the second ionization potential for UO_2^+ that was consistent with a vertical ionization energy obtained by ab initio calculations. Later, Marçalo, and co-workers used laser desorption/ionization and in situ oxidation to generate gas-phase, divalent actinide dioxo cations for subsequent characterization by Fourier transform ion cyclotron resonance mass spectrometry².

The transfer of uranium as monopositive pentavalent $\text{U}^{\text{V}}\text{O}_2^+$, from solution to the gas phase using electrospray ionization (ESI) was first reported in 1992.³ Thereafter, advances in the fundamental understanding of uranyl coordination chemistry have been achieved by using this experimental technique.⁴⁻¹⁹ Most importantly, it has been shown that gas-phase, doubly charged complexes containing the uranyl ion, such as $[\text{UO}_2(\text{L})_n]^{2+}$, with L =acetone (aco) or acetonitrile (acn) and $n=4$ or 5 , can be generated by ESI.¹³ Using small species such as acn and aco, the dominant species observed in the ESI mass spectrum contains the uranyl ion coordinated by 5 ligands.

Studies focusing on gas-phase uranyl complexes have since been extended to include transuranics.²⁰⁻²² For example, ESI was used to generate acn and aco complexes of PuO_2^{2+} and UO_2^{2+} solutions using similar experimental conditions.²² In accord with relative actinyl stabilities, $\text{UO}_2^{2+} > \text{PuO}_2^{2+} > \text{NpO}_2^{2+}$, the yields of plutonyl complexes with acn or aco were significantly lower than those of uranyl, and dipositive neptunyl complexes were not observed. Collision-induced dissociation (CID) of the dipositive coordination complexes in a 3-D quadrupole ion trap produced doubly and singly charged fragment ions; the fragmentation products revealed differences in underlying chemistries of PuO_2^{2+} and UO_2^{2+} , including the lower stability of Pu(VI) as compared with U(VI) . In a subsequent study, it was discovered that micro-solvated NpO_2^{2+} could be generated if the more strongly binding ligand dimethylformamide was used.²³ The chemistry of its complexes was then compared to those of UO_2^{2+} and PuO_2^{2+} .²³

Throughout our past studies of the gas-phase dissociation behavior of actinyl complexes, multiple-stage CID experiments have suggested that doubly charged complexes containing, for example, aco do not shed their full complement of coordinating ligands, but instead generate hydrated product ions (H_2O replacing aco ligands eliminated in the CID reactions), or undergo charge reduction reactions to cations such as $[\text{UO}_2\text{OH}]^+$ and $[\text{UO}_2]^+$ coordinated by aco and/or H_2O .^{13,14,22} Ligand addition reaction rates were so fast that complexes with 2 or 3 coordinating aco ligands hydrated to generate heterogeneous, tetra- or penta-coordinate complexes. As a consequence, gas-phase complex ions containing UO_2^{2+} and two or fewer ligands could not be generated by CID in a “top-down” approach.

In the present study, we used a linear quadrupole ion trap (LIT) to re-examine the fragmentation of uranyl-aco complex ions. The same instrument was used recently to investigate the fragmentation behavior of uranyl complexes with acetonitrile,²⁴ and we showed that the amount of adventitious H_2O and CH_3OH in the LIT is significantly lower than in the 3-D ion trap employed in our previous studies. The low partial pressures of the neutrals therefore allowed the fragmentation chemistry of the species to be studied more completely. For example, we found that CID could be used to drive ligand elimination to completion and furnish the bare uranyl dication, UO_2^{2+} . In addition, fragmentation of $[\text{UO}_2(\text{acn})]^{2+}$ generated $[\text{UO}_2\text{NC}]^+$, which subsequently fragmented to furnish NUO^+ . Creation of the nitrido species by transfer of N from cyanide was confirmed using precursors labeled with ^{15}N , and a formation mechanism involving a cyanate intermediate was proposed based on density functional theory calculations. The bare NUO^+ ion, which is isoelectronic with UO_2^{2+} , had previously been prepared in a “bottom-up” approach by insertion of U^+ into NO in an ion-molecule reaction.²⁵

As described below, the lower partial pressures of adventitious H_2O in the LIT minimized adduct formation and also allowed access to lower uranyl coordination numbers than previously possible for aco-ligated UO_2^{2+} . We have now been able to investigate the fragmentation behavior of the complete series of complex ions, $[\text{UO}_2(\text{aco})_n]^{2+}$, $n=1-5$, with a focus on the tendency for species to undergo ligand elimination versus charge reduction reactions. The low levels of adventitious H_2O and CH_3OH in the ion trap allowed for a more controlled synthesis of adducts for investigation of their fragmentation behavior, and a study of the

general trends in reactivity of specific precursor ions with both neutrals in ion-molecule reactions. These results were compared to data collected on a Fourier-transform ion cyclotron resonance (FT-ICR) MS where the pressure is such that the probability of a collision with a H₂O molecule is essentially zero. IRMPD activation of the uranyl complexes was used in this instrument due to the lack of surrounding gas.

2.0 EXPERIMENTAL METHODS

2.1 CID and IRMPD experiments using a linear ion trap mass spectrometer

ESI followed by CID experiments were performed on a ThermoScientific (San Jose, CA) LTQ-XL LIT mass spectrometer equipped with an Ion Max ESI source. For the ESI experiments, a stock solution (approximately 0.001 molar) of uranyl nitrate hexahydrate ($\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was prepared in water/aco or water/d₆-aco in a 90:10 (v:v) ratio. More dilute solutions were prepared by adding 90:10 water/aco or water/d₆aco to the stock solution. The aco concentration was kept low to prevent its introduction into the ion trap at partial pressures high enough to complicate the studies of reactions between uranyl-aco complexes and H₂O.

The uranyl-H₂O-aco solution was infused into the ESI-MS instrument using the incorporated syringe pump at a flow rate of 5 $\mu\text{L}/\text{min}$. The atmospheric pressure ionization stack settings for the LTQ (lens voltages, quadrupole and octopole voltage offsets, etc.) were optimized for maximum transmission of the doubly-charged ions $[\text{UO}_2(\text{aco})_4]^{2+}$ and $[\text{UO}_2(\text{aco})_5]^{2+}$ to the ion trap mass analyzer by using the auto-tune routine within the LTQ Tune program. Helium was used as the bath/buffer gas to improve trapping efficiency and as the collision gas for CID experiments.

For CID, precursor ions were isolated using an isolation width of 1.0 to 1.5 mass to charge (m/z) units. The exact value was determined empirically to provide maximum ion intensity while ensuring isolation of a single isotopic peak. The (mass) normalized collision energy (NCE, as defined by ThermoScientific) was set between 5 and 18%, which corresponds to application of 0.55 - 0.68 V tickle voltage to the end cap electrodes with the current instrument calibration. The activation Q, which defines the frequency of the applied R.F. potential, was set at 0.30. In all cases, the activation time employed was 30 ms. The mass

spectra displayed represent the accumulation and averaging of at least 30 isolation, dissociation and ejection/detection steps.

The LIT has been modified to accommodate laser beams by cutting a 16-mm diameter hole into the aluminum accessory flange, coaxial with the ion trap. Over this hole sits a replaceable 25.4-mm diameter, 5-mm thick ZnSe window (Thorlabs part WG71050, Newton, NJ, USA), clamped to the aluminum plate with a CF 2-1/8" flange held in place by four socket-cap screws. A high-vacuum seal is made by placing a fluoroelastomer o-ring between the window and the plate. An additional o-ring sits between the window and flange to protect the window from stress-induced deformation or damage. Radiation from a CO₂ laser ($\lambda=10.6\text{ }\mu\text{m}$, Synrad model 48-2, Mukilteo, WA) with output beam radius of 1.75 mm ($1/e^2$ radius) and nominal CW output power of 25 W is shaped before entering the ion trap. The beam is condensed by a factor of ~ 1.5 using a ZnSe Galilean telescope, and then focused with plano-convex ZnSe lens with a nominal focal length of +150 mm, to produce a $1/e^2$ beam radius at the focus (inside the ion trap) of $\sim 250\text{ }\mu\text{m}$ and a Rayleigh range of $\sim 20\text{ mm}$.

The average laser power is controlled by pulse-width modulation of the laser output and by insertion or removal of beam splitters in the beam path. At the highest modulation frequency of 20 kHz the maximum peak-to-peak variation in the laser power is estimated to be $\sim 15\%$. The laser is mounted on an adjacent vibration-isolated optical table approximately 27 cm below the window. A periscope consisting of two gold-plated copper mirrors (Thorlabs NB1-L01) mounted in 2-axis kinematic mounts (Thorlabs KCB1) and an XY translation stage (Thorlabs CXY2) holding the final lens are used to align the laser beam with the ion trap. The total beam path between the laser head and the window is approximately 1.2 m long. This length allows the insertion of removable beamsplitters (for attenuating the laser power), addition of lenses for optimizing the beam diameter and divergence, and optics for incorporating other lasers into the system.

2.2 IRMPD experiments using a FT-ICR mass spectrometer

The experiments were also performed with a custom-built 9.4 T ESI FT-ICR mass spectrometer recently described in detail.²⁶ Samples of $\text{UO}_2(\text{NO}_3)_2 \cdot (\text{H}_2\text{O})_6$ in H_2O and acetone,

prepared as for the LIT experiments, were infused into a tapered 50 μm i.d. fused silica micro-ESI needle^{27,28} at a rate of 300–500 nL min^{-1} at a concentration of $\sim 10\ \mu\text{M}$. ESI conditions were needle voltage 2 kV and heated capillary current 2.5 A. The capillary current was deliberately set to a low value to ensure minimal thermal dissociation of the complex ions. Transport between the quadrupoles was effected with as low a voltage as possible to limit energy of the collisions experienced. A potential of 2 V was applied to the end cap and compensation electrodes of the ICR cell to minimize the axial extent of the ion cloud²⁹. Where possible, the analyte ions of interest were isolated, then accumulated in quadrupole 2 prior to transfer to the ICR cell. Additional or alternate means of isolation were provided by stored waveform inverse Fourier transform (SWIFT)^{30,31} mass-selective ion ejection in the ICR cell. IRMPD experiments were performed by with a Synrad CO_2 laser. The laser is mounted off-axis ($\sim 3.5^\circ$) due to the need to accommodate an axially-mounted electron capture dissociation cathode. To ensure complete irradiation of the ion cloud³², the laser beam diameter (3.5mm) was expanded to $\sim 9\ \text{mm}$ by means of a 2.5-fold beam expander (Synrad). Typical (uncorrected) base pressure for the instrument was $\leq 2 \times 10^{-10}$ Torr, measured by a Bayard-Alpert ionization gauge.

Instrument control, data acquisition, and data analysis were carried out with a modular ICR data station³³. Data acquisition was automated by use of a tool command language script. Each time domain ICR signal (sum of 50 transients) was Hanning apodized, then zero-filled once³⁴, and Fourier transformed to generate a magnitude-mode spectrum that is converted to mass-to-charge ratio by a two-term calibration equation³⁵.

3.0 RESULTS AND DISCUSSION

3.1 CID of $[\text{UO}_2(\text{aco})_5]^{2+}$ and $[\text{UO}_2(\text{aco})_4]^{2+}$

Figure 1 shows the full ESI mass spectrum generated using the LIT mass spectrometer and spray solution of $\text{UO}_2(\text{NO}_3)_2 \cdot (\text{H}_2\text{O})_6$ in 90:10 (v:v) water/aco. As in our previous study,¹³ the most abundant doubly-charged complex ions generated were $[\text{UO}_2(\text{aco})_4]^{2+}$ and $[\text{UO}_2(\text{aco})_5]^{2+}$. Insets in Figure 1 show expanded views of two of the uranyl-aco complexes, which reveal the C-13 isotopic peak spacing that indicates the +2 charge state of the ions.

The CID spectra generated from $[\text{UO}_2(\text{aco})_n]^{2+}$, $n=1-4$, are shown in Figure 2. CID (MS/MS stage) of $[\text{UO}_2(\text{aco})_5]^{2+}$ at m/z 280 generated only $[\text{UO}_2(\text{aco})_4]^{2+}$ at m/z 251 and the product ion spectrum is not shown in Figure 2. The dominant product ion generated by the subsequent CID of $[\text{UO}_2(\text{aco})_4]^{2+}$ (MS³ stage, Figure 2a) was $[\text{UO}_2(\text{aco})_3]^{2+}$ at m/z 222, a result of elimination of a single aco ligand, and the intensity of the monohydrate, $[\text{UO}_2(\text{aco})_3(\text{H}_2\text{O})]^{2+}$ at m/z 231, is $< 10\%$ relative to $[\text{UO}_2(\text{aco})_3]^{2+}$. This observation is in sharp contrast to our earlier study using the 3-D quadrupole ion trap,¹³ in which the relative intensity of $[\text{UO}_2(\text{aco})_3]^{2+}$ was $< 5\%$ relative to the mono- and di-hydrates, $[\text{UO}_2(\text{aco})_3(\text{H}_2\text{O})]^{2+}$ and $[\text{UO}_2(\text{aco})_3(\text{H}_2\text{O})_2]^{2+}$, m/z 231 and 240, respectively. We attribute the difference in the product ion distributions to a lower partial pressure of H_2O in the LIT, whether by change in instrument geometry and design or better vacuum conditions. In any case, it is clear that the tendency to form H_2O adducts to the uranyl complexes in the ion trap is reduced significantly in the present experiments. The same observation was made in our recent investigation of acetonitrile-coordinated uranyl ion.²⁴

3.2 CID of $[\text{UO}_2(\text{aco})_3]^{2+}$

The dominant product ion generated by CID of $[\text{UO}_2(\text{aco})_3]^{2+}$ at m/z 222 (MS⁴ stage, figure 2b) was $[\text{UO}_2(\text{aco})_2]^{2+}$ at m/z 193, again by elimination of a single aco ligand, with an H_2O adduct (m/z 202) observed at $\sim 10\%$ relative intensity. Product ions generated through charge-reduction pathways, at m/z 345, 385 and 403, were observed at relative intensities below 20% relative to the $[\text{UO}_2(\text{aco})_2]^{2+}$ fragment. The ion at m/z 345 is attributed to $[\text{UO}_2\text{OH}(\text{aco})]^+$, the formation of which presumably involves a reactive collision with background H_2O , and elimination of both a neutral and protonated aco ligand as shown in reaction 1. The latter product appears in the CID spectrum at m/z 59. Subsequent CID (spectrum not shown) of the ion at m/z 345 generates a product ion at m/z 287 (UO_2OH^+), consistent with the composition assignment.

We assume that the ion at m/z 403, $[\text{UO}_2\text{OH}(\text{aco})_2]^+$, is generated in a similar process, but without elimination of the neutral aco ligand. The product ions at m/z 345 and 403 were both

observed in our earlier study of $[\text{UO}_2(\text{aco})_n]^{2+}$ ion CID.¹³ However, the relatively low ion intensities of these ions further illustrate the significantly lower partial pressure of (background) H_2O in the LIT instrument.

The relatively abundant product ion at m/z 385 was not observed as a fragment of $[\text{UO}_2(\text{aco})_3]^{2+}$ in our earlier study¹³, and is assigned to a species with composition $[\text{UO}_2(\text{aco-H})(\text{aco})]^+$. We presume that the charge-reduction reaction to generate this ion involves intra-complex proton transfer, elimination of protonated aco, and retention of deprotonated acetone anion (enolate) as shown in reaction 2. Transfer of a D atom to create an $(\text{aco+D})^+$ product was observed in experiments with analogous complexes composed of UO_2^{2+} coordinated by $\text{d}_6\text{-aco}$ (spectrum not shown).

Subsequent CID of the ion at m/z 385 yielded a product ion at m/z 327 (Figure 3a). The neutral loss in this dissociation reaction is 58 mass units, consistent with formation of $[\text{UO}_2(\text{aco-H})]^+$. CID of the ion at m/z 327 (Figure 3b) generated product ions at m/z 270 and 287, assigned as UO_2^+ and UO_2OH^+ , respectively, and at m/z 271 and 288. The latter two are assigned to UO_2H^+ and $\text{UO}_2(\text{H}_2\text{O})^+$, respectively.

At first glance, the appearance of products such as UO_2OH^+ and $\text{UO}_2(\text{H}_2\text{O})^+$ is best explained by invoking dissociation reactions that involve collisions with background H_2O , similar to those reported in our earlier study¹³. To probe the dissociation pathways for $[\text{UO}_2(\text{aco-H})]^+$ further, we examined the CID of the analogous ion generated from precursors that contained $\text{d}_6\text{-aco}$. CID of $[\text{UO}_2(\text{d}_6\text{aco-D})]^+$ (m/z 332, figure 3c) generated UO_2^+ at m/z 270, and UO_2D^+ at m/z 272. The mass shift of 1 unit (m/z 271 to m/z 272) shows that UO_2H^+ (from the unlabeled precursor ion) is generated by hydride transfer from the deprotonated acetone ligand.

CID of $[\text{UO}_2(\text{d}_6\text{aco-D})]^+$ at m/z 332 also generated the product ions at m/z 287 and 288. The intensity of the species at m/z 288 is greater than was observed following CID of $[\text{UO}_2(\text{aco-H})]^+$ (Figure 3b), suggesting that the peak may correspond to formation of UO_2OD^+ . If this is the

case, then the dissociation channel suggests that formation of uranyl hydroxide from $[\text{UO}_2(\text{aco-H})]^+$ (m/z 287 in Figure 3b) may involve, to some extent, decomposition of the deprotonated acetone ligand rather than exclusively reactive collisions with background H_2O .

CID of the ion at m/z 327 also generated a product ion at m/z 299 (Figure 3b). The neutral loss associated with formation of this product ion is 28 mass units, suggesting either elimination of CO or $\text{CH}_2=\text{CH}_2$. For the analogous precursor ions that contained d_6aco , CID of $[\text{UO}_2(\text{d}_6\text{aco-D})]^+$ (Figure 3c), generated peaks at m/z 300 and m/z 304. The peak at m/z 300 would be the

product expected for loss of $\text{CD}_2=\text{CD}_2$, and the composition assignment for the ion at m/z 300 is therefore $[\text{UO}_2(\text{DCO})]^+$ ($[\text{UO}_2(\text{HCO})]^+$ for the unlabeled precursor). The peak at m/z 304 is the product expected for pathway that involves loss of CO from $[\text{UO}_2(\text{d}_6\text{-aco-D})]^+$. Comparing the fragmentation of native and deuterium labeled $[\text{UO}_2(\text{aco-H})]^+$ thus suggests that the elimination of 28 mass involves independent channels that lead to loss of $\text{CH}_2=\text{CH}_2$ or of CO as shown in reactions 4 and 5.

The mechanism by which CO may be eliminated is not known and would benefit from a detailed computation investigation. We note that the conversion of (intact) aco to formaldehyde, with associated elimination of ethylene, has been reported for CID experiments involving aco -coordinated transition metal cations³⁶. Hagelberg, Shvartsburg and coworkers investigated the mechanism for elimination of $\text{CH}_2=\text{CH}_2$ in detail using DFT calculations, and found that the process likely involves a multi-step pathway and formation of an intermediate propionaldehyde ligand³⁶. A particularly interesting feature of reaction 5 is that the product corresponds to an organouranyl complex with discrete uranium-carbon bonding; the most likely structure is $[\text{O}_2\text{U}-\text{CH}_2-\text{CH}_3]^+$.

3.3 CID of $[\text{UO}_2(\text{aco})_2]^{2+}$

In our prior study¹³, collection of product ion spectra for $[\text{UO}_2(\text{aco})_2]^{2+}$ and $[\text{UO}_2(\text{aco})]^{2+}$ required isolation of the species directly from the ESI source rather than by creating them in a

“top-down” approach using multiple-stage CID. With the 3-D ion trap, the product ion spectrum generated from CID of $[\text{UO}_2(\text{aco})_2]^{2+}$ was dominated by $[\text{UO}_2\text{OH}]^+$, $[\text{UO}_2\text{OH}(\text{aco})]^+$ and the mono- and di-hydrates of $[\text{UO}_2\text{OH}(\text{aco})]^+$. Using the LIT in the present study, the high abundance of $[\text{UO}_2(\text{aco})_2]^{2+}$ created by dissociation of $[\text{UO}_2(\text{aco})_3]^{2+}$ allowed us to continue the serial CID (MS^n) experiments. The dominant product ion generated by CID of $[\text{UO}_2(\text{aco})_2]^{2+}$ (MS^5 stage, Figure 2c) appears at m/z 328. This peak is assigned to $[\text{UO}_2(\text{aco})]^+$, which must be generated in a process that involves reduction of uranyl to UO_2^+ , and oxidation of one of the aco ligands. We note that the complementary peak corresponding to (oxidized) aco radical cation is observed at m/z 58 (inset in Figure 2c). Other less abundant (<20% relative intensity) singly-charged product ions included $[\text{UO}_2(\text{aco-H})]^+$ at m/z 327 and $[\text{UO}_2\text{OH}(\text{aco})]^+$ at m/z 345. The former is likely generated in the same type of proton-transfer process that furnishes the product ion at m/z 385 that appears in the CID spectrum of $[\text{UO}_2(\text{aco})_3]^{2+}$.

Also present in the CID spectrum of $[\text{UO}_2(\text{aco})_2]^{2+}$ is a doubly-charged product ion at m/z 179 in the CID spectrum of $[\text{UO}_2(\text{aco})_2]^{2+}$ that arises from the net elimination of 28 mass units (twice the measured neutral loss of 14 m/z from the doubly charged precursor). Subsequent CID of the species at m/z 179 (Figure 1a of the supporting information) generated a peak at m/z 164, consistent with formation of $[\text{UO}_2(\text{aco})]^{2+}$ through the net elimination of 30 mass units (twice the measured neutral loss of 15 m/z). To identify the neutral species eliminated during fragmentation of $[\text{UO}_2(\text{aco})_2]^{2+}$, CID was performed using complex ions that contained d_6 -aco. CID of $[\text{UO}_2(\text{d}_6\text{-aco})_2]^{2+}$ (spectrum not shown) at m/z 199 produced a peak at m/z 183, representing a shift of 4 m/z units relative to the un-labeled complex and indicating that the product ion contains 8 H/D atoms. Subsequent CID of the species at m/z 183 (Figure 1b of the supporting information) produced an ion at m/z 167 (net loss of 32 u), demonstrating that the neutral eliminated to furnish $[\text{UO}_2(\text{aco})]^{2+}/[\text{UO}_2(\text{d}_6\text{-aco})]^{2+}$ contains 2 H/D atoms. The observed shifts in product ion m/z values, and neutral losses during CID, strongly suggest that the ion at m/z 179 in Figure 2c is $[\text{UO}_2(\text{aco})(\text{CH}_2=\text{O})]^{2+}$, created through the elimination of $\text{CH}_2=\text{CH}_2$.

The pathway involving the apparent loss of ethylene was not observed in our previous investigation¹³, primarily because of the lack of access to the ligand elimination reactions of complexes with 2 or 1 aco ligand due to the pronounced formation of H_2O adducts in earlier

CID stages. As noted above, the conversion of *aco* to formaldehyde is not unprecedented, based on the CID experiments reported by Hagelberg, Shvartsburg and coworkers³⁶. Our results demonstrate that similar chemistry is observed for uranyl complexes with *aco*.

3.4 CID of $[\text{UO}_2(\text{aco})]^{2+}$

Another significant finding in the present study was that $[\text{UO}_2(\text{aco})]^{2+}$ was generated in sufficient quantity from dissociation of $[\text{UO}_2(\text{aco})(\text{CH}_2=\text{O})]^{2+}$ to permit an examination of its fragmentation behavior in the multiple-stage CID experiments. The CID spectrum (MS^6 stage) of $[\text{UO}_2(\text{aco})]^{2+}$ is shown in Figure 2d. Fragment ions included the charge reduction products $[\text{UO}_2]^+$ at m/z 270, and $[\text{UO}_2\text{OH}]^+$ at m/z 287 and the complementary ions aco^+ and $(\text{aco}+\text{H})^+$ at m/z 58 and 59, respectively. The $[\text{UO}_2\text{OH}]^+$ and complementary $(\text{aco}+\text{H})^+$ evidently result from a reactive collision with H_2O . It is interesting to note that the bare uranyl ion at m/z 135 was not observed following CID of $[\text{UO}_2(\text{aco})]^{2+}$, while it was observed in our recent investigation of analogous complex ions that contained *acn*.²⁴ Because the ionization energy of UO_2^+ (14.6 ± 0.4 eV³⁷) exceeds that of *acn* (12.2 eV³⁸), we hypothesized that fragmentation by charge separation of $[\text{UO}_2(\text{acn})]^{2+}$ to UO_2^+ and *acn*⁺ should be energetically favored over the elimination of neutral *acn*. The formation of bare UO_2^{2+} from $[\text{UO}_2(\text{acn})]^{2+}$ was therefore attributed to a Coulomb barrier to charge separation to produce UO_2^+ and *acn*⁺.³⁹ The different apparent behavior for complexes containing *acn* and *aco* is consistent with the differences in ionization potential for the two neutrals (ionization energy for *aco* is 9.703 ± 0.006 eV³⁸) and may also reflect a lower coulomb barrier for charge separation.

It should also be pointed out that loss of H_2O from $[\text{UO}_2(\text{aco})_n]^{2+}$, $n=1-4$, was not observed in the experiments that produced the data shown in Figure 2. In a previous study that used ESI of uranyl-*aco* solutions to create gas-phase complex ions, a combination of mass spectrometry experiments¹¹ and quantum chemical calculations¹² revealed H_2O elimination processes that involved aldol dehydration of diacetone alcohol (DAA) ligands, present within the “hypercoordinated” complexes, to produce mesityl oxide (MOX). Because of the lack of product ions corresponding to a net neutral loss of 18 u from any of the $[\text{UO}_2(\text{aco})_n]^{2+}$

precursors, we can conclude that formation of coordinating DAA ligands, or decomposition of DAA to MOX, did not occur in our LIT experiments.

3.5 CID of H₂O and CH₃OH adducts to [UO₂(aco)_n]²⁺, n=2,3.

Though the formation of H₂O adducts to CID products ions was less pronounced in the present study compared to prior ion trap investigations, many of these species could be generated in sufficient abundance by isolating [UO₂(aco)_n]²⁺, n=1-3, for 500-1000 msec without imposed collisional activation. This allowed us to determine the fragmentation pathways of the adduct ions by subsequent CID. As noted earlier, isolation of [UO₂(aco)₅]²⁺ and [UO₂(aco)₄]²⁺ failed to generate adduct ions with intensities suitable for subsequent CID stages.

Figure 4 shows the CID spectra for [UO₂(aco)₃(H₂O)]²⁺ (*m/z* 231, Figure 4a) and [UO₂(aco)₃(CH₃OH)]²⁺ (*m/z* 238, figure 4b). The latter is generated by addition of CH₃OH presumably present in the ion trap because of its use as a co-solvent in unrelated studies by our group of peptide ion fragmentation with the LIT. It was previously demonstrated that [UO₂(aco)₃(O₂)]⁺ is produced by addition of adventitious oxygen to [UO₂(aco)₃]⁺ in an ion trap^{40,41}. The assignment here of the ligand as CH₃OH rather than isobaric O₂ is based on the very different chemistry of U(VI) and U(V), the latter of which is oxidized by addition of O₂, as well as by the distinctive methanol chemistry discussed below. CID of [UO₂(aco)₃(H₂O)]²⁺ leads primarily to formation of [UO₂(aco)₃]²⁺ by simple elimination of H₂O. The CH₃OH adduct (*m/z*

238) is also generated either by a ligand exchange process or by direct addition to the *m/z* 222 product ion. The insets in Figure 3a highlight (aco+H)⁺ and [UO₂OH(aco)₂]⁺ peaks at *m/z* 59 and 403, respectively, which are the products expected for hydrolysis of the bound H₂O ligand during CID (reaction 6).

CID of [UO₂(aco)₃(CH₃OH)]²⁺ also leads primarily to [UO₂(aco)₃]²⁺ by simple elimination of CH₃OH. The methanolysis product, [UO₂OCH₃(aco)₂]⁺ at *m/z* 417, is also observed and is presumably generated in a reaction similar to (6), and is significantly more abundant than the analogous hydroxide complex. This suggests that formation of the methoxide is favored over

the hydroxide, which may be due to stronger binding of CH₃OH to [UO₂(aco)₃]²⁺ and/or different fragmentation mechanisms.

Figure 5 shows the CID spectra for (a) UO₂(aco)₂(H₂O)]²⁺, (b) [UO₂(aco)₂(CH₃OH)]²⁺, (c) [UO₂(aco)₂(H₂O)₂]²⁺ and (d) [UO₂(aco)₂(H₂O)(CH₃OH)]²⁺. For each mono- and di-adduct to [UO₂(aco)₂]²⁺, hydrolysis and methanolysis is observed, with ligated [UO₂OH]⁺ or [UO₂OCH₃]⁺ appearing as prominent, if not dominant, peaks in the product ion spectra. For UO₂(aco)₂(H₂O)]²⁺ at *m/z* 202, direct H₂O loss and formation of the [UO₂OH(aco)]⁺/(aco+H)⁺ pair occur with nearly equal probability. For [UO₂(aco)₂(CH₃OH)]²⁺ at *m/z* 209, direct CH₃OH loss is not observed, and the product ion distribution is dominated by the methanolysis reaction to furnish (aco+H)⁺ and [UO₂OCH₃(aco)]⁺.

Hydrolysis is dominant for [UO₂(aco)₂(H₂O)₂]²⁺ at *m/z* 211. Direct H₂O elimination to generate the monohydrate at *m/z* 202 is a relatively minor pathway compared to formation of [UO₂OH(aco)(H₂O)]⁺ at *m/z* 363. CID of [UO₂(aco)₂(H₂O)(CH₃OH)]²⁺ causes primarily the elimination of H₂O to generate [UO₂(aco)₂(CH₃OH)]²⁺ at *m/z* 209. This result in particular strongly supports the hypothesis that CH₃OH interacts more strongly with UO₂²⁺ than does H₂O, and that this influences in part the relative reaction tendency to generate methoxide products ions in charge reduction reactions. Stronger binding to a metal cation of CH₃OH vs. H₂O is in accord with the comparative gas phase basicities (GBs), which are derived from the proton affinities. The GB of CH₃OH, 724 kJ/mol, is substantially higher than that of H₂O, 660 kJ/mol³⁸, which renders the former a better electron donor that binds more strongly to metal cations such as uranium in uranyl. For [UO₂(aco)₂(H₂O)(CH₃OH)]²⁺, the charge-reduction product generated in greatest abundance is [UO₂OCH₃(aco)(H₂O)]⁺ at *m/z* 377. This composition assignment is preferred over [UO₂OH(aco)CH₃OH]⁺ because the ion at *m/z* 377 dissociates to furnish [UO₂OCH₃(aco)]⁺ at *m/z* 359. This composition assignment is supported by the observed elimination of 58 mass units (neutral aco) to yield [UO₂OCH₃]⁺ in a subsequent CID step. The preferential elimination of protonated aco rather than H₃O⁺, in concert with methoxide formation, is in accord with the higher proton affinity of aco (812 kJ/mol) as compared with H₂O (691 kJ/mol³⁸).

The observations made here using CID of the H₂O or CH₃OH adducts support the conclusions drawn earlier regarding the formation of charge-reduced product ions via reactive collisions of [UO₂(aco)_n]²⁺ with the respective neutrals. Indeed, subjecting the H₂O adduct in particular to CID is akin to isolating the intermediate species likely formed during the fragmentation pathways that lead to aco-coordinated [UO₂OH]⁺ or [UO₂OCH₃]⁺ shown above. The general outcome of the CID reactions, and in particular the tendency to lose H₂O or CH₃OH or to undergo hydrolysis or methanolysis, is interesting and should motivate further DFT studies.

3.6 High-resolution mass measurements and infrared photodissociation of [UO₂(aco)_n]²⁺, n=3-5

As noted above, one significant drawback to the use of the 3-D quadrupole ion trap in our earlier studies was that CID spectra from metal complexes were often dominated by H₂O adducts or by hydrolysis products. One of the aims of the present study was to investigate the fragmentation of acetone-coordinated UO₂²⁺ in a “cleaner” gas-phase environment. Use of an FT-ICR instrument provided both higher vacuum conditions (and presumably lower partial pressure of background H₂O and CH₃OH) and the possibility to perform high-resolution and high-accuracy mass measurements to confirm compositions assignments for precursor and product ions. The desire to maintain high-vacuum conditions in the custom 9.4-T FT-ICR precluded the examination of fragmentation by collisional activation. Instead, ion dissociation by fixed wavelength (10.6 μm) IRMPD was investigated.

The most abundant peak in the FT-ICR spectrum had a measured *m/z* of 280.1254, compared a calculated value of 280.1244 (3.6 ppm error) expected for a molecular formula of UO₇C₁₅H₃₀ and the composition assignment of [UO₂(aco)₅]²⁺. The product ion spectra generated by photodissociation of [UO₂(aco)₅]²⁺, [UO₂(aco)₄]²⁺ and [UO₂(aco)₃]²⁺ are shown in Figure 6a, 6b and 6c, respectively. The IRMPD spectra for [UO₂(aco)₅]²⁺ and [UO₂(aco)₄]²⁺ were collected by direct isolation of the respective species from the ESI source. The IRMPD spectrum of [UO₂(aco)₃]²⁺ was collected in an MS³ experiment following the initial photodissociation of [UO₂(aco)₅]²⁺. Measured and calculated exact masses for the respective precursor and product ions are provided in Table 1.

The most abundant photodissociation product generated from $[\text{UO}_2(\text{aco})_5]^{2+}$ had a measured m/z value of 251.1037, which is within 1 ppm of the calculated m/z of 251.1035 and the molecular formula of $\text{UO}_6\text{C}_{12}\text{H}_{24}$ for $[\text{UO}_2(\text{aco})_4]^{2+}$. Two other product ions were observed at relative intensities greater than 1%. The first had a measured m/z value of 327.0748, compared to a calculated m/z value of 327.0741 for the molecular formula $\text{UO}_3\text{C}_3\text{H}_5^+$ (2.1 ppm error). The accurate mass measurement supports the assignment made in the LIT experiments of UO_2^{2+} coordinated by a deprotonated acetone ligand ($[\text{UO}_2(\text{aco-H})]^+$). The second product ion has a measured m/z value of 385.1176, which agrees well with the calculated value of 385.1159 (4.4 ppm error) and a molecular formula of $\text{UO}_4\text{C}_6\text{H}_{11}$. In this case, the accurate mass measurement supports the composition assignment of $[\text{UO}_2(\text{aco-H})(\text{aco})]^+$. As for the LIT experiments, we suggest that the dissociation pathway that involves elimination of presumed intra-complex proton transfer, elimination of acetone ligands and coordination of UO_2^{2+} of deprotonated acetone.

The dominant product ion generated by photodissociation of $[\text{UO}_2(\text{aco})_4]^{2+}$ was $[\text{UO}_2(\text{aco})_3]^{2+}$ at a measured m/z value of 222.0829, which compares well to the calculated value of 222.0825 (1.8 ppm error) for a molecular formula of $\text{UO}_5\text{C}_9\text{H}_{18}$. As for the $[\text{UO}_2(\text{aco})_5]^{2+}$ precursor, product ions at nominal m/z 327 and 385 were also observed. Other products generated by IRMPD included species with measured m/z values of 270.0419, 287.0450, 299.0452 and 299.0812.

The latter two species, at m/z 299.0452 and 299.0812, were also observed during photodissociation of the $[\text{UO}_2(\text{aco})_3]^{2+}$ precursor and are discussed below. The measured value for the species at nominal m/z 270, agrees well with a calculated value of 270.0400 (7.0 ppm error) for the molecular formula UO_2 . The product ion is thus generated by elimination of 3 neutral acetone ligands, oxidation of the 4th aco ligand, and reduction of the uranyl dication to UO_2^+ . As noted above, similar results were observed during the CID experiments on the LIT when the aco coordination number was reduced to 1.

Appearance of an ion with nominal m/z of 287 in the photodissociation spectrum of $[\text{UO}_2(\text{aco})_4]^{2+}$ was surprising. The accurate m/z measurement for the ion was 287.0450, which agrees well with the calculated value of 287.0428 (7.7 ppm error), a molecular formula of UO_3H ,

and composition assignment of UO_2OH^+ . In the LIT experiments, we assume that UO_2OH^+ is generated primarily by energetic collisions with background H_2O . However, the partial pressure of H_2O in the FT-ICR is significantly lower and an alternative pathway may involve dissociation through an enol-intermediate, with retention of hydroxide by the UO_2^{2+} unit and elimination of $\text{CH}_2=\text{C}-\text{CH}_3^+$. As noted earlier, a potential pathway for generation of UO_2OH^+ by decomposition of deprotonated acetone during CID of $[\text{UO}_2(\text{aco}-\text{H})]^+$ was suggested based on the isotope labeling experiments. In the IR photodissociation experiments conducted with the FT-ICR instrument, UO_2OH^+ may be generated by the fragmentation of energetic $[\text{UO}_2(\text{aco}-\text{H})]^+$ resulting from photodissociation of $[\text{UO}_2(\text{aco})_4]^{2+}$.

The photodissociation spectrum of $[\text{UO}_2(\text{aco})_3]^{2+}$ (figure 6c) contains the same product ions observed following photodissociation of $[\text{UO}_2(\text{aco})_4]^{2+}$, along with a product with (measured) m/z value of 193.0619. This measured value agrees well with a calculated value of 193.0616 (1.6 ppm error) and a molecular formula of $\text{UO}_4\text{C}_6\text{H}_{12}$ (consistent with the assignment of $[\text{UO}_2(\text{aco})_2]^{2+}$). As noted above, product ions were also observed at m/z 299.0452 and 299.0812. Based on the accurate mass measurement (Table 1), the ions have molecular formulae of UO_3CH and $\text{UO}_2\text{C}_2\text{H}_5$, respectively. The former appears to involve conversion of deprotonated acetone to HCO through the elimination of $\text{CH}_2=\text{CH}_2$, as observed in the LIT experiments following CID of $[\text{UO}_2(\text{aco}-\text{H})]^+$. The second likely involves conversion of deprotonated acetone to CO and $\text{CH}_3-\text{CH}_2^-$. The high resolution/high accuracy measurements therefore support the dissociation pathways for $[\text{UO}_2(\text{aco}-\text{H})]^+$ revealed in the LIT experiments. This also provides new evidence of more than one product at nominal m/z 299, indicating at least two fragmentation mechanisms are of relevance here. The mechanisms by which these conversions occur are not clear and would benefit from detailed quantum mechanical calculations.

3.7 Infrared photodissociation in the linear ion trap MS

As noted above, the LIT at Duquesne has been modified to allow IR photodissociation experiments. We are therefore able to make a comparison of photodissociation of the $[\text{UO}_2(\text{aco})_n]^{2+}$ precursor ions at 10.6 μm in the FT-ICR and LIT instruments. In addition, the use

of IRMPD with both types of mass spectrometers allows for further investigation of the potential role(s) background H₂O may play in the appearance of product ions and product ion distributions. As noted earlier, one main goal of this study was to determine the intrinsic fragmentation pathways for the acetone-coordinated uranyl ion, free as much as possible from influence by background H₂O.

Because IRMPD data using the high-resolution FT-ICR instrument could only be collected for [UO₂(aco)₅]²⁺, [UO₂(aco)₄]²⁺ and [UO₂(aco)₃]²⁺, only these species were investigated using the LIT instrument and the photodissociation spectra for the respective ions are shown in Figure 7. In the LIT experiments, each photodissociation spectrum was collected by isolating the precursor directly from the ESI source rather than in an MSⁿ approach.

As in the CID experiments, IR photodissociation of [UO₂(aco)₅]²⁺ (Figure 7a) in the LIT produced only [UO₂(aco)₄]²⁺ at *m/z* 251. Unlike the FT-ICR experiments, generation of [UO₂(aco-H)]⁺ and [UO₂(aco-H)(aco)]⁺ at *m/z* 327 and 385, respectively, was not observed. A likely explanation for this observation is the differences in irradiation times and intensities that were used for IRMPD in the LIT and FT-ICR instruments (ca. 30 ms for the former and 200 ms for the latter), and potential differences in the overlap between the IR laser and the ion cloud.

IR photodissociation of [UO₂(aco)₄]²⁺ in the LIT (Figure 7b) produced primarily [UO₂(aco)₃]²⁺ and *m/z* 222, with [UO₂(aco)₂]²⁺ and UO₂⁺, at *m/z* 193 and 270, respectively, also observed at relative intensities above 1%. Interestingly, no H₂O adduct to [UO₂(aco)₃]²⁺, i.e. [UO₂(aco)₃(H₂O)]²⁺ at *m/z* 237, was observed. The adduct was observed in the product ion spectrum when [UO₂(aco)₄]²⁺ was subjected to CID (Figure 2a), albeit at less than 5% relative intensity.

As in the FT-ICR experiments, IRMPD of [UO₂(aco)₃]²⁺ at *m/z* 222 (Figure 6c) in the LIT generated product ions at *m/z* 193 ([UO₂(aco)₂]⁺) and 270 (UO₂⁺). UO₂OH⁺ at *m/z* 287 was also observed, and is the only species generated by IRMPD in the LIT that contains hydroxide. Despite the higher levels of H₂O in the LIT (compared to the FT-ICR), the photodissociation spectrum appears to contain the same product ions generated in the cleaner gas-phase environment (the FT-ICR). It may therefore be that UO₂OH⁺ is generated by the fragmentation of energetic [UO₂(aco-H)]⁺ resulting from, in this case, initial photodissociation of [UO₂(aco)₃]²⁺.

Most interesting was the appearance of peaks at m/z 299 and 327, which match those observed in the FT-ICR experiments. The resolution of the LIT is not sufficiently high to resolve the peak at nominal m/z 299 into the individual ions suggested by both the high-resolution measurements in the FT-ICR or the isotope labeling study using CID. However, the results here show that the interesting dissociation channels are also activated by IRMPD in the LIT instrument.

4.0 CONCLUSIONS

To summarize, fragmentation of acetone-coordinated uranyl ion, $[\text{UO}_2(\text{aco})_n]^{2+}$ ($n=1-5$), was revisited here using a LIT mass spectrometer in which the level of background H_2O is significantly lower than in 3-D ion traps used in previous studies.^{13,14,22} The lower apparent partial pressure of H_2O in the LIT provided access to the fragmentation behavior of each complex ion. For $n=3-5$, direct elimination of aco ligands is the favored fragmentation pathway. For $n=1$ and 2, charge reduction reactions are dominant: for $[\text{UO}_2(\text{aco})_2]^{2+}$, the most abundant product ion is $[\text{UO}_2(\text{aco})]^+$ while UO_2^+ is observed following CID of $[\text{UO}_2(\text{aco})]^{2+}$. Minor peaks corresponding to ligated UO_2OH^+ are also observed.

We also investigated the CID of H_2O and CH_3OH adducts to $[\text{UO}_2(\text{aco})_3]^{2+}$, $[\text{UO}_2(\text{aco})_2]^{2+}$ and $[\text{UO}_2(\text{aco})]^{2+}$. CID of $[\text{UO}_2(\text{aco})_3(\text{H}_2\text{O})]^{2+}$ and $[\text{UO}_2(\text{aco})_3(\text{CH}_3\text{OH})]^{2+}$ leads primarily to formation of $[\text{UO}_2(\text{aco})_3]^{2+}$ by simple elimination of the solvent molecule. Hydrolysis and methanolysis became the dominant pathways for adducts to $[\text{UO}_2(\text{aco})_2]^{2+}$ that contained 1 or 2 H_2O or CH_3OH ligands. The CID behavior of the adducts both supports the conclusions drawn earlier regarding the formation of charge-reduced product ions via reactive collisions of $[\text{UO}_2(\text{aco})_n]^{2+}$ with the respective neutrals and the hypothesis that 3 aco ligands are necessary to stabilize ligand addition versus charge reduction.

The IRMPD experiments in the FT-ICR yielded highly accurate mass measurements that strongly support composition assignments, and shed light on dissociation reactions in a gas-phase environment that is free of H_2O . For $[\text{UO}_2(\text{aco})_n]^{2+}$, $n=3-5$, the primary photodissociation channel is direct aco elimination, along with charge-reduction pathways that involve intra-

complex proton transfer and formation of species that contain enolate ligands. Similar pathways are observed for IMRPD measurements in the LIT.

The IRMPD investigations, particularly those in the FT-ICR instrument, along with CID using deuterium labeled acetone, helped identify new reaction pathways for decomposition of $[\text{UO}_2(\text{aco-H})]^+$ that involve elimination of 28 mass units. The isotope labeling studies suggested that loss of 28 mass units from $[\text{UO}_2(\text{aco-H})]^+$ involves elimination of either CO or $\text{CH}_2=\text{CH}_2$. These two pathways were confirmed by high-accuracy mass measurements in the FT-ICR instrument. While the mechanisms by which CO or $\text{CH}_2=\text{CH}_2$ are eliminated are not clear, the reactions further illustrate the rich chemistry of these complexes that may be accessed in the relatively clean gas-phase environment of the LIT instrument.

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SUPPORTING INFORMATION

A schematic of the modified linear ion trap, and CID spectra of the m/z 179 product derived from fragmentation of $[\text{UO}_2(\text{aco})_2]^{2+}$, and the m/z 183 product derived from fragmentation of $[\text{UO}_2(\text{d}_6\text{-aco})_2]^{2+}$ are provided as Figures S1 and S2, respectively, of the supporting information.

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LIST OF FIGURES AND TABLES

- Figure 1. Electrospray ionization mass spectrum generated from uranyl nitrate hexahydrate dissolved in H₂O with 5% by volume of aco. The insets show high-resolution scans centered on [UO₂(aco)₄]²⁺ and [UO₂(aco)₅]²⁺.
- Figure 2. Collision induced dissociation spectra generated from uranyl-aco complex ions: (a) fragmentation of [UO₂(aco)₄]²⁺, (b) fragmentation of [UO₂(aco)₃]²⁺, (c) fragmentation of [UO₂(aco)₂]²⁺, and (d) fragmentation of [UO₂(aco)]²⁺. Asterisks in each spectrum indicate adducts (H₂O and/or CH₃OH) generated by ion-molecule reactions. The circle and arrow legends identifies the sequence of CID stages that produces a given product in spectra. Filled circles indicate the ions specifically isolated for collisional activation. Open circles symbolize product ions generated in the last CID step in a given sequence.
- Figure 3. Collision induced dissociation spectra generated from singly charged uranyl-aco complex ions: (a) fragmentation of [UO₂(aco-H)(aco)]⁺ at *m/z* 385, (b) fragmentation of [UO₂(aco-H)]⁺ at *m/z* 327 (c) fragmentation of [UO₂(d₆aco-D)]⁺ at *m/z* 332. Asterisks in each spectrum indicate adducts (H₂O and/or CH₃OH) generated by ion-molecule reactions. The circle and arrow legends identifies the sequence of CID stages that produces a given product in spectra. Filled circles indicate the ions specifically isolated for collisional activation. Open circles symbolize product ions generated in the last CID step in a given sequence.
- Figure 4. Collision induced dissociation spectra generated from H₂O and CH₃OH adducts of [UO₂(aco)₃]²⁺: (a) CID of (a) [UO₂(aco)₃(H₂O)]²⁺ and (b) [UO₂(aco)₃(CH₃OH)]²⁺. The circle and arrow legends identifies the sequence of CID stages that produces a given product in spectra. Partially shaded circles indicate species isolated but not subjected to collisional activation. Filled circles indicate the ions specifically isolated for collisional activation. Open circles symbolize product ions generated in the last CID step in a given sequence.
- Figure 5. Collision induced dissociation spectra generated from H₂O and CH₃OH adducts of [UO₂(aco)₂]²⁺: (a) [UO₂(aco)₂(H₂O)]²⁺, (b) [UO₂(aco)₂(CH₃OH)]²⁺, (c) [UO₂(aco)₂(H₂O)₂]²⁺ and (d) [UO₂(aco)₂(H₂O)(CH₃OH)]²⁺. The circle and arrow legends identifies the sequence of CID stages that produces a given product in spectra. Partially shaded circles indicate species isolated but not subjected to

collisional activation. Filled circles indicate the ions specifically isolated for collisional activation. Open circles symbolize product ions generated in the last CID step in a given sequence.

Figure 6. IR photodissociation spectra generated from uranyl-aco complex ions: (a) fragmentation of $[\text{UO}_2(\text{aco})_5]^{2+}$, (b) fragmentation of $[\text{UO}_2(\text{aco})_4]^{2+}$ and (c) fragmentation of $[\text{UO}_2(\text{aco})_3]^{2+}$. Photodissociation spectra were collected using the FT-ICR mass spectrometer.

Figure 7. IR photodissociation spectra generated from uranyl-aco complex ions: (a) fragmentation of $[\text{UO}_2(\text{aco})_5]^{2+}$, (b) fragmentation of $[\text{UO}_2(\text{aco})_4]^{2+}$ and (c) fragmentation of $[\text{UO}_2(\text{aco})_3]^{2+}$. Photodissociation spectra were collected using the linear ion trap mass spectrometer.

Table 1. Measured and calculated exact masses for the uranyl-acetone precursor and product ions.

Figure 1.

Figure 3.

Figure 4.

Figure 5.

Figure 6.

Figure 7.

Table 1.

Measured m/z	Calculated m/z	Error (ppm)	Molecular formula	Composition assignment
280.1254	280.1244	3.6	UO ₇ C ₁₅ H ₃₀	[UO ₂ (aco) ₅] ²⁺
251.1037	251.1035	0.8	UO ₆ C ₁₂ H ₂₄	[UO ₂ (aco) ₄] ²⁺
222.0829	222.0825	1.8	UO ₅ C ₉ H ₁₈	[UO ₂ (aco) ₃] ²⁺
193.0619	193.0616	1.6	UO ₄ C ₆ H ₁₂	[UO ₂ (aco) ₂] ²⁺
385.1176	385.1159	4.4	UO ₄ C ₆ H ₁₁	[UO ₂ (aco-H)(aco)] ⁺
327.1748	327.0741	2.1	UO ₃ C ₃ H ₅	[UO ₂ (aco-H)] ⁺
299.0452	299.0428	8.0	UO ₃ CH	[UO ₂ (HCO)] ⁺
299.0812	299.0792	6.7	UO ₂ C ₂ H ₅	[UO ₂ (CH ₂ CH ₃)] ⁺
287.0450	287.0428	7.7	UO ₃ H	[UO ₂ OH] ⁺
271.0497	271.0478	7.0	UO ₂ H	[UO ₂ H] ⁺
270.0419	270.04	7.0	UO ₂	[UO ₂] ⁺