Using Tandem Mass Spectrometry and IRMPD Spectroscopy to Determine the Intrinsic Reactions of Uranyl-Containing Ions

Irena Tatosian

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USING TANDEM MASS SPECTROMETRY AND IRMPD SPECTROSCOPY TO DETERMINE THE INTRINSIC REACTIONS OF URANYL-CONTAINING IONS

A Thesis
Submitted to Duquesne University

Duquesne University
In partial fulfillment of the requirements for the degree of Master of Science

By
Irena J. Tatosian

May 2020
USING TANDEM MASS SPECTROMETRY AND IRMPD SPECTROSCOPY TO
DETERMINE THE INTRINSIC REACTIONS OF URANYL-CONTAINING IONS

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ABSTRACT

USING TANDEM MASS SPECTROMETRY AND IRMPD SPECTROSCOPY TO
DETERMINE THE INTRINSIC REACTIONS OF URANYL-CONTAINING IONS

By
Irena J. Tatosian
May 2020

Thesis supervised by Dr. Michael J. Van Stipdonk

Developing a comprehensive understanding of the intrinsic reactivity of uranium-containing species remains an important goal, as it may influence future developments in areas ranging from new approaches to nuclear fuel processing to studies of the migration and fate of the element in the environment. At a more fundamental level, such studies contribute to the understanding of the role that 5-f electrons may play in chemical bonding, the so-called “f-electron challenge”. Electrospray ionization (ESI) is an effective way to generate gas-phase complexes containing uranium and uranyl ions for subsequent studies of intrinsic structure and reactivity. Studies in the gas-phase are important and necessary because investigation of reactivity in the condensed phase, in a species-specific fashion, is complicated by the presence of solvent molecules and counter ions and complex equilibria between metallic species in different form.
Recent experiments have demonstrated that state-of-the art linear ion traps (LIT) can provide access to a wide range of fragmentation pathways and reactions for gas-phase uranium species, whether using collision-induced dissociation (CID) and ion-molecule reactions (IMRs), including ones that were masked in previous experiments by high partial pressures of adventitious H$_2$O present in 3-D ion traps.

The goal was to survey the types of unimolecular (by CID) and bimolecular (IMR) reactions of precursor and product ions. The experiments outlined in this thesis were undertaken to investigate the intrinsic reactivity of uranium-containing complexes with a variety of ligands including nitrate, perchlorate, acetate, propionate, acrylate, benzoate, and combinations of different halides. However, a general limitation of mass spectrometry approaches to the study of intrinsic chemistry is that no direct structural information is produced, and determinations of structure rely heavily either on chemical intuition or theoretical calculations - understanding gas-phase reactivity requires a clearer idea of ion structure. Therefore, an addition goals was to use density functional theory (DFT) calculations, and infrared multiple-photon photodissociation (IRMPD) spectroscopy were used to identify the conformations of selected gas-phase uranyl complexes to enhance the understanding of the relationship between structure and reactivity.
DEDICATION

To my mother, Gina Tatosian, thank you for always being there for me, cooking my favorite meals, and for answering endless phone calls at all hours of the night. I wouldn’t be where I am today, without you.
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LIST OF ABBREVIATIONS

LIT: Linear Ion Trap
ESI: Electrospray Ionization
CID: Collision-Induced Dissociation
IMR: Ion-Molecule Reactions
IRMPD: Infrared Multiple-Photon Photodissociation
FT-ICR: Fourier Transform Ion Cyclotron Resonance
FELIX: Free Electron Laser for Infrared Experiments
DFT: Density Functional Theory
EE: Electronic Energies
Chapter 1

Introduction to Fragmentation of Uranium Containing Ions

Understanding the intrinsic reactivity of uranium species is important in many technical areas of actinide science, including the development of new approaches for nuclear fuel processing and waste storage, to predicting the migration and the fate of the element in the environment. On a fundamental level, there is great interest in the identification of new ways to activate and/or functionalize the “yl” oxo ligands of the uranyl ion, UO$_2^{2+}$, which is thermodynamically stable, and kinetically inert, in the condensed phases. Also, there is interest in probing intrinsic interactions between actinyl ions and ligands and identifying reactions mediated by the actinides, as the chemistry of these elements can differ from those exhibited by transition metal ions. Lastly, it is with the 5-f elements that the f-electrons may participate in chemical bonding, and studies of intrinsic structure and reactivity may contribute to the so-called “f-electron challenge”.

The principal advantage of gas-phase studies is their ability to provide fundamental information that may be used to further understand reactivity in the condensed phase by allowing for the investigation of reactivity at the molecular level, free of solvent, while maintaining control over the composition of the reactants and their energies [1-10]. Electrospray ionization (ESI) has been very effective for producing gas-phase complexes that contain uranium in high oxidation states (+5 and +6) [11], and the van Stipdonk group was among the first to use ESI to generate gas-phase, doubly charged complexes containing the uranyl ion (true uranyl species) for studies for intrinsic structure and reactivity in a species-specific fashion [2-8]. For example, ESI was used to generate, for the first time, gas-phase ions that contained U$^{VI}$O$_2^{2+}$ coordinated by ligands
such as acetone or acetonitrile for studies of both unimolecular fragmentation (using CID) and bimolecular IMR reactions using ion trap mass spectrometry [2,3]. Since then, ESI has been used to create gas-phase uranyl species for wide a range of mass spectrometry, ion mobility, and anion photoelectron spectroscopy experiments [12-37], as well as transuranic species [1, 38-45]. For example, ESI was used to produce acn and aco complexes of Pu^{VI}O_{2}^{2+} and U^{VI}O_{2}^{2+} solutions for an “apple-apples” comparison of CID behavior under similar experimental conditions [38].

Recent experiments by the van Stipdonk group indicated that newer, 2-dimensional linear ion trap (LIT) instruments will provide access to fragmentation pathways and reactions when used to investigate species that were initially studied using 3-dimensional ion traps [46-50]. For example, the dissociation behavior of gas-phase uranyl ions, such as those with acetone or acetonitrile ligands, using a 3-dimensional ion trap was difficult to interpret because of the appearance and high yields of reaction products created by collisions with background H_{2}O. The relatively high partial pressures of H_{2}O in older generation ion traps (ca. 10^{-6} Torr) can lead to formation of hydrated ions (adducts created by association reactions) or to charge reduction reactions that leave [U^{VI}O_{2}(OH)]^{+} and [U^{V}O_{2}]^{+} complexes [2,3,38]. However, experiments using the newer LIT, for which conductance of gases out of the mass analyzer is higher (thus leading to lower levels of background H_{2}O and/or O_{2}) suggested that more accurate descriptions of intrinsic fragmentation pathways would be produced for gas-phase uranyl complexes. For example, in the LIT multiple-stage CID ultimately produced bare U^{VI}O_{2}^{2+} by sequential elimination of acetonitrile ligands from [U^{VI}O_{2}(N≡C-CH_{3})_{4}]^{2+} and, more importantly, generated the nitrido species NU^{VI}O^{+} from [U^{VI}O_{2}(NC)]^{+}. While gas-
phase NU\textsuperscript{VI}O\textsuperscript{+} had been previously created by insertion of U\textsuperscript{+} into NO \textsuperscript{51}, the LIT experiments showed that the product can also be generated by CID reaction in a pathway that involves activation and substitution of an “yl” oxo ligand of the uranyl ion. Later experiments were conducted with acetone-coordinated U\textsuperscript{VI}O\textsuperscript{2+}, and interesting product ions such as [U\textsuperscript{VI}O\textsubscript{2}-HCO]\textsuperscript{+} and [U\textsuperscript{VI}O\textsubscript{2}-CH\textsubscript{2}CH\textsubscript{3}]\textsuperscript{+} have been identified using extensive isotope labeling and high-resolution/high-accuracy mass measurements \textsuperscript{47}. These experiments in particular demonstrated the exciting and interesting new type of gas-phase experiments that may be conducted with uranyl species.

ESI and MS\textsuperscript{n} tandem mass spectrometry were later used to create ions from uranyl-formate and -acetate precursor anions \textsuperscript{48}. Multiple-stage CID experiments showed that [UO\textsubscript{2}(O\textsubscript{2}C-H)\textsubscript{3}]\textsuperscript{-} dissociates by decarboxylation and elimination of CH\textsubscript{2}=O, leaving the [UO\textsubscript{2}(O)(H)]\textsuperscript{-} as the final product ion. For [UO\textsubscript{2}(O\textsubscript{2}C-CH\textsubscript{3})\textsubscript{3}]\textsuperscript{-}, the initial fragmentation step was elimination of acetyloxyl radical, CH\textsubscript{3}CO\textsuperscript{•}, with associated reduction of UO\textsubscript{2}\textsuperscript{2+} to UO\textsubscript{2}\textsuperscript{+}. CID of the [UO\textsubscript{2}(O\textsubscript{2}C-CH\textsubscript{3})\textsubscript{2}]\textsuperscript{-} ion then created [UO\textsubscript{2}(CH\textsubscript{3})(O\textsubscript{2}C-CH\textsubscript{3})]\textsuperscript{-} (and organometallic complex) through the elimination of CO\textsubscript{2}. The organometallic product then reacted with H\textsubscript{2}O to make [UO\textsubscript{2}(OH)(O\textsubscript{2}C-CH\textsubscript{3})]\textsuperscript{-} (with CH\textsubscript{4} eliminated as the neutral product) when independently isolated for IMR with H\textsubscript{2}O. CID of [UO\textsubscript{2}(CH\textsubscript{3})(O\textsubscript{2}C-CH\textsubscript{3})]\textsuperscript{-} caused the elimination of (neutral) CH\textsubscript{4}, likely through intra-complex proton transfer, to make [UO\textsubscript{2}(O\textsubscript{2}C=CH\textsubscript{2})]\textsuperscript{-}. This species then fragmented to generate [UO\textsubscript{2}(O)]\textsuperscript{-} as the terminal product ion.

The experiments with the acetate anion precursor ions were important for a couple of reasons. First, the reaction pathways identified in experiments in which the levels of background H\textsubscript{2}O were relatively low were very different than those reported by Luo et al.
[37], who listed species such as $\text{[UO}_2\text{(CH}_3\text{)(OH)}\text{]}^-$ and $\text{[UO}_2\text{(OH)}_2\text{]}^-$ as the terminal dissociation products. The experiments performed using the LIT strongly suggest that the $\text{[UO}_2\text{(CH}_3\text{)(OH)}\text{]}^-$ and $\text{[UO}_2\text{(OH)}_2\text{]}^-$ ions are actually artifacts created by reactions between CID products and background H$_2$O in the study by Luo et al. This lends support to the idea that the experiments performed under the condition of lower partial pressure of background H$_2$O provide a more accurate survey of intrinsic unimolecular chemistry. Also, to note from these experiments described above, new interesting ions can be generated by the LIT experiments that will allow for exploration of intrinsic reactivity.

Another focus of the uranyl ion research effort has been on the use of wavelength selective infrared multiple photon photodissociation (IRMPD) spectroscopy to determine precursor and product ion structure(s), and also to determine how much the position of the asymmetric O=U=O stretch ($v_3$) [8-10, 46, 52] is influenced by the number and identify of coordinating ligands. It is known that the uranium-oxygen bonds in UO$_2^{2+}$ and UO$_2^+$ are weakened by electron donation to the uranium metal center by coordinating nucleophiles [53-61]. The gas-phase infrared spectra of discrete UO$_2^{2+}$ complexes coordinated by acetone and acetonitrile were used in a past study [8], to systematically measure systematic trends of the position of $v_3$ versus ligand number and identity, and for comparison with computed frequencies generated using DFT. In terms of the position of the $v_3$ vibration, important data about the interactions between ligands and UO$_2$ was generated. The $v_3$ value systematically red shifted from 1017 cm$^{-1}$ for $\text{[UO}_2\text{(acetone)}_2\text{]}^{2+}$ to 1000 and 988 cm$^{-1}$ for $\text{[UO}_2\text{(acetone)}_3\text{]}^{2+}$ and $\text{[UO}_2\text{(acetone)}_4\text{]}^{2+}$, respectively, which was consistent with the idea that increased donation of electron density to the U center with higher coordination number will weaken the O=U bonds. Similar trends were
observed for analogous [UO$_2$(acetonitrile)$_n$]$_{2+}$ complexes, although the $v_3$ frequencies were greater than those measured for acetone complexes having the same coordination number. This observation is consistent difference in strength of the two ligands as nucleophiles (acetonitrile is greater than acetone). Another important take-home point is the comparison of the vibrational spectra generated by IRMPD, to computed frequencies from DFT calculations, allow for the assignment of structure – different potential isomers and structures have specific vibrational patterns. Therefore, the IRMPD work to date shows that important information about both intrinsic structure and ligand-metal interactions can be generated by examining the vibrational spectra of gas-phase uranyl species.

The goals of this thesis were to determine probe the intrinsic interactions between actinyl ions and ligands and to identify reactions mediated by the actinides that may contribute to a better understanding of the potential role of f-electrons in chemical bonding and to the chemistry of the elements in general. The specific objectives of this research are to develop an understanding of the dissociation pathways of uranyl complexes coordinated by different ligands, focusing on ion-molecule reactivity, and structure determination using computational methods in combination with IRMPD spectroscopy.
Sample Preparation:

The experiments outlined in this thesis involved use of uranyl nitrate, uranyl perchlorate and uranyl-carboxylate precursor solutions. Of the precursor, only uranyl nitrate hexahydrate is commercially available. The uranyl nitrate hexahydrate (U\(^{VI}\)O\(_2\)(NO\(_3\))\(_2\)\(\cdot\)6H\(_2\)O) was purchased from Fluka/Sigma-Aldrich (St. Louis, MO) and used as received. The remaining uranyl precursor materials were synthesized in house by combining ca. 2-3 mg of U\(^{VI}\)O\(_3\) (Strem Chemicals, Newburyport MA), corresponding to approximately 7 x 10\(^{-6}\) to 1 x 10\(^{-5}\) moles, with a 2-fold mole excess of each respective acids (Sigma Aldrich, St. Louis MO, nitric acid, perchloric acid, acetic acid, propionic acid, acrylic acid, and benzoic acid) 400 \(\mu\)L of deionized/distilled H\(_2\)O contained in a glass scintillation vial. The solutions were allowed to incubate on a hot plate at 70°C for 12 h. The uranyl complexes were synthesized in house because the salts are not commercially available.

When cooled, 20 \(\mu\)L of the resulting solution was diluted with 800 \(\mu\)L of 50:50 (by volume) H\(_2\)O/ethanol (EtOH) and used without further work up as the spray solution for ESI-MS. EtOH has been used in our most recent experiments to avoid any ambiguity when looking for potential molecular O\(_2\) adducts to certain product ions [62-65]. With the limited mass measurement accuracy of the LIT, O\(_2\) and CH\(_3\)OH adducts cannot be distinguished.

Special Safety Precautions
Uranium oxide is radioactive and proper shielding, waste disposal, and personal protective gear must be used when handling the material. The half-life of $^{238}\text{U}$ is $4.5 \times 10^9$ years, which makes the activity of the radionuclide very low, and thus danger from exposure minimal. The primary decay channel for $^{238}\text{U}$ is by $\alpha$-emission. Because the distance an $\alpha$-particle travels in air is on the order of a few centimeters, the risk from damage due to exposure from the small quantities of $\text{UO}_3$ used in these experiments is also low. Because the penetrating power of $\alpha$-particles is low, the primary hazard for exposure to $^{238}\text{U}$ from inhalation or ingestion (few $\alpha$-particles will penetrate the dead layer to reach the germinal layer of skin). Risk is therefore minimized greatly by use of nitrile gloves, a respiratory mask and a face shield.

In ESI experiments, solutions are used at a rate of 5 microliters per minute, with experiments lasting approximately 30 to 60 minutes at a time. Stock solutions of uranyl salts are prepared at a 0.5 – 1 milliliter volume and can be used for several months. The amount of waste generated is therefore low, and excess solutions, once experiments are finished, are confined to a dedicated waste container with appropriate labeling.

*Linear ion trap mass spectrometry*

ESI and CID experiments were performed on a Thermo-Scientific (San Jose, CA) LTQ-XL LIT mass spectrometer. The uranyl-ligand spray solutions were infused into the ESI-MS instrument using the incorporated syringe pump at a flow rate of 5 $\mu\text{L}/\text{min}$.

In the positive ion mode, the atmospheric pressure ionization stack setting for the LTQ (lens voltages, quadrupole and octupole voltage offsets, etc) were optimized for maximize transmission of singly charged ions to the LIT 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 a width of 1.0 to 1.5 m/z units. The exact value was determined empirically to provide maximum ion intensity while ensuring isolation of a single isotopic peak. To probe CID behavior in general, the (mass) normalized collision energy (NCE, as defined by ThermoScientific) was set between 5% and 18%, which corresponds to 0.075 to 0.27 V applied for CID with the current instrument calibration. The activation Q, which defines the frequency of the applied radio frequency potential, was set at 0.30, and a 30-ms activation time was used.

To probe gas-phase reactions of selected precursor ions with background neutrals, ions were isolated using widths of 1 to 2 m/z units. Ions were stored in the LIT for periods ranging from 1 ms to 10 s. Despite the lower H₂O levels in the 2-D LIT under normal operating conditions, there is still a sufficient partial pressure of the neutral to permit an investigation of IMRs, particularly when using long isolation times. Our intent was to not measure or report rates or rate constants but to identify the pathways by which ions react with neutrals such as H₂O or O₂ in the LIT. The levels of these natural species in the LIT are too low to allow a rigorous examination of H₂O addition rates to specific uranyl complexes for comparison to earlier studies, and our instrument is not configured to allow controlled addition of neutral reagents for IMR.

In each CID spectrum, the bold peak label indicates the precursor selected for CID while labels in italics represent the products from dissociation or ion-molecule reactions as indicated in the text. Filled circles correspond to species isolated for
dissociation in the MS\textsuperscript{n} sequence. H\textsubscript{2}O adducts to product ions are indicated with an asterisk.

In the negative ion mode, the atmospheric pressure ionization stack settings for the LTQ (lens voltages, quadrupole and octupole voltage offsets, etc.) were optimized for maximum transmission of the singly-charged anions to the ion trap mass analyzer by using the auto-tune routine with the LTQ Tune program.

**High-resolution and high mass accuracy measurements**

High-accuracy ion mass measurements were carried out on an FT-ICR mass spectrometer (Bruker SolariX XR, Bruker Daltonics, Billerica MA). Sample preparation for ESI-MS using the FT-ICR instrument were carried out as described above. Instrument parameters were optimized for maximum transmission of precursor ions using the Bruker control software. External m/z calibration for high-accuracy measurements was carried out using sodium formate cluster anions with general composition [(NaO\textsubscript{2}CH\textsubscript{n}O\textsubscript{2}CH\textsuperscript{-}].

Single stage CID experiments were also carried out using a collision quadrupole (QCID) placed before the ion transfer lenses to the ICR cell. Dry N\textsubscript{2} was used as the collision gas. To carry out pseudo MS\textsuperscript{3} experiments, in-source fragmentation was used to generate product ions from a particular precursor anion. These product ions were then subjected to QCID in the quadrupole collision cell, with ion accumulation times (i.e. collision time) of 500 ms and a collision gas flow rate of 35%.

High-resolution/high-accuracy measurements were also performed on a ThermoScientific (San Jose, CA) LTQ-Orbitrap Elite mass spectrometer using experimental conditions similar to those outlined above for the LTQ-XL instrument. With
the Orbitrap instrument, the experiments were performed with the 120,000-resolution setting, NCE values of 8-16%, activation Q setting of 0.25, and a 10-ms activation time. Mass spectra were collected for 1 minute at each MS

**Infrared Multiple-Photon Photodissociation (IRMPD) Spectroscopy**

IRMPD experiments were performed at the Free Electron Laser for Infrared eXperiments (FELIX) laboratory [35]. Specific precursor ions, such as [UO$_2$(X)$_3$]$^-$, were generated by ESI using the prepared solutions as discussed above. IRMPD spectra were acquired using a quadrupole ion trap mass spectrometer (Bruker) which has been modified [1] such that the high-intensity tunable IR beam from FELIX can be directed into the ion packet, resulting in multiphoton dissociation that is appreciable only when the IR frequency is in resonance with an adequately high absorption vibrational mode of the particular mass-selected complex being studied. The FEL produces ~5 μs long IR pulses with an energy of typically 40 mJ, which are in the form of a sequence of ~1 ps long micropulse at a 1 GHz repetition rate. The wavelength of the radiation was tuned between 10 and 12 μm in our experiments.

**Density functional theory (DFT) calculations**

Geometry optimizations for potential product ion structures were performed using the B3LYP [38–40], PBE0 [41, 42], M06-L [43] or SVWN [44] functionals, or a combination for comparison purposes, the MWB60 pseudopotential and associated basis set on U, MWB46 pseudopotential and associated bases set on larger atoms (i.e. > I), and the triple-zeta 6-311 + G(d), aug-cc-pvtz or 6-311 + G(3df) basis set on all other atoms.
The pseudopotential and functionals were chosen because they have been used in previous studies of gas-phase U species, including measurements of the O=U=O stretching frequencies. The basis sets used here have also been employed in previous studies. In all cases, geometry optimizations were performed with an ultrafine integration grid and a tight convergence criterion. Vibrational frequency calculations were performed, using the respective optimized geometries, to ensure that all species were true minima (i.e. no imaginary frequencies) and for comparison to experimental IRMPD spectra. The Gaussian 09 software package [51] was used for all calculations.
As discussed above, recent experiments by our group have demonstrated that the relatively low levels of residual H$_2$O in a 2-D LIT makes it possible to examine fragmentation pathways and reactions not observed in earlier studies conducted with 3-D ion traps (Van Stipdonk et al. J. Am. Soc. Mass Spectrom. 14, 1205-1214, 2003). In the present study, we revisited the dissociation of complexes composed of uranyl nitrate cation [U$^{VI}$O$_2$(NO$_3$)]$^+$ coordinated by alcohol ligands (methanol and ethanol) using the 2-D LIT. The goal of the present study was to determine whether additional, previously obscured dissociation pathways would be revealed under gas-phase conditions in which the level of residual H$_2$O was lower. As discussed below, the dominant product ion following CID of [U$^{VI}$O$_2$(NO$_3$)]$^+$ is [U$^V$O$_2$(O$_2$)]$^+$, rather than [U$^V$O$_2$(H$_2$O)]$^+$. To determine whether this result was due to the use of a different mass spectrometer, H$_2$O was deliberately added to the vacuum system of the LIT. Under conditions that included higher levels of background H$_2$O, CID of [U$^{VI}$O$_2$(NO$_3$)]$^+$ created [U$^V$O$_2$(H$_2$O)]$^+$ and U$^V$O$_2^+$, consistent with our earlier study using the 3-D ion trap [4]. No formation of [U$^V$O$_2$(O$_2$)]$^+$ was observed with the higher levels of residual H$_2$O. The experiments in the LIT allow for a revision of the previously proposed mechanism for the decomposition
of \([U^{VI}O_2(NO_3)]^+\) to one that involves a two-step process: initial formation of

\([U^{V}O_2(O_2)]^+\) followed by rapid exchange of \(O_2\) for \(H_2O\) by ion-molecule reaction. Our

experiments further illustrate the extent to which the presence of residual \(H_2O\) in ion trap

instruments influences dissociation patterns and pathways and provide a more accurate
description of the intrinsic dissociation pathway for \([U^{VI}O_2(NO_3)]^+\).

The multiple-stage CID spectra initiated with the dissociation of, for example,

\([U^{VI}O_2(NO_3)(CH_3OH)_3]^+\) were complexed and contained product ions from

fragmentation reactions and \(H_2O\) adducts to those product ions formed by association

reactions with \(H_2O\) present as a contaminant in the He buffer/bath gas. In the earlier

experiments, the \(H_2O\) adducts were identified by characteristic peak tails and chemical

mass shifts (shifts of 0.2-0.3 \(u\) lower than expected mass). It has been proposed that the

asymmetric peak shapes and mass deficits may be tied to the formation of fragment ions

from particularly “fragile” precursors because of the application of resonance ejection,

and the magnitude of the resonant ejection amplitude for ion ejection during mass

analysis using ion traps [66]. The ejection of the fragment ions, which “appears as

premature ejection of the fragile ion, leads to the appearance of peak fronting and a mass

shift” [66]. The reader is directed to reports by Yost and coworkers [66] and Vachet et al.

[67], for specific details.

Formation of adducts can also be confirmed by isolating expected product ions in

the ion trap for periods of 10-100 ms, without an applied collision voltage (NCE). During

the isolation step, all ionized species except the one chosen for storage are resonantly

ejected from the ion trap. The appearance of peaks 18 \(u\) higher than the isolated ion is
indicative of the formation of \( \text{H}_2\text{O} \) adducts and their abundance increased as the isolation and storage time was extended.

The multiple-stage CID experiments initiated with the \([\text{U}^{\text{VI}}\text{O}_2(\text{NO}_3)(\text{CH}_3\text{OH})_3]^+\) precursor ultimately generated \([\text{U}^{\text{VI}}\text{O}_2(\text{OCH}_3)]^+\) as the dominant product ion (through the elimination of \( \text{HNO}_3 \) from \([\text{U}^{\text{VI}}\text{O}_2(\text{NO}_3)(\text{CH}_3\text{OH})]^+\)). The relatively intensity of \([\text{U}^{\text{VI}}\text{O}_2(\text{NO}_3)]^+\) produced by CID of \([\text{U}^{\text{VI}}\text{O}_2(\text{NO}_3)(\text{CH}_3\text{OH})]^+\) was \( \sim 5\% \). In the same study, the \( \text{MS}^n \) CID of \([\text{U}^{\text{VI}}\text{O}_2(\text{NO}_3)(\text{H}_2\text{O})_3]^+\) produced \([\text{U}^{\text{VI}}\text{O}_2(\text{NO}_3)]^+\), and subsequent dissociation of this led to product ions of at \( m/z \) 270 (\( \text{U}^{\text{V}}\text{O}_2^+ \)) and \( m/z \) 288. Because there was no reasonable explanation for the elimination of 44 u from \([\text{U}^{\text{VI}}\text{O}_2(\text{NO}_3)]^+\), the product ion at \( m/z \) 288 was assigned as the hydrated, reduced uranyl ion, \([\text{U}^\text{V}\text{O}_2(\text{H}_2\text{O})]^+\).

CID of \([\text{U}^{\text{V}}\text{O}_2(\text{H}_2\text{O})]^+\) caused the elimination of 18 u, consistent with the loss of \( \text{H}_2\text{O} \) to form \( \text{U}^{\text{V}}\text{O}_2^+ \) at \( m/z \) 270. Curiously, the \( m/z \) 288 product ion was significantly higher after CID of \([\text{U}^{\text{VI}}\text{O}_2(\text{NO}_3)]^+\) than when \( \text{U}^{\text{V}}\text{O}_2^+ \) was isolated independently for association reactions with \( \text{H}_2\text{O} \), which led to the conclusion that it was unlikely that the \( m/z \) 288 ion (produced by CID of \([\text{U}^{\text{VI}}\text{O}_2(\text{NO}_3)]^+\) resulted from addition of \( \text{H}_2\text{O} \) to the \( m/z \) 270 (\( \text{U}^{\text{V}}\text{O}_2^+ \)) product ion by IMR. Instead, we proposed at the time that \([\text{U}^{\text{V}}\text{O}_2(\text{H}_2\text{O})]^+\) was generated via reaction 1:
\[
[U^{VI}_2(\text{NO}_3)]^+ + \text{H}_2\text{O} \rightarrow [U^{VI}_2\text{NO}_3(\text{H}_2\text{O})]^+ \rightarrow [U^{V}_2\text{O}_2(\text{H}_2\text{O})]^+ + \text{NO}_3^-
\] (1)

In which an energetic collision with \( \text{H}_2\text{O} \) in the ion trap mass causes the formation of an activated ternary complex, rapidly followed by the reductive elimination of \( \text{NO}_3^+ \) radical (with electron transfer to the uranyl ion) to leave the hydrated, reduced uranyl ion. It was this result in particular that prompted the study presented here.

The ESI and MS\( ^n \) CID spectra collected on the 2-D LIT instrument, using a solution of (commercially available) uranyl nitrate in a mixture of \( \text{H}_2\text{O} \) and \( \text{CH}_3\text{OH} \), are shown in Figure 1. With this solution, ESI (Figure 1a) generates \([U^{VI}_2(\text{OCH}_3)(\text{CH}_3\text{OH})_2]^+\), \([U^{VI}_2(\text{NO}_3)(\text{CH}_3\text{OH})_2]^+\), and \([U^{VI}_2(\text{NO}_3)(\text{CH}_3\text{OH})_3]^+\) at \( m/z \) 365, 396, and 428, respectively. CID of \([U^{VI}_2(\text{NO}_3)(\text{CH}_3\text{OH})_3]^+\) (MS/MS stage, Figure 1b) causes elimination of a single \( \text{CH}_3\text{OH} \) ligand to produce \([U^{VI}_2(\text{NO}_3)(\text{CH}_3\text{OH})_2]^+\), which in a subsequent stage (MS\( ^3 \) stage, Figure 1c) loses another \( \text{CH}_3\text{OH} \) ligand to create \([U^{VI}_2(\text{NO}_3)(\text{CH}_3\text{OH})]^+\) at \( m/z \) 364, of \( \text{HNO}_3 \) to leave \([U^{VI}_2(\text{OCH}_3)(\text{CH}_3\text{OH})]^+\) at \( m/z \) 333. Subsequent CID of \([U^{VI}_2(\text{NO}_3)(\text{CH}_3\text{OH})]^+\) (MS\( ^4 \) stage, Figure 1d) primarily causes the elimination of \( \text{HNO}_3 \) to leave \([U^{VI}_2(\text{OCH}_3)]^+\) at \( m/z \) 301, and \([U^{VI}_2(\text{NO}_3)]^+\) at \( m/z \) 332 was also observed at \( \sim10\% \) relative intensity. In general, the fragmentation reactions...
to this point are in agreement with our earlier study that used the 3-D ion trap [4]. However, one notable difference is that the number and intensity of H$_2$O adducts are greatly diminished in the present experiments, consistent with several recent studies by our group [46-50]. For example, the only adduct observed at relative intensity greater than 1% appears at m/z 382 (addition of H$_2$O to [U$^{\text{VI}}$O$_2$(NO$_3$)(CH$_3$OH)]$^+$ at m/z 364.

CID of [U$^{\text{VI}}$O$_2$(OCH$_3$)]$^+$ at m/z 301 (MS$^5$ stage, data not shown) generates U$^{\text{V}}$O$_2^+$ at m/z 270 and U$^{\text{V}}$O$_2$H$^+$ at m/z 271, in agreement with a recent comparison of the fragmentation pathways of [U$^{\text{VI}}$O$_2$(OCH$_3$)]$^+$ and [U$^{\text{VI}}$O$_2$(OCH$_2$CH$_3$)]$^+$ [49]. More importantly, CID of [U$^{\text{VI}}$O$_2$(NO$_3$)]$^+$ at m/z 301 (MS$^5$ stage, Figure 1e) generates U$^{\text{V}}$O$_2^+$ at m/z 270, and the dominant fragment ion appears at m/z 302. The neutral loss to make the ion at m/z 302 corresponds to 30 u, and given the composition of the precursor ([U$^{\text{VI}}$O$_2$(NO$_3$)]$^+$), it is reasonable to conclude that this corresponds to elimination of NO to leave an ion with a formula of UO$_4^+$ as shown in reaction 2.

\[
[U^{\text{VI}}O_2(NO_3)]^+ \rightarrow [U^{\text{V}}O_4]^+ + \cdot NO \tag{2}
\]

This reaction pathway was not observed in our previous examination of the CID of H$_2$O and alcohol-coordinated [U$^{\text{VI}}$O$_2$(NO$_3$)]$^+$. Subsequent CID of UO$_4^+$ cause the formation of U$^{\text{V}}$O$_2^+$ by elimination of O$_2$ (MS$^5$ stage, data not shown). While the appearance of the ion at m/z 302 in the CID spectrum of [U$^{\text{VI}}$O$_2$(NO$_3$)]$^+$ was a surprise, generation of a product with a formula of UO$_4$ is not without precedent. For example, in a recent study of gas-phase binary and complex oxide anion molecules of protactinium and uranium, the oxalate species [U$^{\text{V}}$O$_2$(C$_2$O$_4$)]$^+$ exhibited the spontaneous replacement of the oxalate ligand by O$_2$ to leave U$^{\text{V}}$O$_4^-$ and two CO$_2$ molecules [45]. Quantum chemical calculations suggested that the structure of U$^{\text{V}}$O$_4^-$ includes a distorted U$^{\text{VI}}$O$_2^{2+}$ core
coordinated in the equatorial plane by two equivalent O atoms. We note that a UO$_4^-$ ion has also been observed in CID experiments initiated with precursor anions such as [U$^{VI}$O$_2$(NO$_3$)$_3$]$^-$, [U$^{VI}$O$_2$(ClO$_4$)$_3$]$^-$, and [U$^{VI}$O$_2$(CH$_3$COO)$_3$]$^-$ [36].

More important to the present study, a UO$_4^+$ cation was produced by Duncan and coworkers by laser vaporization and supersonic expansion and studied with infrared laser photodissociation spectroscopy using Ar atom pre-dissociation [68]. The IR action spectrum of UO$_4^+$ Ar$_2$ was collected in the O=U=O and O=O stretching regions, and spectral and structure assignments were made with the assistance of high-level computational quantum chemistry. UO$_4^+$ was found to have a central U$^{V}$O$_2$ core, with O$_2$ bound side-on in a $\eta^2$ coordination mode, as suggested in previous experimental and theoretical studies of the addition of molecular O$_2$ to U$^{V}$O$_2^+$ complexes in the gas-phase [62-65]. Therefore, the composition of the ion at $m/z$ 302, created in the present study by CID of [U$^{VI}$O$_2$(NO$_3$)]$,^+$, is assigned as [U$^{V}$O$_2$(O$_2$)]$^+$ and is assumed to have the structure revealed in the pre-dissociation experiments [68].
Formation of $[\text{U}^{\text{VI}}\text{O}_2\text{O}_2]^+$ by CID in the LIT instrument was not dependent on the specific precursor used for the multiple-stage CID experiments. For example, multiple-stage CID initiated with either $[\text{U}^{\text{VI}}\text{O}_2\text{O}_2\text{N}_3\text{(CH}_3\text{CH}_2\text{OH})_2]^+$ or $[\text{U}^{\text{VI}}\text{O}_2\text{O}_2\text{N}_3\text{(H}_2\text{O})_2]^+$, using the commercially available nitrate salt, led to formation of $[\text{U}^{\text{VI}}\text{O}_2\text{N}_3]^+$, which subsequently dissociated to leave $[\text{U}^{\text{VI}}\text{O}_2\text{O}_2]^+$ and $\text{U}^{\text{VI}}\text{O}_2^+$ (spectra not shown). We also investigated whether or not the formation of $[\text{U}^{\text{VI}}\text{O}_2\text{O}_2]^+$ was an artifact of the uranyl nitrate starting material. The ESI and multiple-stage CID spectra resulting from the use of fresh uranyl nitrate synthesized from $\text{U}^{\text{VI}}\text{O}_3$ are shown in Figure 2. The dominant ions generated by ESI using the synthetic salt in H$_2$O/CH$_3$CH$_2$OH were $[\text{U}^{\text{VI}}\text{O}_2\text{O}_2\text{N}_3\text{(CH}_3\text{CH}_2\text{OH})_2]^+$ and $[\text{U}^{\text{VI}}\text{O}_2\text{N}_3\text{(CH}_3\text{CH}_2\text{OH})_2]^+$ at m/z 407 and 424, respectively. CID of $[\text{U}^{\text{VI}}\text{O}_2\text{N}_3\text{(CH}_3\text{CH}_2\text{OH})_2]^+$ (MS/MS stage, Figure 2b) caused the elimination of a CH$_3$CH$_2$OH ligand to leave $[\text{U}^{\text{VI}}\text{O}_2\text{N}_3\text{(CH}_3\text{CH}_2\text{OH})]^+$ at m/z 378, or loss of HNO$_3$ to generate $[\text{U}^{\text{VI}}\text{O}_2\text{O}_2\text{O}_2\text{N}_3\text{(CH}_3\text{CH}_2\text{OH})_2]^+$ at m/z 361.

Subsequent CID of $[\text{U}^{\text{VI}}\text{O}_2\text{O}_2\text{O}_2\text{N}_3\text{(CH}_3\text{CH}_2\text{OH})]^+$ at m/z 361 created $[\text{U}^{\text{VI}}\text{O}_2\text{O}_2\text{O}_2\text{(CH}_3\text{CH}_2\text{OH})]^+$ at m/z 315 (spectrum not shown), consistent with our earlier
The investigation of uranyl alkoxide cations [49]. The dominant product ion generated by CID of [U\textsuperscript{VI}O\textsubscript{2}(NO\textsubscript{3})(CH\textsubscript{3}CH\textsubscript{2}OH)]\(^+\) at m/z 378 (MS\(^3\) stage, Figure 2c) was [U\textsuperscript{VI}O\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}]\(^+\) at m/z 315, with [UO\textsubscript{2}(NO\textsubscript{3})]\(^+\) at m/z 332 appearing at a relative intensity of ~5%. CID of [U\textsuperscript{VI}O\textsubscript{2}(OCH\textsubscript{2}CH\textsubscript{3})]\(^+\) (MS\(^5\) stage, data not shown) generated products such as [U\textsuperscript{V}O\textsubscript{2}(O=CH\textsubscript{2})]\(^+\), [U\textsuperscript{VI}O\textsubscript{2}(CH\textsubscript{3})]\(^+\), and U\textsuperscript{V}O\textsubscript{2}\(^+\) (m/z 300, 285, and 270, respectively), consistent with a previous study by our group using the LIT [49]. As with the other experiments performed with the LIT in this study, including those that used the commercially available salt, subsequent CID of [U\textsuperscript{VI}O\textsubscript{2}(NO\textsubscript{3})]\(^+\) (MS\(^4\) stage, Figure 2d) created [U\textsuperscript{V}O\textsubscript{2}(O\textsubscript{2})]\(^-\) and U\textsuperscript{V}O\textsubscript{2}\(^+\).

The last goal in this study was to determine whether the difference between the previous and current results, with respect to the dissociation of [U\textsuperscript{VI}O\textsubscript{2}(NO\textsubscript{3})]\(^+\), is due to the presence of significant levels of background H\textsubscript{2}O, or the specific ion trap used in the MS\(^n\) experiment. The LIT was vented and kept at ambient temperature and pressure for 12 h. Our hypothesis was that the typical humidity of the ambient air would lead to relatively higher H\textsubscript{2}O levels in the vacuum system and ion trap for a short period of time after pump down. Therefore, after the instrument returned to typical operating pressure (ca. 1.0 x 10\(^{-6}\) Torr in a vacuum chamber), the MS\(^n\) experiment using ethanol-coordinated [U\textsuperscript{VI}O\textsubscript{2}(NO\textsubscript{3})]\(^+\) was repeated to make a direct comparison to the experiments run under the “low” H\textsubscript{2}O level conditions. The CID spectra initiated using the
[U\text{VI}O_2(NO_3)(CH_3CH_2OH)_2]^+ precursor, are provided in Figure 3. Under the high H_2O conditions, the dominant product ion observed following CID of [U\text{VI}O_2(NO_3)(CH_3CH_2OH)_2]^+ (MS/MS stage, Figure 3a) appears at m/z 396 (throughout Figure 3, H_2O adducts to CID product ions are indicated with an asterisk). The product ion at m/z 396 corresponds to the H_2O adduct to [U\text{VI}O_2(NO_3)(CH_3CH_2OH)]^+ (m/z 378). Other true dissociation products at the MS/MS stage include [U\text{VI}O_2(OCH_2CH_3)(CH_3CH_2OH)]^+ at m/z 361 and [U\text{VI}O_2(OCH_2CH_3)]^+ at m/z 315. Prominent H_2O adducts to these fragment ions appear at m/z 442, 414, 379, 351, and 333, demonstrating that the level of background H_2O was indeed higher.

Subsequent CID of [U\text{VI}O_2(NO_3)(CH_3CH_2OH)]^+ at m/z 378 (MS^3 stage, Figure 3b) primarily generated [U\text{VI}O_2(OCH_2CH_3)]^+ at m/z 315 and mono and di-hydrates of the ion at m/z 333 and 351. The [U\text{VI}O_2(NO_3)]^+ ion was also generated at nearly the same relative intensity as in the low H_2O conditions. In contrast to the experiments under low H_2O conditions, subsequent CID of [U\text{VI}O_2(NO_2)]^+ (MS^4 stage Figure 3c) under the high H_2O conditions produced [U\text{V}O_2(H_2O)]^+ at m/z 288 and U\text{V}O_2^+ at m/z 270, exactly the results obtained in our previous investigation using the
3-D ion trap [4]. This result strongly suggests that the differences in product ion formation are not due to the specific ion trap used for the experiments, but instead to the presence of higher levels of background H$_2$O in the earlier study.

One additional hypothesis tested was that [U$^{V}$O$_2$(O$_2$)]$^+$ would undergo a ligand exchange reaction with H$_2$O. Our motivation for this was a set of earlier studies by our group which showed that (a) gas-phase complexes containing U$^{V}$O$_2^+$ ligated with two or three $\sigma$-donating acetone ligands react with O$_2$ to form complexes with composition [U$^{V}$O$_2$(A)$_{2,3}$(O$_2$)]$^+$ (A = acetone, acetonitrile, etc.) [62-64] and (b) the O$_2$ ligand is easily eliminated by CID or exchanges for neutral ligands such as H$_2$O, acetone, or acetonitrile by IMR [64].

Using the relatively low residual H$_2$O conditions in the LIT, the ion at $m/z$ 302 (presumed to be [U$^{V}$O$_2$(O$_2$)]$^+$) was generated by MS$^n$ CID of the [U$^{VI}$O$_2$(NO$_3$)(CH$_3$CH$_2$OH)$_2$]$^+$ precursor, and then isolated and allowed to react with background H$_2$O for periods ranging from 10 to 1000 ms (Figure 4a–c). Despite the low levels of background H$_2$O, reactions with the neutral species can still be observed, especially when using relatively long isolation/reaction times. The spectra shown in Figure 4a–c clearly show that the product ion generated by IMR appears at $m/z$ 288, consistent with the exchange of O$_2$ for H$_2$O by reaction 3.

$$[U^{V}O_2(O_2)]^+ + H_2O \rightarrow [U^{V}O_2(H_2O)]^+ + O_2$$  (3)
Subsequent CID (Figure 4d) of the ion at m/z 288 causes formation of UV_O2^+ by loss of H_2O. This behavior is therefore consistent with our earlier studies of ligand exchange reactions of O_2 adducts to UV_O2^+ complexes, and with the composition assignment of [UV_O2(O_2)]^+ for the m/z 302 ion.

One remaining question is the mechanism by which NO is released from [UV_O2(NO_3)]^+ to make [UV_O2(O_2)]^+. A study by Frański [69] showed that NO is eliminated from Ca^{2+}, Sr^{2+}, and Ba^{2+} complexes with nitrate, but mechanistic details and energetics were not provided. Schröder and coworkers [70] demonstrated that decomposition of nitrate will occur for gas-phase complexes of Co and Ni. For the case of Co, NO^+ was observed and attributed to the dissociation of [CoNO_3]^+. For the Ni system, loss of (neutral) NO was observed from the mono-hydrate of [NiNO_3]^+. An alternative to direct ejection of NO would be isomerization of nitrate to peroxynitrite (reaction 4), followed by decomposition and elimination of (neutral) NO.

[UV_O2(NO_3)]^+ \rightarrow [UV_O2O_2NO]^+ \rightarrow [UV_O2(O_2)]^+ + NO \quad (4)

This is the reverse of the well-known isomerization of peroxynitrite to nitrate (and hydrogen peroxynitrite to nitric acid) after creation of the former by reaction of NO and
superoxide ion [71-75]. The exact mechanism by which \([U^{VI}\mathrm{O}_2(O_2)]^+\) is generated in the present study remains unclear and would benefit from a detailed quantum chemical study. Whatever the mechanism, our results strongly suggest that the decomposition of \([U^{VI}\mathrm{O}_2(NO_3)]^+\) involves the initial elimination of NO.

To summarize, in this study, we revisited the dissociation of complexes composed of uranyl nitrate cation \([U^{VI}\mathrm{O}_2(NO_3)]^+\) coordinated by alcohol ligands (methanol and ethanol) using the 2-D LIT. With relatively low levels of background \(H_2O\), CID of \([U^{VI}\mathrm{O}_2(NO_2)]^+\) primarily creates \([U^{V}\mathrm{O}_2(O_2)]^+\) by the ejection of NO (reaction 2). However, under conditions in which the level of residual \(H_2O\) is higher, CID of \([U^{VI}\mathrm{O}_2(NO_3)]^+\) instead leads to formation of \([U^{V}\mathrm{O}_2(H_2O)]^+\) and \(U^{V}\mathrm{O}_2^+\), consistent with our earlier investigation of similar systems on a 3-D quadrupole ion trap. Our experiments further illustrate the impact of residual \(H_2O\) in ion trap instruments on the product ions generated by CID and reveal the correct dissociation pathway for \([U^{VI}\mathrm{O}_2(NO_3)]^+\).

Based on these new results, we can revise the apparent intrinsic dissociation reaction for \([U^{VI}\mathrm{O}_2(NO_3)]^+\). It is reasonable to assume that CID of \([U^{VI}\mathrm{O}_2(NO_3)]^+\) initially creates \([U^{V}\mathrm{O}_2(O_2)]^+\) by elimination of NO (reaction 2). The \([U^{V}\mathrm{O}_2(O_2)]^+\) product can further dissociate by loss of \(O_2\) to leave \(U^{V}\mathrm{O}_2^+\), consistent with the dissociation pattern observed on the LIT instrument. Knowing that \([U^{V}\mathrm{O}_2(O_2)]^+\) can undergo a spontaneous and rapid exchange of \(O_2\) for \(H_2O\) (reaction 3), the earlier results on the 3-D ion trap may have involved a two-step process: the initial formation of \([U^{V}\mathrm{O}_2(O_2)]^+\), followed by rapid exchange with \(H_2O\) to leave the species at \(m/z\) 288. This is essentially reactions 2 and 3 in rapid succession. Both \([U^{V}\mathrm{O}_2(O_2)]^+\) and \([U^{V}\mathrm{O}_2(H_2O)]^+\)
may dissociate to leave U^{VI}O_2^{+} at m/z 270. We therefore conclude that dissociation
reactions in our previous study using the 3-D trap were influenced by the relatively high
levels of residual H_2O, and the results obtained on the 2-D ion trap more accurately
reflect the intrinsic CID pathway for [U^{VI}O_2(NO_3)]^{+}. 
Chapter 4

**CID of $[\text{U}^{\text{VI}}\text{O}_2(\text{ClO}_4)]^+$ Revisited: Production of $[\text{U}^{\text{VI}}\text{O}_2(\text{Cl})]^+$ and Subsequent Hydrolysis to Create $[\text{U}^{\text{VI}}\text{O}_2(\text{OH})]^+$**

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In this study, the CID of uranyl perchlorate species, $[\text{U}^{\text{VI}}\text{O}_2(\text{ClO}_4)]^+$, was re-examined using the 2-D LIT in a similar fashion to the uranyl nitrate species discussed above. As with the uranyl nitrate species, the goal of this study was to determine whether previous dissociation pathways were obscured by high levels of residual H$_2$O. As discussed below, under conditions of relatively “low” background H$_2$O, the dominant product ion generated by CID of $[\text{U}^{\text{VI}}\text{O}_2(\text{ClO}_4)]^+$ is actually $[\text{U}^{\text{VI}}\text{O}_2(\text{Cl})]^+$, rather than $[\text{U}^{\text{VI}}\text{O}_2(\text{OH})]^+$. Subsequent isolation of $[\text{U}^{\text{VI}}\text{O}_2(\text{Cl})]^+$ for reaction with H$_2$O causes hydrolysis and formation of $[\text{U}^{\text{VI}}\text{O}_2(\text{OH})]^+$. The experiments using the LIT allow for revision of the previously proposed intrinsic pathway for the decomposition of $[\text{U}^{\text{VI}}\text{O}_2(\text{ClO}_4)]^+$, and further illustrate the role of residual H$_2$O in ion trap instruments has on dissociation patterns and pathways.

**4.1 CID of $[\text{U}^{\text{VI}}\text{O}_2\text{ClO}_4(\text{H}_2\text{O})_n]^+$**

In the prior study using the 3-D trap, the MS$^n$ CID of $[\text{U}^{\text{VI}}\text{O}_2(\text{ClO}_4)(\text{H}_2\text{O})_3]^+$ caused the serial elimination of H$_2$O ligands to generate $[\text{U}^{\text{VI}}\text{O}_2(\text{ClO}_4)]^+$ [76]. The primary dissociation products observed from CID of $[\text{U}^{\text{VI}}\text{O}_2(\text{ClO}_4)]^+$ were $[\text{U}^{\text{VI}}\text{O}_2(\text{OH})]^+$ and $[[\text{U}^{\text{VI}}\text{O}_2]^+$ at $m/z$ 287 and $m/z$ 270, respectively. Because the hydroxide product was observed, it was reasonable at the time to assume that the intrinsic CID pathways involved hydrolysis of a hydrated intermediate complex as in reaction 5.
\[ [\text{U}^{\text{VI}} \text{O}_2(\text{ClO}_4)]^+ + \text{H}_2\text{O} \rightarrow [\text{U}^{\text{VI}} \text{O}_2(\text{ClO}_4)(\text{H}_2\text{O})]^+ \rightarrow [\text{U}^{\text{VI}} \text{O}_2(\text{OH})]^+ + \text{HClO}_4 \] (5)

The MS\textsuperscript{n} CID spectra collected on the 2-D LIT instrument in the present study are shown in Figure 5. CID of [U\text{VI}O\text{2}(\text{ClO}_4)(\text{H}_2\text{O})_3]^+ at m/z 423 (MS/MS stage, Figure 5a) caused elimination of a single H\textsubscript{2}O ligand to generate [U\text{VI}O\text{2}(\text{ClO}_4)(\text{H}_2\text{O})_2]^+ at m/z 405. Subsequent CID of [U\text{VI}O\text{2}(\text{ClO}_4)(\text{H}_2\text{O})_2]^+ (MS\textsuperscript{3} stage, Figure 5b) caused elimination of a second H\textsubscript{2}O ligand to produce [U\text{VI}O\text{2}(\text{ClO}_4)(\text{H}_2\text{O})]^+ at m/z 387. CID of [U\text{VI}O\text{2}(\text{ClO}_4)(\text{H}_2\text{O})]^+ (MS\textsuperscript{4} stage, Figure 5c), created [U\text{VI}O\text{2}(\text{ClO}_4)]^+ (m/z 369) by loss of the final H\textsubscript{2}O ligand, and all of the fragmentation reactions to this point were in general agreement with the earlier study that used a 3-D ion trap [76]. One notable difference, however, was that the number and relative abundance of H\textsubscript{2}O was significantly lower in the present experiments.

Unlike the earlier study with the 3-D ion trap, subsequent CID of [U\text{VI}O\text{2}(\text{ClO}_4)]^+ (MS\textsuperscript{5} stage, Figure 5d), using the 2-D ion trap, produced by [U\text{VI}O\text{2}(\text{Cl})]^+ at m/z 305. Formation of [U\text{VI}O\text{2}(\text{Cl})]^+ from [U\text{VI}O\text{2}(\text{ClO}_4)]^+ presumably involves the elimination of 2 O\textsubscript{2} molecules, as shown in reaction 6. Subsequent CID of [U\text{VI}O\text{2}(\text{Cl})]^+ produced [U\text{V}O\text{2}]^+ at m/z 270, via elimination of Cl radical as in reaction 7.

![Figure 5: ESI and multiple-stage CID spectra derived from UO\textsubscript{2}(ClO\textsubscript{4})\textsubscript{2} (prepared in house) in 1 mL of H\textsubscript{2}O. (a) CID (MS/MS) of [UO\textsubscript{2}(ClO\textsubscript{4})(H\textsubscript{2}O\textsubscript{3})]^+ at m/z 423, (b) CID (MS\textsuperscript{3}) of [UO\textsubscript{2}(ClO\textsubscript{4})(H\textsubscript{2}O\textsubscript{2})]^+ at m/z 405, (c) CID (MS\textsuperscript{4}) of [UO\textsubscript{2}(ClO\textsubscript{4})(H\textsubscript{2}O)]^+ at m/z 387, (d) CID (MS\textsuperscript{5}) of [UO\textsubscript{2}(ClO\textsubscript{4})]^+ at m/z 369 and (e) CID (MS\textsuperscript{6}) of [UO\textsubscript{2}(Cl)]^+ at m/z 305.](image-url)
\[ [\text{UVI}_2(\text{ClO}_4)]^+ \rightarrow [\text{UVI}_2(\text{Cl})]^+ + 2 \text{O}_2 \] (6)

\[ [\text{UVI}_2(\text{Cl})]^+ \rightarrow [\text{U}^\text{VI}_2]^+ + \bullet \text{Cl} \] (7)

Another minor product observed in the CID spectrum of \([\text{UVI}_2(\text{ClO}_4)]^+\) (MS^5 stage, Figure 5d) was \([\text{UVI}_2]^+\), produced at approximately 1% relative intensity. We attribute this product to the loss of chlorate (ClO_3), and this reaction pathway was not observed in our previous examination of the CID of water coordinated \([\text{UVI}_2(\text{ClO}_4)]^+\) [76].

Evidence to support our conclusion that \([\text{UVI}_2(\text{ClO}_4)]^+\) and \([\text{UVI}_2(\text{Cl})]^+\) were formed was obtained by examining the CID of the ^{37}\text{Cl} isotopic species (spectra not shown). The MS^n CID of \([\text{UVI}_2(^{37}\text{ClO}_4)(\text{H}_2\text{O})_3]^+\) caused the same cascade of dissociation reactions reported in Figure 5 for the ^{35}\text{Cl} isotopic species. CID of \([\text{UVI}_2(^{37}\text{ClO}_4)(\text{H}_2\text{O})_3]^+\) ultimately to produce \([\text{UVI}_2(^{37}\text{ClO}_4)]^+\) at m/z 371 and \([\text{UVI}_2(^{37}\text{Cl})]^+\) at m/z 307. The apparent decomposition of ClO_4^- to generate Cl^-, with elimination of O_2, is in the line with the known thermal decomposition of inorganic perchlorate compounds [77-81]. Our results are also in accord with other MS-based investigations of metal- and ammonium salts compounds subjected to in-source CID [2] or laser-electrospray ionization [82] within the context of forensic analysis of explosive compounds.

To test the hypothesis that earlier experiments may have been influenced by the presence of background H_2O, the \([\text{UVI}_2(^{35}\text{ClO}_4)]^+\) and \([\text{UVI}_2(^{35}\text{Cl})]^+\) ions at m/z 369 and 305, respectively, were isolated and allowed to react with background H_2O for periods ranging from 10 ms to 10 s. Despite the low levels of background H_2O, reactions with the neutral species can still be observed, especially when using relatively long isolation/reaction times.
Isolation of [U\textsuperscript{VI}O\textsubscript{2}(\textsuperscript{35}ClO\textsubscript{4})\textsuperscript{+}] for periods ranging from 10 ms to 10 s (spectra not shown) caused the formation of mono-, di-, and tri-hydrates of the species at m/z 387, 405, and 425, respectively. No spontaneous hydrolysis of [U\textsuperscript{VI}O\textsubscript{2}(\textsuperscript{35}ClO\textsubscript{4})\textsuperscript{+}] to leave [U\textsuperscript{VI}O\textsubscript{2}(OH)]\textsuperscript{+} and (neutral) H\textsuperscript{35}ClO\textsubscript{4} was observed. The product ion spectra generated by isolation of [U\textsuperscript{VI}O\textsubscript{2}(\textsuperscript{35}Cl)]\textsuperscript{+} (Figure 6a-d) instead clearly show that an IMR product ion appears at m/z 287, consistent with spontaneous formation of [U\textsuperscript{VI}O\textsubscript{2}(OH)]\textsuperscript{+} by hydrolysis and elimination of HCl, as shown in reaction 8.

\[
[U^{\text{VI}}O_2(Cl)]^+ + H_2O \rightarrow [U^{\text{VI}}O_2(OH)]^+ + HCl \quad (8)
\]

This result shows that the [U\textsuperscript{VI}O\textsubscript{2}(Cl)]\textsuperscript{+} will undergo a gas-phase hydrolysis reaction with H\textsubscript{2}O to leave the hydroxide product. We suggest that dissociation spectrum generated from [U\textsuperscript{VI}O\textsubscript{2}(ClO\textsubscript{4})]\textsuperscript{+} in the earlier experiments was actually the result of a two-step process: initial formation of [U\textsuperscript{VI}O\textsubscript{2}(Cl)]\textsuperscript{+} by CID followed by hydrolysis to create [U\textsuperscript{VI}O\textsubscript{2}(OH)]\textsuperscript{+}. The high levels of background H\textsubscript{2}O in the 3-D ion trap may have made the latter step sufficiently rapid that the [U\textsuperscript{VI}O\textsubscript{2}(Cl)]\textsuperscript{+} intermediate was not observed.
4.2 CID of [U\textsuperscript{VI}O\textsubscript{2}ClO\textsubscript{4}(CH\textsubscript{3}OH)\textsubscript{n}]\textsuperscript{+}

In the previous study using the 3-D ion trap, the MS\textsuperscript{n} CID of [U\textsuperscript{VI}O\textsubscript{2}(ClO\textsubscript{4})(CH\textsubscript{3}OH)]\textsubscript{n}\textsuperscript{+} was also investigated. The same species was investigated in the present study for the sake of the comparison. The product ion spectra from MS\textsuperscript{n} CID initiated with the [U\textsuperscript{VI}O\textsubscript{2}(\textsuperscript{35}ClO\textsubscript{4})(CH\textsubscript{3}OH)\textsubscript{3}]\textsuperscript{+} precursor are shown in Figure 7. CID of [U\textsuperscript{VI}O\textsubscript{2}(\textsuperscript{35}ClO\textsubscript{4})(CH\textsubscript{3}OH)\textsubscript{3}]\textsuperscript{+} at m/z 465 (MS/MS stage, Figure 7a) caused the elimination of a single CH\textsubscript{3}OH ligand to produce [U\textsuperscript{VI}O\textsubscript{2}(\textsuperscript{35}ClO\textsubscript{4})(CH\textsubscript{3}OH)\textsubscript{2}]\textsuperscript{+} at m/z 433. An adduct was observed at only 10% relative intensity, again illustrating the significantly lower levels of background H\textsubscript{2}O in the LIT. Subsequent CID of [U\textsuperscript{VI}O\textsubscript{2}(\textsuperscript{35}ClO\textsubscript{4})(CH\textsubscript{3}OH)\textsubscript{2}]\textsuperscript{+} (MS\textsuperscript{3} stage, Figure 7b) resulted in the loss of a second CH\textsubscript{3}OH ligand to leave [U\textsuperscript{VI}O\textsubscript{2}(\textsuperscript{35}ClO\textsubscript{4})(CH\textsubscript{3}OH)]\textsuperscript{+} at m/z 401. Two dissociation channels were observed following CID of [U\textsuperscript{VI}O\textsubscript{2}(\textsuperscript{35}ClO\textsubscript{4})(CH\textsubscript{3}OH)]\textsuperscript{+} (Figure 7c). One involved the elimination of the last CH\textsubscript{3}OH ligand to leave [U\textsuperscript{VI}O\textsubscript{2}(\textsuperscript{35}ClO\textsubscript{4})]\textsuperscript{+}. Subsequent CID lead again to the formation of [U\textsuperscript{VI}O\textsubscript{2}(\textsuperscript{35}Cl)]\textsuperscript{+} at m/z 305 (MS\textsuperscript{5} stage, Figure 7d). The other dissociation pathway lead to formation of [U\textsuperscript{VI}O\textsubscript{2}(OCH\textsubscript{3})]\textsuperscript{+} at m/z 301 by loss of HClO\textsubscript{4} as shown in reaction 9. Elimination of
HClO$_4$ was confirmed by noting the shift in neutral loss from 99 to 101 mass units following CID of the $^{37}$Cl isotopic peak (data not shown). CID of the peak at $m/z$ 301 (spectrum not shown) lead primarily to product ions at $m/z$ 270 and 271, consistent with an earlier study by our group of the CID of [U$^{VI}$O$_2$(OCH$_3$)$_2$]$^+$ [49].

\[
[U^{VI}O_2(ClO_4)(CH_3OH)]^+ \rightarrow [U^{VI}O_2(OCH_3)]^{+} + \text{HClO}_4
\]  

(9)

The preferred elimination of HClO$_4$ acid at the MS$^4$ stage suggests that a proton is transferred from the alcohol ligand to the perchlorate anion during the dissociation reaction. Such a proton transfer process is consistent with our previous studies of H$_2$O and alcohol-coordinated uranyl-nitrate, halide and perchlorate cations [14, 36, 76, 83]. A strong tendency to form alkoxide species may be a driving force for the apparent proton transfer step and subsequent elimination of HClO$_4$ is even more pronounced during CID of complexes containing ethanol and n-propanol. A comprehensive examination of the competition between alcohol ligand loss and elimination of (neutral) acids such as HNO$_3$ and HClO$_4$ from similar cationized uranyl complexes is currently underway and will be reported at a later date.

To summarize, in this set of experiments we revisited the dissociation of complexes composed of the uranyl perchlorate cation [U$^{VI}$O$_2$(ClO$_4$)]$^+$ coordinated by CH$_3$OH and H$_2$O ligands using the 2-D LIT. The experiments conducted under conditions of low levels of background H$_2$O allow for the revision of the previously proposed dissociation pathway for the decomposition of [U$^{VI}$O$_2$(ClO$_4$)]$^+$ to one that involves the loss of 2 O$_2$ molecules to generate [U$^{VI}$O$_2$(Cl)]$^+$, which can then undergo an ion molecule reaction to generate [U$^{VI}$O$_2$(OH)]$^+$. Formation of [U$^{VI}$O$_2$(Cl)]$^+$ is more in line with the known thermal decomposition of inorganic perchlorate compounds. Our
experiments further illustrate the role residual H$_2$O in ion trap instruments may play in influencing the observed dissociation patterns and pathways for metal ion complexes.
Chapter 5

Formation and hydrolysis of gas-phase $[\text{UO}_2(\text{R})]^+$: $\text{R} = \text{CH}_3$, $\text{CH}_2\text{CH}_3$, $\text{CH}=$CH$_2$, and C$_6$H$_5$

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Experiments with formate and acetate complexes followed a previous study in which a 3-D quadrupole ion trap was used to investigate the dissociation reactions of anionic actinyl complexes with carboxylate ligands. Precursor ions with the general formula $[\text{AnO}_2(\text{O}_2\text{C-R})_3]^{-}$, when An = U, Np, and Pu and R = CH$_3$ (methyl), CH$_3$C≡C (1-propynyl), C$_6$H$_5$ (phenyl), and C$_6$F$_5$ (pentafluorophenyl), were subjected to CID. Product ions such as $[(\text{R})\text{AnO}_2(\text{O}_2\text{C-R})_2]^{-}$ and $[(\text{R})_2\text{AnO}_2(\text{O}_2\text{C-R})]^{-}$ were generated by decarboxylation, and this was the first report of such species that included discrete Np-C and Pu-C bonds.

Given the interesting actinyl complexes generated in the negative ion mode, the goals of the present study were (a) to determine whether similar, cationic uranyl-alkyl or -aryl complexes with general formula $[\text{UO}_2(\text{R})]^+$ could be produced by decarboxylation of $[\text{UO}_2(\text{O}_2\text{C-R})]^+$ precursors and (b) to identify the pathways by which the species, if formed, dissociate by collisional activation or otherwise react when exposed to gas-phase H$_2$O. Our hypothesis was that lower levels of adventitious H$_2$O would improve the likelihood that the organometallic species would be generated by multiple-stage CID.

5.1 Creation of $[\text{UO}_2(\text{R})]^+$ species and reactions with gas-phase H$_2$O

As noted earlier, one aim of this study was to create cationic uranyl-alkyl and
aryl complexes by decarboxylation using MS\textsuperscript{n} CID. This approach has been used extensively to create a range of organometallic species, including some that contain UO\textsubscript{2}\textsuperscript{2+}, for gas-phase studies \cite{[44, 48, 83-87]}. In several cases, the positively and negatively charged organometallic species were created for subsequent study of hydrolysis in a species-specific fashion \cite{[44, 48, 84, 85, 87]}. The MS\textsuperscript{n} CID of [UO\textsubscript{2}(O\textsubscript{2}C-CH\textsubscript{3})(CH\textsubscript{3}CH\textsubscript{2}OH)\textsubscript{n}]\textsuperscript{+}, n = 0-3, was discussed in our previous report \cite{[48]}. For the sake of comparison with the respective carboxylate precursors presented below, the MS\textsuperscript{n} spectra are briefly summarized here. The most abundant positively charged species generated by ESI of uranyl acetate in 50:50 H\textsubscript{2}O/CH\textsubscript{3}CH\textsubscript{2}OH was [UO\textsubscript{2}(O\textsubscript{2}C-CH\textsubscript{3})(CH\textsubscript{3}CH\textsubscript{2}OH)\textsubscript{2}]\textsuperscript{+} at m/z 421, CID of [UO\textsubscript{2}(O\textsubscript{2}C-CH\textsubscript{3})(CH\textsubscript{3}CH\textsubscript{2}OH)\textsubscript{2}]\textsuperscript{+} caused elimination of single CH\textsubscript{3}CH\textsubscript{2}OH ligands in sequential stages to generate [UO\textsubscript{2}(O\textsubscript{2}C-CH\textsubscript{3})]\textsuperscript{+} at m/z 329. Subsequent CID of [UO\textsubscript{2}(O\textsubscript{2}C-CH\textsubscript{3})]\textsuperscript{+} generated [UO\textsubscript{2}(OH)]\textsuperscript{+} at m/z 287. The product ion shifted to m/z 288 for CID of [UO\textsubscript{2}(O\textsubscript{2}C-CD\textsubscript{3})]\textsuperscript{+} \cite{[3 R=paper]}, consistent with a dissociation reaction pathway that involves intramolecular H\textsuperscript{+}(D\textsuperscript{+}) transfer and elimination of ketene O=C=CH\textsubscript{2} (O=C=CD\textsubscript{2} for the deuterated labeled analog) as suggested by Waters et al. \cite{[88]}. Formation of [UO\textsubscript{2}(CH\textsubscript{3})]\textsuperscript{+} by decarboxylation of [UO\textsubscript{2}(O\textsubscript{2}C-CH\textsubscript{3})]\textsuperscript{+} did not occur.

Graul and Squires used CID of (bare) ethoxide to synthesize the methyl carbanion for studies of gas-phase reactivity in a flowing afterglow instrument \cite{[89]}. We found that sufficient abundance of ethanol-coordinated uranyl-ethoxide cation [UO\textsubscript{2}(OCH\textsubscript{2}CH\textsubscript{3})((CH\textsubscript{3}CH\textsubscript{2}OH)\textsubscript{2}]\textsuperscript{+}, was created by ESI of the uranyl-acetate solution (in 50:50 H\textsubscript{2}O: CH\textsubscript{3}CH\textsubscript{2}OH) to allow preparation of [UO\textsubscript{2}(OCH\textsubscript{2}CH\textsubscript{3})]\textsuperscript{+} by MS\textsuperscript{n} CID. Subsequent CID of [UO\textsubscript{2}(OCH\textsubscript{2}CH\textsubscript{3})]\textsuperscript{+} created [UO\textsubscript{2}(CH\textsubscript{3})]\textsuperscript{+} \cite{[49]}.
The CID of $[\text{UO}_2(\text{CH}_3)]^+$ was probed in our previous study [48]; the sole fragmentation pathway is creation of $[\text{UO}_2]^+\,(m/z\,270)$ by elimination of $\text{CH}_3$ radical. The product ion spectra generated by isolation of $[\text{UO}_2(\text{CH}_3)]^+$ at $m/z\,285$, without imposed collisional excitation, for reaction with background neutrals (presumed to be primarily $\text{H}_2\text{O}$ and $\text{O}_2$) over time periods ranging from 1 ms to 1 s are shown in Figure 8.

At isolation times of 10 and 100 ms (Figure 8a-b, respectively), $[\text{UO}_2(\text{H}_2\text{O})]^+$ and $\text{UO}_2^+$ product ions at $m/z\,288$ and 270, respectively, were observed. At isolation times of 1 and 10 s (Figure 8c-d, respectively), larger hydrates such as $[\text{UO}_2(\text{H}_2\text{O})_2]^+$ and $[\text{UO}_3(\text{H}_2\text{O})_3]^+$ at $m/z\,306$ and 324, along with the $\text{O}_2$ adduct $[\text{UO}_2(\text{H}_2\text{O})(\text{O}_2)]^+$ [62-64], are also formed.

The appearance of the $[\text{UO}_2(\text{H}_2\text{O})]^+$ is likely the result of reaction 10, in which the energy associated with binding of $\text{H}_2\text{O}$ drives the elimination of $\cdot\text{CH}_3$ and reduction of uranyl to $\text{UO}_2^{2+}$. The formation of $\text{UO}_2^+$ may involve either collisions with $\text{He}$ or $\text{H}_2\text{O}$ with sufficient energy to cause reductive elimination of $\cdot\text{CH}_3$ directly or the loss of $\text{H}_2\text{O}$ from the $[\text{UO}_2(\text{H}_2\text{O})]^+$ product created in reaction 10.

\[
\text{[UO}_2(\text{CH}_3)(\text{H}_2\text{O})]^+ \rightarrow \text{[UO}_2(\text{H}_2\text{O})]^+ + \cdot\text{CH}_3
\]  

$$[\text{UO}_2(\text{H}_2\text{O})]^+ + \cdot\text{CH}_3 \quad (10)$$
While a hydrolysis pathway was observed for anionic actinyl organometallic complexes in earlier studies, [3,15] the formation of \([\text{UO}_2(\text{OH})]^+\) \((m/z\ 287)\) and elimination of \(\text{CH}_4\) (reaction 11) was not detected above background in the present study (Figure 8).

\[
[\text{UO}_2(\text{CH}_3)]^+ + \text{H}_2\text{O} \rightarrow [\text{UO}_2(\text{CH}_3)(\text{H}_2\text{O})]^{++} \rightarrow [\text{UO}_2(\text{OH})(\text{CH}_4)]^{++} \rightarrow [\text{UO}_2(\text{OH})]^+ + \text{CH}_4
\]  

(11)

Because the electron affinity of a neutral can be used to assess the stability of an anion, we propose that the exclusive formation of \([\text{UO}_2(\text{H}_2\text{O})]^+\) upon isolation of \([\text{UO}_2(\text{CH}_3)]^+\) for IMR likely reflects the low electron affinity of the methyl radical \(+0.080 \pm 0.002\ \text{eV}\) [89-90].

The next step was to create the positively charged complex \([\text{UO}_2(\text{CH}_2\text{CH}_3)]^+\).

However, the MS\(^n\) CID or the uranyl-propionate complex, \([\text{UO}_2(\text{O}_2\text{C-CH}_2\text{CH}_3)(\text{CH}_3\text{CH}_2\text{OH})_2]^+\), (spectra not shown) produced essentially the same results observed for the acetate-containing precursor: \(\text{CH}_3\text{CH}_2\text{OH}\) ligands were eliminated in sequential steps (MS/MS and MS\(^3\) stages, respectively), and subsequent CID of \([\text{UO}_2(\text{O}_2\text{C-CH}_2\text{CH}_3)]^+\) (MS\(^4\) stage) created \([\text{UO}_2(\text{OH})]^+\) at \(m/z\ 287\). The 1-propoxide complex \([\text{UO}_2(\text{OCH}_2\text{CH}_2\text{CH}_3)(\text{CH}_3\text{CH}_2\text{CH}_2\text{OH})_2]^+\) was a prominent ion in the ESI spectrum of the uranyl-propionate solution prepared in 50:50 \(\text{H}_2\text{O}: \text{CH}_3\text{CH}_2\text{CH}_2\text{OH}\). Initiating MS\(^n\) CID experiments with this precursor, we were able to generate \([\text{UO}_2(\text{CH}_2\text{CH}_3)]^+\) (MS\(^4\) stage, spectrum not shown).

CID of \([\text{UO}_2(\text{CH}_2\text{CH}_3)]^+\) (MS\(^5\) stage, spectrum not shown) primarily caused elimination of \(\text{CH}_2\text{CH}_3\) radical to leave \([\text{UO}_2]^+\) at \(m/z\ 270\). Isolation of \([\text{UO}_2(\text{CH}_2\text{CH}_3)]^+\)
for 1 ms to 1 s (spectra not shown) to react with H₂O generated only [UO₂(H₂O)]⁺ at m/z 288, presumably through a reaction similar to 10. Hydrolysis to generate [UO₂(OH)]⁺ at m/z 287 was not observed. Exclusive loss of the CH₂CH₃ radical, with reduction of UO₂²⁺ to U⁴⁺, after association of the precursor complex with H₂O in an IMR is consistent with the negative electron affinity for the ethyl radical (-0.263±0.089 eV) [91], which indicates an “unbound” state (unstable towards electron detachment [92]).

We next examined the CID of the uranyl-acrylate precursor and began MSⁿ experiments with [UO₂(O₂C-CH=CH₂)(CH₃CH₂OH)₂]⁺ at m/z 433. Our hypothesis was that the significantly higher electron affinity of the vinyl radical (+0.667±0.024 eV) [93] compared with the ethyl radical would make formation of the vinyl carbanion by decarboxylation more favorable. As for the acetate and propionate precursors, CID of [UO₂(O₂C-CH=CH₂)(CH₃CH₂OH)₂]⁺ caused
the sequential elimination (MS/MS and MS$^3$ stages, Figure 9a,b, respectively) of CH$_3$CH$_2$OH ligands to leave [UO$_2$(O$_2$C-CH=CH$_2$)]$^+$. However, unlike the acetate and propionate precursors, subsequent CID of [UO$_2$(O$_2$C-CH=CH$_2$)]$^+$ (MS$^4$ stage, Figure 9c) caused decarboxylation (reaction 12) to leave [UO$_2$(CH=CH$_2$)]$^+$ at m/z 297, along with [UO$_2$(OH)]$^+$ and UO$_2^+$. 

\[
[UO_2(O_2C-CH=CH_2)]^+ \rightarrow [UO_2(CH=CH_2)]^+ + CO_2 \tag{12}
\]

CID of [UO$_2$(CH=CH$_2$)]$^+$ generated UO$_2^+$ by elimination of vinyl radical, •CH=CH$_2$ (MS$^5$ stage, Figure 9d). Isolation of [UO$_2$(CH=CH$_2$)]$^+$ (MS$^5$ stage, Figure 10) for reaction periods of 10 and 100 ms (Figure 10a,b, respectively) produced [UO$_2$(OH)]$^+$ through a hydrolysis reaction similar to 11. At longer reaction times (1 and 10 s, Figure 10 c,d, respectively), the mono-, di-, and tri-hydrates [UO$_2$(OH)(H$_2$O)]$^+$, [UO$_2$(OH)(H$_2$O)$_2$]$^+$, and [UO$_2$(OH)(H$_2$O)$_3$]$^+$ were observed at m/z 305, 323, and 341, respectively. The [UO$_2$(H$_2$O)]$^+$ ion, the dominant product when [UO$_2$(CH$_3$)]$^+$ and
[UO₂(CH₂CH₃)]⁺ were isolated and allowed to react with H₂O, was not observed for [UO₂(CH=CH₂)]⁺. This result is consistent with the relatively high electron affinity of the vinyl radical and the fact that formation of UO₂⁺ required collisional activation.

The multiple-stage CID spectra derived from the uranyl-benzoate precursor, [UO₂(O₂C-C₆H₅)(CH₃CH₂OH)₂]⁺, is discussed below. CID of [UO₂(O₂C-C₆H₅)(CH₃CH₂OH)₂]⁺ (spectra not shown) and [UO₂(O₂C-C₆H₅)(CH₃CH₂OH)]⁺ caused the elimination of single CH₃CH₂OH ligands. Subsequent CID of [UO₂(O₂C-C₆H₅)]⁺ at m/z 391 produced the uranyl complex with the benzoate carbanion, [UO₂(C₆H₅)]⁺ by decarboxylation, and [UO₂]⁺ by elimination of C₆H₅CO₂ radical. CID of [UO₂(C₆H₅)]⁺ generated UO₂⁺ at m/z 270 by elimination of the benzoate radical. Isolation of [UO₂(C₆H₅)]⁺ (MS² stage, Figure 11) for reaction periods of 10 ms to 10 s produced only [UO₂(OH)]⁺ by hydrolysis and the hydrates [UO₂(OH)(H₂O)]⁺, [UO₂(OH)(H₂O)₂]⁺, and [UO₂(OH)(H₂O)₃]⁺ by subsequent H₂O addition. The [UO₂(H₂O)]⁺ product was not observed following isolation of [UO₂(C₆H₅)]⁺ to react with H₂O, consistent with the electron affinity of the benzoate radical (+1.0860 ± 0.0060 eV) [94], which is higher than those of both the methyl and vinyl radicals.

![Figure 11: Product ion spectra generated by isolation and storage of [UO₂(C₆H₅)]⁺ (m/z 347) for reaction with background H₂O: (a) 10 ms, (b) 100 ms, (c) 1 s, and (d) 10 s.](image)
5.2 DFT calculation of reaction energies

The appearance of either [UO$_2$(H$_2$O)]$^+$ or [UO$_2$(OH)]$^+$ as reaction products, as described above, implicates collisions with gas-phase H$_2$O in the LIT. Given the different reactivity displayed by [UO$_2$(CH$_3$)]$^+$ and [UO$_2$(CH$_2$CH$_3$)]$^+$ on the one hand and [UO$_2$(CH=CH$_2$)]$^+$ and [UO$_2$(C$_6$H$_5$)]$^+$ on the other, we used DFT to compute zero-point corrected relative electronic energy and reaction free energy changes for reactions 10 and 11. Computed Gibbs free energies (298 K) for reactions 10 and 11 are provided in Table 1 along with the experimentally measured branching ratios. The zero-point corrected electronic energies for the same reactions were performed (data not shown).

Regardless of the precursor organo-uranyl species investigated, the relative change in corrected electronic energy and free energy for hydrolysis (reaction 11) is significantly more negative than for loss of a neutral radical to generate [UO$_2$(H$_2$O)]$^+$ (reaction 10). Therefore, the computed energy changes are in agreement with the reactivity measured for [UO$_2$(CH=CH$_2$)]$^+$ and [UO$_2$(C$_6$H$_5$)]$^+$ but not with our results for [UO$_2$(CH$_3$)]$^+$ and [UO$_2$(CH$_2$CH$_3$)]$^+$, which both generate [UO$_2$(H$_2$O)]$^+$ when exposed to gas-phase H$_2$O. This led to us to determine the extent to which the transition state energy for proton transfer, necessary to create [UO$_2$(OH)]$^+$ and neutral CH$_4$, CH$_3$-CH$_3$, etc., may influence the competition between reactions 10 and 11.
Structures for the respective minima and transition states for reactions 10 and 11, using species on the reaction coordinate for \([\text{UO}_2(\text{CH}_3)]^+\) as respective examples, are provided in Figure 12.

![Figure 12: Computed structures for minima and transition state for reactions 10 and 11 in the text, using species on the reaction coordinate for \([\text{UO}_2(\text{CH}_3)]^+\) as a representative example.]

Table 1: Computed free energies and branching ratios for the reaction of \([\text{UO}_2(\text{CH}_3)]^+, \ [\text{UO}_2(\text{CH}_2\text{CH}_3)]^+, \ [\text{UO}_2(\text{CH}==\text{CH}_2)]^+, \) and \([\text{UO}_2(\text{C}_6\text{H}_5)]^+\) with H_2O

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<th>CH(_2\text{CH}_3)</th>
<th>CH(=\text{CH}_2)</th>
<th>C(_6\text{H}_5)</th>
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<td>([\text{UO}_2(R)]^+ + \text{H}_2\text{O} \rightarrow [\text{UO}_2(\text{H}_2\text{O})]^+ + \bullet \text{R})</td>
<td>-55.5</td>
<td>-29.8</td>
<td>-2.4</td>
<td>9.4</td>
<td></td>
</tr>
<tr>
<td>([\text{UO}_2(R)]^+ + \text{H}_2\text{O} \rightarrow [\text{UO}_2(\text{OH})]^+ + \text{HR})</td>
<td>-177.4</td>
<td>-122.9</td>
<td>-135.4</td>
<td>-128.3</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Reaction</th>
<th>(\Delta G, \text{kJ/mol, M06-2X})</th>
<th>CH(_3)</th>
<th>CH(_2\text{CH}_3)</th>
<th>CH(=\text{CH}_2)</th>
<th>C(_6\text{H}_5)</th>
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</thead>
<tbody>
<tr>
<td>Reaction</td>
<td>CH3</td>
<td>CH2CH3</td>
<td>CH=CH2</td>
<td>C6H5</td>
<td></td>
</tr>
<tr>
<td>----------</td>
<td>-----</td>
<td>--------</td>
<td>--------</td>
<td>------</td>
<td></td>
</tr>
<tr>
<td>[UO2(R)]^+ + H2O → [UO2(H2O)]^+ + ● R</td>
<td>-53.0</td>
<td>-27.8</td>
<td>1.0</td>
<td>10.2</td>
<td></td>
</tr>
<tr>
<td>[UO2(R)]^+ + H2O → [UO2(OH)]^+ + HR</td>
<td>-157.5</td>
<td>-116.2</td>
<td>-128.8</td>
<td>-128.0</td>
<td></td>
</tr>
</tbody>
</table>

$\Delta G$, kJ/mol, PBE0

<table>
<thead>
<tr>
<th>Reaction</th>
<th>CH3</th>
<th>CH2CH3</th>
<th>CH=CH2</th>
<th>C6H5</th>
</tr>
</thead>
<tbody>
<tr>
<td>[UO2(R)]^+ + H2O → [UO2(H2O)]^+ + ● R</td>
<td>-68.5</td>
<td>-40.3</td>
<td>-12.6</td>
<td>1.6</td>
</tr>
<tr>
<td>[UO2(R)]^+ + H2O → [UO2(OH)]^+ + HR</td>
<td>-168.9</td>
<td>-116.6</td>
<td>-136.3</td>
<td>-130.9</td>
</tr>
</tbody>
</table>

Percentage of product yield

<table>
<thead>
<tr>
<th>Reaction</th>
<th>CH3</th>
<th>CH2CH3</th>
<th>CH=CH2</th>
<th>C6H5</th>
</tr>
</thead>
<tbody>
<tr>
<td>[UO2(R)]^+ + H2O → [UO2(H2O)]^+ + ● R</td>
<td>100.0</td>
<td>100.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>[UO2(R)]^+ + H2O → [UO2(OH)]^+ + HR</td>
<td>0.0</td>
<td>0.0</td>
<td>100.0</td>
<td>100.0</td>
</tr>
</tbody>
</table>

Electronic energies (EE), zero-point energy-corrected EEs, and the sum of electron and thermal free energies are available upon request. We note here that one consideration when surveying potential minima and transition structures was that the [UO2(H2O)]^+ species might isomerize to generate the dihydroxide [U(O)(OH)2]^+ through a proton transfer step (Scheme 1). This specific reaction was investigated for ThO2, PaO2^+, UO2^{2+}, and UO2^+ in detail by Vasiliu et al [95] using coupled-cluster method calculations. In their study, it was determined that the “physisorbed” H2O adduct ([UO2(H2O)]^+) is approximately 50 kJ/mol more stable than the “chemisorbed” species ([U(O)(OH)2]^+). Moreover, the transition state energy for proton transfer to create the dihydroxide was computed to lie.

Scheme 1: Isomerization of [UO2(H2O)]^+ to create [UO(OH)2]^+.
only 5.43 kJ/mol below the reactant energy asymptote, and the computed reaction energies were in good agreement with experimental investigations of the rates of axial oxo ligand exchange for the species [1, 96]. Because isomerization appears to be energetically unfavorable for [UO$_2$(H$_2$O)]$^+$, we neglected the energetics of this step and based our evaluation of the reactivity of the organometallic species, [UO$_2$(R)]$^+$, on formation either of [UO$_2$(H$_2$O)]$^+$ or [UO$_2$(OH)]$^+$ by reaction with H$_2$O.

Reaction energy diagrams for generation of [UO$_2$(H$_2$O)]$^+$ and [UO$_2$(OH)]$^+$ from [UO$_2$(R)]$^+$ computed using the M06-L functional are shown in Figure 13. The diagrams constructed from structures computed with the B3LYP, M06-2X, and PBE0 functionals are available upon request. Relative free energies for the minima and transition state structures for all species are provided in Table 2.
Table 2: Relative computed Gibbs free energies for minima I, II, III, IV, V, and for TSII→IV, calculated relative to sum of reactant species energies (structure I + H2O)

<table>
<thead>
<tr>
<th></th>
<th>ΔG, R=CH3</th>
<th>ΔG, R=CH2CH3</th>
<th>ΔG, R=CH2</th>
<th>ΔG, R=C2H5</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>M06-</td>
<td>M06-</td>
<td>M06-</td>
<td>M06-</td>
</tr>
<tr>
<td>I</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>II</td>
<td>-107.4</td>
<td>-111.3</td>
<td>-115.1</td>
<td>-100.8</td>
</tr>
<tr>
<td>III</td>
<td>-55.5</td>
<td>-73.6</td>
<td>-65.8</td>
<td>-29.8</td>
</tr>
<tr>
<td>TS II → IV</td>
<td>-28.5</td>
<td>-22.5</td>
<td>-42.9</td>
<td>-14.3</td>
</tr>
<tr>
<td>IV</td>
<td>-193.2</td>
<td>-184.8</td>
<td>-181.3</td>
<td>-160.8</td>
</tr>
<tr>
<td>V</td>
<td>-177.4</td>
<td>-167.4</td>
<td>-157.5</td>
<td>-122.9</td>
</tr>
</tbody>
</table>

Referring to the structures provided in Figure 12, association of H2O with [UO2(CH3)]+ (structure I) creates the hydrate II. Direct elimination of CH3 radical from II leaves [UO2(H2O)]+ (structure III). The ion-molecule complex IV, created by intracomplex proton transfer, is created from II through the transition state structure TS II → IV. Elimination of CH4 leaves [UO2(OH)]+ (structure V).

As shown in the reaction energy diagram in Figure 13A, addition of H2O to [UO2(CH3)]+ and [UO2(CH2CH3)]+ to create structure II is computed to be exergonic by approximately 107 and 101 kJ/mol, respectively. The computed energies for generation of [UO2(H2O)]+ (structure III) by elimination of CH3 or CH2CH3 radical from the respective hydrates lie 55.5 and 30 kJ/mol below the entrance asymptote and 51.5 and 71 kJ/mol above the energy of structure II, respectively. For both precursor ions, the computed energy for the proton-transfer transition state (TSII→IV) lies below the reactant asymptote, 78 and 87 kJ/mol above the hydrate structures (II), and (more
importantly) 26.5 and 15.5 kJ/mol above the energy required to eject either CH$_3$ or CH$_2$CH$_3$ radical to leave [UO$_2$(H$_2$O)]$^+$ (structure III), respectively.

For [UO$_2$(CH=CH$_2$)]$^+$ and [UO$_2$(C$_6$H$_5$)]$^+$ (Figure 13b), the calculations predict that reaction with H$_2$O is also exergonic by 105.5 and 96.1 kJ/mol, respectively. However, for these two precursors, the proton transfer transition state energy lies approximately 81 and 61 kJ/mol above the energy of the hydrate (structure II) but 21.5 and 44.1 kJ/mol below the energies required for direct elimination of the respective radicals to generate [UO$_2$(H$_2$O)]$^+$ (structure III). We note also that the relative energy to generate [UO$_2$(H$_2$O)]$^+$ by elimination of CH=CH$_2$ or C$_6$H$_5$ radical is comparable or slightly higher than the entrance channel (-2.7 and 9.4 kJ/mol for CH=CH$_2$ and C$_6$H$_5$ radical, respectively), which likely reflects the significantly higher electron affinities compared with those of the CH$_3$ and CH$_2$CH$_3$ radicals.

While our intent was not to try to determine absolute reaction thermochemistry for the respective organouranyl ions, the trends in computed energies support are consistent with experimental observations (i.e., ejection of neutral radicals versus hydrolysis during reaction with H$_2$O) and, in particular, support the hypothesis that the transition state energy for proton transfer influences the competition between the two pathways. We note that similar trends were observed when using the B3LYP, PBE0, and M06-2X functionals (data not shown), thus leading to confidence in the match between theory and experiment for these species.

To summarize, the goals of this study were (a) to create positively charged organo-uranyl complexes with general formula [UO$_2$(R)]$^+$ (e.g., R = CH$_3$, CH$_2$CH$_3$, etc.) by decarboxylation of [UO$_2$(O$_2$C-R)]$^+$ precursors and (b) to identify the pathways by
which the complexes, if formed, dissociate by collisional activation or otherwise react when exposed to gas-phase H$_2$O. CID of both [UO$_2$(O$_2$C-CH$_3$)]$^+$ and [UO$_2$(O$_2$C-CH$_2$CH$_3$)]$^+$ causes H$^+$ transfer and elimination of a ketene to leave [UO$_2$(OH)]$^+$. However, CID of the alkoxide species [UO$_2$(OCH$_2$CH$_3$)]$^+$ and [UO$_2$(OCH$_2$CH$_2$CH$_3$)]$^+$ produced [UO$_2$(CH$_3$)]$^+$ and [UO$_2$(CH$_2$CH$_3$)]$^+$, respectively. Isolation of [UO$_2$(OCH$_2$CH$_3$)]$^+$ and [UO$_2$(OCH$_2$CH$_2$CH$_3$)]$^+$ for reaction with H$_2$O caused formation of [UO$_2$(H$_2$O)]$^+$ by elimination of •CH$_3$ and •CH$_2$CH$_3$: Hydrolysis was not observed. CID of the acrylate and benzoate versions of the complexes, [UO$_2$(O$_2$C-CH=CH$_2$)]$^+$ and [UO$_2$(O$_2$C-C$_6$H$_5$)]$^+$, caused decarboxylation to leave [UO$_2$(CH=CH$_2$)]$^+$ and [UO$_2$(C$_6$H$_5$)]$^+$, respectively. These organometallic species react with H$_2$O to produce [UO$_2$(OH)]$^+$, and loss of the respective radicals to leave [UO$_2$(H$_2$O)]$^+$ was not detected. DFT calculations suggest that the [UO$_2$(OH)]$^+$ product is energetically favored over the hydrated [UO$_2$]$^+$ cation, regardless of the precursor species. However, for the [UO$_2$(CH$_3$)]$^+$ and [UO$_2$(CH$_2$CH$_3$)]$^+$ precursors, the transition state energy for proton transfer to generate [UO$_2$(OH)]$^+$ and the associated neutral alkanes is higher than the path involving direct elimination of the organic neutral to form [UO$_2$(H$_2$O)]$^+$. The situation is reversed for the [UO$_2$(CH=CH$_2$)]$^+$ and [UO$_2$(C$_6$H$_5$)]$^+$ precursors: The transition state for proton transfer is lower than the energy required for creation of [UO$_2$(H$_2$O)]$^+$ and elimination of C=CH$_2$ or C$_6$H$_5$ radical.
Measurement of the asymmetric UO$_2^{2+}$ stretching frequency for [U$^{VI}$O$_2$(F)$_3$]$^-$ using IRMPD spectroscopy

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In an earlier experiment [97], the IRMPD spectra of negatively charged complexes, [UO$_2$(X)$_3$]$^-$ (where X = Cl$^-$, Br$^-$, and I$^-$), were collected. Within this group, the $\nu_3$ frequency shifted to lower values, following the trend I > Br > Cl; however, no (experimental) photodissociation signal was observed for the [UO$_2$(F)$_3$]$^-$ complex, which prevented a comprehensive comparison of measured $\nu_3$ positions to computed frequencies from DFT calculations. Because the shift in $\nu_3$ is predicted to be most dramatic when X = F, we revisited these species using wavelength-selective infrared photodissociation in a quadrupole ion trap mass spectrometer. The specific goals in this study were: (a) to measure $\nu_3$ for [UO$_2$(F)$_3$]$^-$, (b) to compare $\nu_3$ for [UO$_2$(F)$_3$]$^-$ to values for [UO$_2$(Cl)$_3$]$^-$, [UO$_2$(Br)$_3$]$^-$, and [UO$_2$(I)$_3$]$^-$ measured under similar experimental conditions and (c) establish the extent to which the trend in experimentally-measured shift to $\nu_3$ is captured by DFT calculations.

6.1 IRMPD measurements

In our earlier investigation [58], abundant [UO$_2$(X)$_3$]$^-$ complexes were generated by ESI using each of the four uranyl-halide materials. Different photofragmentation behavior was noted for the respective precursors: no photodissociation products were observed for [UO$_2$(F)$_3$]$^-$; [UO$_2$(Cl)$_3$]$^-$ dissociated solely by loss of (neutral) [UO$_2$(Cl)$_2$] to form Cl$^-$ (shown in general reaction 13); [UO$_2$(I)$_3$]$^-$ eliminated iodine radical to create [UO$_2$(I)$_2$] (shown in reaction 14) and the [UO$_2$(Br)$_3$]$^-$ precursor fragmented by both
pathways. The trends in dissociation behavior were in good general agreement with computed reaction energetics [58].

\[
[U^{VI}O_2(X)_3]^- \rightarrow [U^{VI}O_2(X)_2]^o + X^- \quad (13)
\]

\[
[U^{VI}O_2(X)_3]^- \rightarrow [U^{V}O_2(X)_2]^+ + X^o \quad (14)
\]

Using IRMPD in the FT-ICR instrument, the uranyl \( \nu_3 \) frequencies measured for the three complexes that exhibited dissociation channels ranged from 935 cm\(^{-1} \) for [UO\(_2\)(Br)_3]\(^-\) to 948 cm\(^{-1} \) for [UO\(_2\)(I)_3]\(^-\).

In the present study, all four anionic complexes were also generated using ESI and the quadrupole ion trap analyzer. For [UO\(_2\)(Cl)_3]\(^-\), [UO\(_2\)(Br)_3]\(^-\), and [UO\(_2\)(I)_3]\(^-\), the position of \( \nu_3 \) was determined by measuring the yield of the [UO\(_2\)(X)_2]\(^-\) photodissociation product (reaction 14) as a function of photon energy. This approach was necessary because the halide product generated by reaction 13 lies below the low-mass cutoff of the quadrupole instrument for each of the three precursors. It is not clear why reaction 14 was not observed in the earlier experiments performed using the FT-ICR instrument.

In the present study, no photodissociation product ions were observed for the [UO\(_2\)(F)_3]\(^-\) precursor. For this species, the position of \( \nu_3 \) was instead measured.
by monitoring the depletion in precursor ion intensity as a function of photon energy. Previous DFT calculations suggest that the reaction energy to produce [UO₂(F)₂]⁻ by loss of neutral fluorine radical would be ~37-70 kcal/mol higher than for the other precursor ions [58], making dissociation by reaction 14 unlikely. The F⁻ product ion (m/z 19) that might be generated by reaction 13 also lies below the low-mass cutoff of the quadrupole ion trap. To ensure that there is no loss in accuracy by measuring ν₃ by precursor ion depletion, the IRMPD of [UO₂(Cl)₃]⁻ was examined using both modes. As shown in Figure 14, the spectrum produced by monitoring depletion of [UO₂(Cl)₃]⁻ as a function of photon energy (top trace) mirrors the spectrum generated by monitoring the photodissociation product ion yield (bottom trace, using formation of the [UO₂(Cl)₂]⁻ by reaction 14).

Figure 15: Comparison of vibrational action spectra for (a) [UVO₂(F)]⁻, (b) [UVO₂(Cl)]⁻, (c) [UVO₂(Br)]⁻, and (d) [UVO₂(I)]⁻ using irradiation in a quadrupole ion trap instrument.
The IRMPD spectra for all four \([\text{UO}_2(\text{X})_3]^-\) complexes are compared in Figure 15. No peaks corresponding to symmetric \(\text{O}=\text{U}=\text{O}\) stretch were observed in the IRMPD spectra, regardless of the species. All \(\text{U-X}\) stretch frequencies (expected to be in the range of 200 cm\(^{-1}\) to 600 cm\(^{-1}\)) lie below the lower frequency limit on the free electron laser under the operating conditions used in these experiments and were not measured. The measured asymmetric stretching frequencies \((v_3)\) values for \([\text{UO}_2(\text{I})_3]^-\), \([\text{UO}_2(\text{Br})_3]^-\), and \([\text{UO}_2(\text{Cl})_3]^-\) were 948 cm\(^{-1}\), 942 cm\(^{-1}\), and 936 cm\(^{-1}\), respectively. These results are in excellent agreement with the measured values from our previous study and demonstrates the reproducibility of the IRMPD experiments when using different ion trapping instruments.

More importantly, the \(v_3\) value measured for \([\text{UO}_2(\text{F})_3]^-\) was 893 cm\(^{-1}\), which is 43 cm\(^{-1}\) lower than the one measured for \([\text{UO}_2(\text{Cl})_3]^-\).

3.2 Computed asymmetric \(\text{O}=\text{U}=\text{O}\) stretching frequencies

As in the initial study of these species, the single minimum identified here for \([\text{UO}_2(\text{X})_3]^-\) has trigonal bipyramidal geometry with axial oxo ligands, and the halide ligands occupying equatorial sites (Figure 15). As noted earlier, we use multiple
functionals and basis sets to ensure that a consistent trend with respect to the shift in \( \nu_3 \) frequency with change in halide ligand was predicted by DFT. The unscaled computed \( \nu_3 \) frequencies generated in the present study using the B3LYP functional, MWB46 and MWB60 pseudopotential on I and U, respectively, and either the 6-311 + G(d), 6-311 + G(3df) or aug-cc-pvtz basis set on O, F, Cl, and Br are compared in Table 3.

Table 3: Unscaled, computed asymmetric \( \text{O=U=O} \) stretching frequencies for \([\text{U}^{\text{VI}}\text{O}_2(X)_3]^-\) , \(X=\text{F, Cl, Br, and I}\), using B3LYP functional and either the 6-311 + G(d), 6-311 + G(3df), or aug-cc-pvtz basis set on O, F, Cl, and Br. *The MWB46 and MWB60 pseudopotentials with associated basis sets were used on I and U, respectively.

<table>
<thead>
<tr>
<th>Halide</th>
<th>Basis Set*</th>
<th>IRMPD</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>6-311 + G(d)</td>
<td>6-311 + G(3df)</td>
</tr>
<tr>
<td>F</td>
<td>917</td>
<td>914</td>
</tr>
<tr>
<td>Cl</td>
<td>962</td>
<td>963</td>
</tr>
<tr>
<td>Br</td>
<td>968</td>
<td>970</td>
</tr>
<tr>
<td>I</td>
<td>978</td>
<td>981</td>
</tr>
</tbody>
</table>

The computed \( \nu_3 \) frequencies generated using B3LYP, M06-L, PBE0, and SVWN functional and the MWb46 and MWB60 pseudopotential on I and U, respectively, and the 6-311 + G(d) set on O, F, Cl, and Br are compared in Table 4. As in the earlier study, the difference between the computed frequency for \([\text{UO}_2(\text{Cl})_3]^-\), \([\text{UO}_2(\text{Br})_3]^-\), and \([\text{UO}_2(\text{I})_3]^-\) is \(\sim 7-10 \text{ cm}^{-1}\). Importantly, the computer \( \nu_3 \) frequency for \([\text{UO}_2(\text{F})_3]^-\) is 45 cm\(^{-1}\), 49 cm\(^{-1}\), and 51 cm\(^{-1}\) is lower than the frequency predicted for \([\text{UO}_2(\text{Cl})_3]^-\) when using
the 6-311 + G(d), 6-311 + G(3df), and qug-cc-pvtz basis set, respectively, on O, F, Cl, and Br. A difference of 48 cm$^{-1}$ was predicted in the earlier study.

Table 4: Unscaled, computed asymmetric O=U=O stretching frequencies for [U$^{VI}$O$_2$(X)$_3$], X= F, Cl, Br, and I, using the MWB46 and MWB60 pseudopotential on I and U, respectively, 6-311 + G(d) basis set on O, F, Cl, and Br and either the B3LYP, M06-L, PBE0, or SVWN functional.

<table>
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<th>IRMPD</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>B3LYP</td>
<td>M06-L</td>
</tr>
<tr>
<td>F</td>
<td>917</td>
<td>905</td>
</tr>
<tr>
<td>Cl</td>
<td>962</td>
<td>957</td>
</tr>
<tr>
<td>Br</td>
<td>968</td>
<td>962</td>
</tr>
<tr>
<td>I</td>
<td>978</td>
<td>971</td>
</tr>
</tbody>
</table>

The unscaled computed $v_3$ frequencies computed using the B3LYP functional, MWB60 and MWB46 effective core potential/basis set on U and I, respectively, and either the 6-311 + G(d), 6-311 + G(3df), or aug-cc-pvtz basis set on O, F, Cl, and Br, are compared to the experimental values in Figure 17 and Figure 18. In Figure 18, the measured values are compared to the computed $v_3$ frequencies generated using the B3LYP, M06-L, PBE0, or SVWN functional, the MWB60 and MWB46 effective core potential/basis set on U and I, respectively, and either the 6-311 + G(d) basis set on the O, F, Cl, and Br atoms. The comparison shows that the computed frequencies for $v_3$ are sensitive to the choice in functional, however, each functional/basis set combination accurately captures the trend with respect to the dependence of $v_3$ on the halide ligand X.
In general, the local spin density approximation (SVWN functional) provides computed frequencies that lie closest to the measured values, while the PBE0 functional appears to be least accurate for predicting $\nu_3$. The better agreement when using the SVWN functional is in accord with earlier investigations of U species [8, 9, 98-100]. When used for comparison to IRMPD measurements, unscaled computed $\nu_3$ frequencies using the local density approximation were between 10 and 15 cm$^{-1}$ higher for [UO$_2$(aco)$_n$]$^{2+}$ (n=2-4) and 5 to 10 cm$^{-1}$ higher for [UO$_2$(acn)$_n$]$^{2+}$ (n=3-5) ions, whereas the discrepancy was greater by nearly a factor of 2 when using B3LYP [8]. Similar results were observed in an IRMPD study of the uranyl-nitrate anion [UO$_2$(NO$_3$)$_3$]$^-$. [9]

As noted above, the $\nu_3$ stretching frequency is sensitive to the degree to which electron density is donated to UO$_2^{2+}$ by coordinating nucleophiles [35, 53-61, 101-103], with significant evidence for this coming from species-specific measurements in the gas-phase [8-10, 58, 104-105]. The $\nu_3$ value for [UO$_2$(F)$_3$]$^-$ of 893 cm$^{-1}$, reported here, can be compared to those for a series of cationic and anionic complexes with ligands of varying basicity. In the first systematic species-specific investigation using IRMPD, the lowest
frequencies measured were 988 cm\(^{-1}\) and 1019 cm\(^{-1}\) for 
\([UO_2(aco)_4]^{2+}\) and 995 cm\(^{-1}\) for 
\([UO_2(acn)_5]^{2+}\), respectively [9]. In 
a later study with a larger set of 
ligands, the \(v_3\) value for cations 
with general formula \([UO_2(L)_3]^{2+}\), 
where \(L = \text{acetone, dimethylformamide (DMF), dimethyl sulfoxide (DMSO),}
\text{tetramethyl urea (TMU), and tetramethylthiourea (TMTU) were 1000 cm}^{-1}, 979 \text{ cm}^{-1}, 973 \text{ cm}^{-1}, 965 \text{ cm}^{-1}, \text{and 954 cm}^{-1}, \text{respectively [105]. The values measured with TMU and}
\text{TMTU as the coordinating ligands were lower than the} v_3 \text{ frequency for U}^{VI}\text{O}_2^{2+}
\text{coordinated by 2 oxo-glutaramide ligands (measured at 965 cm}^{-1} [104]). The values 
observed when using the urea, thiourea, and glutaramide ligands approached those 
measured for the reduced complexes \([UO_2(H_2O)]^+\) and \([UO_2(CH_3OH)]^+\), (952 cm\(^{-1}\) and 
945 cm\(^{-1}\), respectively) [9] which demonstrated the high degree of donation from ligand 
to the metal center. For anionic species, a \(v_3\) value of 949 cm\(^{-1}\) was measured for 
\([UO_2(NO_3)_3]^-\) [10]; and at 929 cm\(^{-1}\) and 938 cm\(^{-1}\) for the acetate and benzoate complexes 
\([UO_2(O_2C-CH_3)_3]^-\) and \([UO_2(O_2C-C_6H_5)_3]^-, \text{respectively [106]. Therefore, to the best of}
\text{our knowledge, the} \(v_3\) \text{ value for} [UO_2(F)_3]^-, \text{at 893 cm}^{-1}, \text{is the lowest yet reported for} \(v_3\)
in an IRMPD measurement.
To summarize, these experiments demonstrate that earlier predictions about the influence of halide ligands on the position of the $v_3$ vibration in suite of complexes $[\text{UO}_2(X)_3]^-$ hold, with a modest red shift following the trend I $<$ Br $<$ Cl and significantly greater red shift for $X = F$. Based on our new experiments, we now show that the value measured for $[\text{UO}_2(F)_3]^-$ is $\sim 43$ cm$^{-1}$ lower than the one measured for $[\text{UO}_2(\text{Cl})_3]^-$, which is consistent with predictions made using DFT calculations.

The trends predicted by DFT, regardless of the limited group of functionals and basis sets employed here, are in excellent agreement with the measured shift in $v_3$ frequency. With addition in the present study of F$^-$ as a coordinating ligand, the trend with respect to the measured values of $v_3$ in $[\text{UO}_2(X)_3]^-$ is consistent with the relative strengths of the halides as donor ligands. For example, based on a joint computational and gas-phase photoelectron spectroscopy study, Wang, Li, and coworkers [101] reported that U-X bonding within $[\text{UO}_2(X)_3]^-$ species, in which primarily ionic in character, is strongest for $X = F$, and progressively weaker for $X = \text{Cl, Br, and I}$. In particular, they suggested that U-O orbitals are destabilized and become the frontier molecular orbitals in the fluoride complex through mixing with the low-energy F 2p orbitals. The U-O orbitals are instead stabilized and lie below the halogen lone-pair orbitals for the chloro-, bromo-, and iodo-complexes. In total, the trend in $v_3$ frequency is also consistent with the relative positions of the halides in the spectrochemical series, and the relative strengths of the respective nucleophiles polar, aprotic solvents.
Chapter 7

Gas-Phase Reactions of Ions Derived from Uranyl Propionate and Uranyl Acrylate Complexes

In a previous experiment, the fragmentation of anionic uranyl formate and acetate complexes (general formula \([\text{UO}_2(\text{O}_2\text{C-R})_3]^\text{-}\) where R = H or CH₃, respectively) was investigated using a linear ion trap (LIT) mass spectrometer [48]. In multiple-stage CID experiments, the anionic uranyl formate complex, \([\text{U}^{\text{VI}}\text{O}_2(\text{O}_2\text{C-H})_3]^\text{-}\), fragmented by decarboxylation and elimination of CH₂=O, ultimately to produce the oxo-hydride species \([\text{U}^{\text{VI}}\text{O}_2(\text{O})]^\text{-}\). Cationic species ultimately dissociated to make \([\text{UO}_2(\text{OH})]^\text{+}\). Our experiments also allowed for the revision of the intrinsic dissociation pathways [48] for the anionic uranyl-acetate complex, \([\text{UO}_2(\text{O}_2\text{C-CH}_3)_3]^\text{-}\). The dominant fragmentation pathway, at the MS/MS stage, for \([\text{UO}_2(\text{O}_2\text{C-CH}_3)_3]^\text{-}\) was elimination of acetyloxyl radical, \(\text{CH}_3\text{CO}_2^\text{•}\), with reduction of \(\text{U}^{\text{VI}}\text{O}_2^{2+}\) to \(\text{U}^{\text{V}}\text{O}_2^+\). Subsequent CID of \([\text{U}^{\text{V}}\text{O}_2(\text{O}_2\text{C-CH}_3)_2]^\text{-}\) caused decarboxylation to generate \([\text{U}^{\text{V}}\text{O}_2(\text{OH})(\text{O}_2\text{C-CH}_3)]^\text{-}\), which reacted spontaneously with H₂O to create \([\text{U}^{\text{V}}\text{O}_2(\text{OH})(\text{O}_2\text{C-CH}_3)]^\text{-}\) and neutral CH₄. CID of \([\text{U}^{\text{V}}\text{O}_2(\text{CH}_3)(\text{O}_2\text{C-CH}_3)]^\text{-}\) also caused the loss of CH₄ to create \([\text{U}^{\text{V}}\text{O}_2(\text{O}_2\text{C=CH}_2)]^\text{-}\), which subsequently fragmented to generate \([\text{U}^{\text{V}}\text{O}_2(\text{O})]^\text{-}\).

In the study reported here, our experiments with uranyl carboxylate anions was expanded to include the intrinsic reactions of ions derived from the anionic uranyl-propionate complex \([\text{U}^{\text{VI}}\text{O}_2(\text{O}_2\text{CCH}_2\text{CH}_3)_3]^\text{-}\) and acrylate complex \([\text{U}^{\text{VI}}\text{O}_2(\text{O}_2\text{CCHCH}_2)_3]^\text{-}\). Our hypothesis was that use of the more complex propionate/acrylate ligands might provide access to new reaction pathways (for example, \(\beta\)-hydride transfer and/or dehydrogenation) as compared to our previous experiments.
with formate and acetate. Initial CID and IMR experiments were conducted in a linear ion trap (LIT).

The negative ion mass spectrum generated from uranyl propionate in H$_2$O/CH$_3$CH$_2$OH is shown in Figure 19a. The multiple-stage CID spectra, created initially isolating [U$V^I$O$_2$(O$_2$CCH$_2$CH$_3$)$_3$]$^-$ for dissociation, are shown in Figures 19b-d.

The dominant ion produced by ESI of the uranyl propionate solution is [U$V^I$O$_2$(O$_2$CCH$_2$CH$_3$)$_3$]$^-$ at m/z 489. The dominant product ion generated by CID of [U$V^I$O$_2$(O$_2$CCH$_2$CH$_3$)$_3$]$^-$ (MS$^2$ stage, Figure 19b) was [U$V^V$O$_2$(O$_2$CCH$_2$CH$_3$)$_2$]$^-$ at m/z 416, created by elimination of the propionyloxyl radical, •O$_2$CCH$_2$CH$_3$ and reduction of U$V^I$O$_2^{2+}$ to U$V^V$O$_2^+$ (reaction 15).

\[
[U^{VI}O_2(O_2CCH_2CH_3)_3]^- \rightarrow [U^{V}O_2(O_2CCH_2CH_3)_2]^- + \cdot O_2CCH_2CH_3 \quad (15)
\]

Similar behavior was observed for dissociation of the analogous uranyl-acetate complex in our previous study [48]. Other minor peaks (less than 10% relative intensity) were observed following CID of [U$V^I$O$_2$(O$_2$CCH$_2$CH$_3$)$_3$]$^-$ appeared at m/z 433 and 360. The peak at m/z 433 is attributed to formation of [U$V^I$O$_2$(OH)(O$_2$CCH$_2$CH$_3$)$_2$] through an energetic reaction with H$_2$O as

Figure 19: Multiple-stage collision-induced dissociation (CID) spectra derived from uranyl propionate in 50:50 H$_2$O/CH$_3$CH$_2$OH: (a) Full negative ion mass spectrum, (b) CID (MS/MS) of [U$V^I$O$_2$(O$_2$CCH$_2$CH$_3$)$_3$]$^-$ at m/z 489, (c) CID (MS$^3$) of [U$V^I$O$_2$(O$_2$CCH$_2$CH$_3$)$_3$]$^-$, and (d) CID (MS$^4$) of [U$V^I$O$_2$(O$_2$CCH$_2$CH$_3$)(H)]$^-$. 
shown in reaction 16. In similar fashion, the peak at \( m/z \) 360 can be attributed to an energetic reaction of \([\text{U}^{\text{VI}}\text{O}_2(\text{O}_2\text{CCH}_2\text{CH}_3)_2]\)− with \( \text{H}_2\text{O} \), as depicted in reaction 17.

\[
[\text{U}^{\text{VI}}\text{O}_2(\text{O}_2\text{CCH}_2\text{CH}_3)_3]^- + \text{H}_2\text{O} \rightarrow [\text{U}^{\text{V}}\text{O}_2(\text{OH})(\text{O}_2\text{CCH}_2\text{CH}_3)_2]^- + \text{HO}_2\text{CCH}_2\text{CH}_3 \quad (16)
\]

\[
[\text{U}^{\text{VI}}\text{O}_2(\text{O}_2\text{CCH}_2\text{CH}_3)_2]^- + \text{H}_2\text{O} \rightarrow [\text{U}^{\text{V}}\text{O}_2(\text{OH})(\text{O}_2\text{CCH}_2\text{CH}_3)]^- + \text{HO}_2\text{CCH}_2\text{CH}_3 \quad (17)
\]

The \([\text{U}^{\text{VI}}\text{O}_2(\text{O}_2\text{CCH}_2\text{CH}_3)_2]\)− product at \( m/z \) 416 was isolated and stored in the LIT, without imposed collisional activation, for periods ranging from 1 ms to 10 s to probe for ion molecule reactions (IMR) with \( \text{H}_2\text{O} \) and \( \text{O}_2 \) (data not shown). It is important to note that in these experiments, all species except for the one initially isolated for storage in the LIT for the specified are resonantly ejected. Other peaks that appear after the imposed isolation time therefore are the result of IMR with background neutral species such as \( \text{H}_2\text{O} \) and \( \text{O}_2 \) present in the LIT. No reaction was observed at isolation times of 1 and 10 ms. However, at 1 s and 10 s isolation times, at peak \( m/z \) 448 appeared (32 mass units higher than the \( m/z \) ratio of the precursor \([\text{U}^{\text{V}}\text{O}_2(\text{O}_2\text{CCH}_2\text{CH}_3)_2(\text{O}_2)]\)− via reaction 18. An \( \text{H}_2\text{O} \) adduct, which would appear at \( m/z \) 434, by (reaction 19) was not observed at any isolation time.

\[
[\text{UO}_2(\text{O}_2\text{CCH}_2\text{CH}_3)_2]^- + \text{O}_2 \rightarrow [\text{UO}_2(\text{O}_2\text{CCH}_2\text{CH}_3)_2(\text{O}_2)]^- \quad (18)
\]

\[
[\text{UO}_2(\text{O}_2\text{CCH}_2\text{CH}_3)_2]^- + \text{H}_2\text{O} \rightarrow [\text{UO}_2(\text{O}_2\text{CCH}_2\text{CH}_3)_2(\text{H}_2\text{O})]^- \quad (19)
\]

Earlier studies have shown that cationic \( \text{U}^{\text{V}}\text{O}_2^+ \) complexes will reversibly bind molecular \( \text{O}_2 \), but \( \text{U}^{\text{VI}}\text{O}_2^{2+} \) will not reversibly add \( \text{O}_2 \) [13]. The tendency to add \( \text{O}_2 \) in an IMR can therefore be used to reveal those species that formally contain a \( \text{U}^{\text{V}}\text{O}_2^+ \) core. The addition of \( \text{O}_2 \) to \([\text{U}^{\text{V}}\text{O}_2(\text{O}_2\text{CCH}_2\text{CH}_3)_2]\)− is consistent with the suggestion that the product ion contains a \( \text{U}^{\text{V}}\text{O}_2^+ \) core.
Two prominent product ions were observed following CID of \([\text{U}^\text{V} \text{O}_2(\text{O}_2\text{CCH}_2\text{CH}_3)_2]^+\) at \(m/z\) 416 (MS\(^3\) stage, Figure 19c). One appeared at \(m/z\) 344, and the peak is assigned as \([\text{U}^\text{V} \text{O}_2(\text{O}_2\text{CCH}_2\text{CH}_3)(\text{H})]^+\) formed by supposed \(\beta\)-hydride transfer and elimination of [O\(_2\)C\(_3\)H\(_4\)]. The second product was the product ion \(m/z\) 360, assigned above as \([\text{U}^\text{V} \text{O}_2(\text{O}_2\text{CCH}_2\text{CH}_3)_2]^+\) generated by an energetic reaction of \([\text{U}^\text{V} \text{O}_2(\text{O}_2\text{CCH}_2\text{CH}_3)_2]^+\) with H\(_2\)O.

Isolation of the peak at \(m/z\) 344, without imposed collisional activation, for periods ranging from 1 ms to 1 s (data not shown) demonstrated that the peak at \(m/z\) 360 is also formed by spontaneous reaction of \([\text{U}^\text{V} \text{O}_2(\text{O}_2\text{CCH}_2\text{CH}_3)(\text{H})]^+\) with H\(_2\)O. The mass difference of 16 units is consistent with reaction of the hydride species with H\(_2\)O, retention of hydroxide and elimination of H\(_2\) as shown in reaction 20. At 10 s reaction time, an O\(_2\) adduct, \([\text{U}^\text{V} \text{O}_2(\text{OH})(\text{O}_2\text{CCH}_2\text{CH}_3)(\text{O}_2)]^-\), at \(m/z\) 392 was also observed.

\[
\text{[UO}_2(\text{O}_2\text{CCH}_2\text{CH}_3)(\text{H})]^+ + \text{H}_2\text{O} \rightarrow \text{[UO}_2(\text{OH})(\text{O}_2\text{CCH}_2\text{CH}_3)]^- + \text{H}_2
\]  

(20)

CID of \([\text{U}^\text{V} \text{O}_2(\text{O}_2\text{CCH}_2\text{CH}_3)(\text{H})]^+\) at \(m/z\) 344 (Figure 19d) produced several product ions. The dominant dissociation product was a peak at \(m/z\) 342, assigned as \([\text{U}^\text{V} \text{O}_2(\text{O}_2\text{CC}_2\text{H}_4)]^-\) generated by loss of H\(_2\). Also observed was an ion at \(m/z\) 340, consistent with a second elimination of H\(_2\), is assigned as \([\text{U}^\text{V} \text{O}_2(\text{O}_2\text{CC}_2\text{H}_2)]^-\).
Additional minor peaks apparent in Figure 19d appear at \( m/z \) 326, 314, 304, and 286. The peak at \( m/z \) 326 may represent the elimination of \( \text{H}_2\text{O} \) to create \([\text{U}^\text{V}\text{O}_2(\text{O}_2\text{CCH}_2\text{CH}_2)]^+\). The product ion at \( m/z \) 314 represents the elimination of 30 mass units (\( \text{C}_2\text{H}_6 \)) to generate \([\text{U}^\text{V}\text{O}_2(\text{CO}_2)]^+\) by reaction 21.

\[
[\text{U}^\text{V}\text{O}_2(\text{O}_2\text{CCH}_2\text{CH}_3)(\text{H})]^+ \rightarrow [\text{U}^\text{V}\text{O}_2(\text{O}_2\text{C})]^+ \\
+ \text{C}_2\text{H}_6 \quad (21)
\]

Isolation of the product ion at \( m/z \) 314, without imposed collisional activation, for periods ranging from 1 ms to 1 s (Figure 20a-d), generated the product ion at \( m/z \) 304. The spontaneous reaction involves a via net loss of 10 mass units, and the \( m/z \) 304 product has been identified in our previous study of anionic uranyl-acetate complexes as \([\text{U}^\text{V}\text{O}_2(\text{O})(\text{H}_2\text{O})]^+\) or \([\text{U}^\text{V}\text{O}_2(\text{OH})_2]^+\). The pathway to the \( m/z \) 304 may therefore proceed as shown in reaction 22a or 22b.

\[
[\text{U}^\text{V}\text{O}_2(\text{O}_2\text{C})]^+ + \text{H}_2\text{O} \rightarrow [\text{U}^\text{V}\text{O}_2(\text{O})(\text{H}_2\text{O})]^+ \\
+ \text{CO} \quad (22a)
\]

Figure 20: Product ion spectra generated by isolation and storage of \([\text{UO}_2(\text{CO}_2)]^+ (m/z \text{ 314})\) for reaction with background \( \text{H}_2\text{O} \): (a) 1 ms, (b) 10 ms, (c) 100 ms, and (d) 1 s.
Serial elimination of H$_2$ was observed for CID of [UO$_2$O$_2$(OCC$_2$H$_4$)]$^-$ at m/z 342 (MS$^5$ stage, Figure 21b), producing [UO$_2$O$_2$(CC$_2$H$_2$)]$^-$ at m/z 340 and [UO$_2$O$_2$(CC$_2$)]$^-$ at m/z 338. Also, observed at the MS$^5$ stage were the m/z 314 and 286 product ions, attributed above to formation of [UO$_2$O$_2$(OC)$_2$]$^-$ and [UO$_2$(O)]$^-$ at m/z 286. Subsequent CID of the ion at m/z 338 (Figure 21d) caused elimination of 44 mass units (loss of CO$_2$) to yield a product ion at m/z 294. This species is assigned a composition of [UO$_2$(C)$_2$]$,^-$, or UO$_2^+$ coordinated to a C$_2$ dianion. When isolated to react with H$_2$O for periods ranging from 1 ms to 1 s (data not shown), [UO$_2$(C)$_2$]$^-$ produces [UO$_2$(O)]$^-$ at m/z 286 by reaction 23.

$$[\text{UO}_2\text{O}_2(\text{C}_2)]^- + \text{H}_2\text{O} \rightarrow [\text{UO}_2\text{O}(\text{O})]^- + \text{C}_2\text{H}_2 \quad (23)$$

Deuterated propionic acid (HO$_2$CCD$_2$CH$_3$) was purchased to identify which hydrogen was retained in the supposed β-hydride transfer mentioned above. The ESI mass spectrum generated of deuterated uranyl propionate in H$_2$O/CH$_3$CH$_2$OH. The dominant species generated is [UO$_2$O$_2$(CCD$_2$CH$_3$)$_3$]$^-$ at m/z 495 (data not shown). CID of [UO$_2$O$_2$(CCD$_2$CH$_3$)$_3$]$^-$ yielded [UO$_2$O$_2$(CCD$_2$CH$_3$)$_2$]$^-$ at m/z
420 via elimination of the propionyloxyl radical, \( \bullet \text{O}_2 \text{CCD}_2 \text{CH}_3 \), and reduction of \( \text{U}^{\text{VI}} \text{O}_2^{2+} \) to \( \text{U}^{\text{V}} \text{O}_2^+ \). Subsequent CID of \( [\text{U}^{\text{VI}} \text{O}_2(\text{O}_2 \text{CCD}_2 \text{CH}_3)_2]^+ \) generated two product ions \( [\text{U}^{\text{VI}} \text{O}_2(\text{O}_2 \text{CCD}_2 \text{CH}_3)(\text{H})]^+ \) at \( m/z \) 346, and \( [\text{U}^{\text{VI}} \text{O}_2(\text{O}_2 \text{CCD}_2 \text{CH}_3)(\text{OH})]^+ \) at \( m/z \) 362. The loss of 74 mass units demonstrated the retention of a methyl hydrogen.

The positive ion mass spectrum was generated from uranyl-propionate in \( \text{H}_2\text{O}/\text{CH}_3\text{CH}_2\text{OH} \). The most abundant positively charged species produced from ESI appeared at \( m/z \) 435 and was initially assigned the formula \( [\text{U}^{\text{VI}} \text{O}_2(\text{O}_2 \text{CCH}_2 \text{CH}_3)(\text{CH}_3\text{CH}_2\text{OH})_2]^+ \). The dominant pathways for the multiple-stage CID of the \( m/z \) 435 precursor (data not shown) caused the elimination of single ethanol ligands to ultimately generate \( [\text{U}^{\text{VI}} \text{O}_2(\text{O}_2 \text{CCH}_2 \text{CH}_3)]^+ \) at \( m/z \) 343. A water adduct was also formed at \( m/z \) 361 with formula \( [\text{U}^{\text{VI}} \text{O}_2(\text{O}_2 \text{CCH}_2 \text{CH}_3)(\text{H}_2\text{O})]^+ \). Subsequent CID of \( [\text{U}^{\text{VI}} \text{O}_2(\text{O}_2 \text{CCH}_2 \text{CH}_3)]^+ \) at \( m/z \) 343 generated \( [\text{U}^{\text{VI}} \text{O}_2(\text{OH})]^+ \) at \( m/z \) 287 and \( [\text{U}^{\text{VI}} \text{O}_2]^+ \) at \( m/z \) 270 (data not shown). The dissociation reaction chemistry of the positively charged propionate-containing complex was therefore identical to that of the analogous acetate precursor used in the previous study [48].

**Energetics for \( \text{H}_2\text{O} \) and \( \text{O}_2 \) Adduct Formation**

One interesting observation in the MS\(^n\) experiments, was the lack of an \( \text{H}_2\text{O} \) adduct to \( [\text{U}^{\text{VI}} \text{O}_2(\text{O}_2 \text{CCH}_2 \text{CH}_3)_2]^+ \), given the high abundance of the \( \text{O}_2 \) adduct (\( m/z \) 448 product ion, data not shown). The energy minimized structures for \( [\text{U}^{\text{VI}} \text{O}_2(\text{O}_2 \text{CCH}_2 \text{CH}_3)_2]^+; [\text{U}^{\text{VI}} \text{O}_2(\text{O}_2 \text{CCH}_2 \text{CH}_3)_2(\text{H}_2\text{O})]^+; \) and \( [\text{U}^{\text{VI}} \text{O}_2(\text{O}_2 \text{CCH}_2 \text{CH}_3)_2(\text{O}_2)]^- \) and the electronic energy data is available upon request.

For \( [\text{U}^{\text{VI}} \text{O}_2(\text{O}_2 \text{CCH}_2 \text{CH}_3)_2(\text{H}_2\text{O})]^+ \), \( \text{H}_2\text{O} \) is bound to the complex by H-bonding interactions with one “yl” oxo ligand and an O atom of a propionate ligand, with some
apparent interaction of the O atom of H$_2$O and the U metal center. Consistent with prior calculations for other positively and negatively charged complexes that contain UO$_2^+$ and molecular O$_2$, the calculated structure for [U$^{\text{V}}$O$_2$(O$_2$CCH$_2$CH$_3$)$_2$(O$_2$)]$^-$ involves O$_2$ bound side on (η$^2$-O$_2$). No stable structure was found in which the O$_2$ ligand was bound end-on.

Representations of the highest occupied molecular orbital (HOMO) for both adduct species can be provided upon request. The HOMO for the H$_2$O adduct is primarily on the UO$_2^+$ core. The HOMO for [U$^{\text{V}}$O$_2$(O$_2$CCH$_2$CH$_3$)$_2$(O$_2$)]$^-$ instead involves strong overlap between the U$^{\text{V}}$O$_2^+$ 5f$_\psi$ and O$_2$ π*$_{xy}$ orbitals, as suggested in our earlier investigation of the bonding interactions within complexes UO$_2^+$ coordinated by a single acetone or dimethylsulfoxide ligand. Calculations of overall reaction energies suggest that addition of O$_2$ or H$_2$O is exothermic. However, addition of O$_2$ favored over H$_2$O by ca. 60 kcal/mol. The modest exothermicity of H$_2$O explains the observation that [U$^{\text{V}}$O$_2$(O$_2$CCH$_2$CH$_3$)$_2$(H$_2$O)]$^-$ is not generated following isolation of [U$^{\text{V}}$O$_2$(O$_2$CCH$_2$CH$_3$)$_2$]$^-$ for IMR.

The negative ion mass spectrum generated from uranyl acrylate in H$_2$O/CH$_3$CH$_2$OH is shown in Figure 22. The multiple-stage CID spectra, created initially isolating [U$^{\text{VI}}$O$_2$(O$_2$CCH=CH$_2$)$_3$]$^-$ for dissociation, are shown in Figures 22b-e.

The dominant ion produced by ESI of the uranyl acrylate solution is [U$^{\text{VI}}$O$_2$(O$_2$CCH=CH$_2$)$_3$]$^-$ at m/z 483. The dominant product ion generated by CID of
[UVIIO2(O2CCH=CH2)2]+ (MS² stage, Figure 22b) was
[UVO2(O2CCH=CH2)2]+ at m/z 412, created by
elimination of the acryloxyl radical, •O2CCH=CH2
and reduction of UVIIO2²⁺ to UVO2⁺ (reaction 24).

\[ [UVIIO2(O2CCH=CH2)2]+ \rightarrow [UVO2(O2CCH=CH2)2]+ + •O2CCH=CH2 \]  \hspace{1cm} (24)

The [UVO2(O2CCH=CH2)2]+ product at m/z 412 was isolated and stored in the LIT, without
imposed collisional activation, for periods ranging
from 1 ms to 10 s to probe for ion molecule reactions
(IMR) with H₂O and O₂. No reaction was observed at
isolations times of 1 ms, 10 ms, and 100 ms (data not
shown). However, at 1 s and 10 s isolation times, at
peak m/z 444 appeared (32 mass units higher than the
m/z ratio of the precursor [UVO2(O2CH2CH3)2(O2)]⁻
via reaction 25. An H₂O adduct, which would appear
at m/z 430, by (reaction 26) was not observed at any
isolation time.

\[ [UO2(O2CCH=CH2)2]+ + O₂ \rightarrow [UO2(O2CCH=CH2)(O2)]⁻ \]  \hspace{1cm} (25)

\[ [UO2(O2CCH=CH2)2]+ + H₂O \rightarrow [UO2(O2CCH=CH2)2(H₂O)]⁻ \]  \hspace{1cm} (26)
As previously stated, the addition of O\textsubscript{2} to [U\textsuperscript{V}O\textsubscript{2}(O\textsubscript{2}CCH=CH\textsubscript{2})\textsubscript{2}]\textsuperscript{-} is consistent with the suggestion that the product ion contains a U\textsuperscript{V}O\textsubscript{2}\textsuperscript{+} core.

The prominent product ion observed following CID of [U\textsuperscript{V}O\textsubscript{2}(O\textsubscript{2}CCH=CH\textsubscript{2})\textsubscript{2}]\textsuperscript{-} at m/z 412 (MS\textsuperscript{3} stage, Figure 22c) appeared at m/z 368 and assigned as [U\textsuperscript{V}O\textsubscript{2}(O\textsubscript{2}CCH=CH\textsubscript{2})(CH=CH\textsubscript{2})]\textsuperscript{-} via decarboxylation. A smaller peak was also observed at m/z 324 which was assigned as [U\textsuperscript{V}O\textsubscript{2}(CH=CH\textsubscript{2})\textsubscript{2}]\textsuperscript{-}. The elimination of •O\textsubscript{2}CCH=CH\textsubscript{2} and CO\textsubscript{2} to generate these product ions is consistent with earlier CID using acetate [14].

Isolation of the product ion at m/z 368, for periods as long as 1 s generated an ion at m/z 358 with formula [U\textsuperscript{V}O\textsubscript{2}(O\textsubscript{2}CCH=CH\textsubscript{2})(OH)]\textsuperscript{-}, the formation of which likely involves a reaction with background H\textsubscript{2}O and elimination of ethylene (CH\textsubscript{2}=CH\textsubscript{2}). Subsequent CID of the product ion at m/z 368 (MS\textsuperscript{4} stage, Figure 22d) caused the loss of CO to create [U\textsuperscript{V}O\textsubscript{2}(OCH=CH)(CH\textsubscript{2}=CH\textsubscript{2})]\textsuperscript{-} at m/z 340. A minor peak was also generated at m/z 288, attributed to the addition of water to [U\textsuperscript{V}O\textsubscript{2}]\textsuperscript{-}.

CID of the ion at m/z 340 (MS\textsuperscript{5} stage, Figure 22e) generates [U\textsuperscript{V}O\textsubscript{2}(O)]\textsuperscript{-} at m/z 286, as well as a product at m/z 294 ([U\textsuperscript{V}O\textsubscript{2}(C\textsubscript{2})]\textsuperscript{-}, a product also observed during the CID of the uranyl propionate precursor. In addition, CID at the MS\textsuperscript{5} stage generated a peak at m/z 314, where the structure is discussed below.

Isolation of the ion at m/z 294 for periods up to 1 s generated [U\textsuperscript{V}O\textsubscript{3}]\textsuperscript{-} at m/z 286, in a similar fashion to the uranyl propionate complexes. Isolation of the ion at m/z 314 for the same time period instead generated [U\textsuperscript{V}O\textsubscript{2}(OH)\textsubscript{2}]\textsuperscript{-} at m/z 304.

Interestingly, CID of the m/z 324 (MS\textsuperscript{5} stage, Figure 23e) created from the [U\textsuperscript{V}O\textsubscript{2}(O\textsubscript{2}CCH=CH\textsubscript{2})(CH\textsubscript{2}=CH)]\textsuperscript{-} precursor lead to the ultimate formation of [U\textsuperscript{V}O\textsubscript{2}]\textsuperscript{-}.

Isolation of the [U\textsuperscript{V}O\textsubscript{2}(CH\textsubscript{2}=CH\textsubscript{2})\textsubscript{2}]\textsuperscript{-} at m/z 324 (Figure 24) for IMR generates
[U\textsuperscript{6+}O\textsubscript{2}(OH)\textsubscript{2}\textsuperscript{-}] at m/z 304. Because the step-wise elimination of CH\textsubscript{2}=CH\textsubscript{2} neutrals following IMR with H\textsubscript{2}O is *not* observed (i.e., as in reaction 27), the formation of [U\textsuperscript{6+}O\textsubscript{2}(OH)\textsubscript{2}\textsuperscript{-}] suggests the two vinyl anions may actually be coupled while bound to the U\textsuperscript{6+}O\textsubscript{2} core to create butadiene. Isolation of m/z 324 at 10 s generates an ion consistent with an O\textsubscript{2} adduct, [U\textsuperscript{6+}O\textsubscript{2}(OH)\textsubscript{2}(O\textsubscript{2})\textsuperscript{-}].

[U\textsuperscript{6+}O\textsubscript{2}(CH\textsubscript{2}=CH)\textsubscript{2}\textsuperscript{-}] \rightarrow [U\textsuperscript{6+}O\textsubscript{2}(OH)\textsubscript{2}\textsuperscript{-}] + 2CH\textsubscript{2}=CH\textsubscript{2} \hspace{1cm} (27)

Through use of the FT-ICR, accurate masses were used to confirm assignment of precursor and product ions.

The positive ion mass spectrum was generated from uranyl-acrylate in H\textsubscript{2}O/CH\textsubscript{3}CH\textsubscript{2}OH. The most abundant positively charge species produced from ESI appeared at m/z 433 and was assigned as [U\textsuperscript{VI}O\textsubscript{2}(O\textsubscript{2}CCH=CH\textsubscript{2})(CH\textsubscript{3}CH\textsubscript{2}OH)\textsubscript{2}]\textsuperscript{+}. CID of

Figure 23: Multiple-stage collision-induced dissociation (CID) spectra derived from uranyl propionate in 50:50 H\textsubscript{2}O/CH\textsubscript{3}CH\textsubscript{2}OH: (a) Full negative ion mass spectrum, (b) CID (MS\textsubscript{2}) of [U\textsuperscript{6+}O\textsubscript{2}(O\textsubscript{2}CCH=CH\textsubscript{2})\textsuperscript{2}], (e) CID (MS\textsubscript{3}) of [U\textsuperscript{6+}O\textsubscript{2}(O\textsubscript{2}CCH=CH\textsubscript{2})\textsuperscript{3}], (d) CID (MS\textsubscript{4}) of [U\textsuperscript{6+}O\textsubscript{2}(O\textsubscript{2}CCH=CH\textsubscript{2})(CH\textsubscript{2}=CH)\textsuperscript{2}], (e) [U\textsuperscript{6+}O\textsubscript{2}(C\textsubscript{4}H\textsubscript{6})\textsuperscript{+}]
$[\text{U}^{\text{VI}}\text{O}_2(\text{O}_2\text{CCH}═\text{CH})\text{(CH}_3\text{CH}_2\text{OH})_2]^+$ caused the elimination of a single ethanol ligands to generate $[\text{U}^{\text{V}}\text{O}_2(\text{O}_2\text{CCH}═\text{CH})]^+$. A water adduct was also formed at $m/z$ 359 with formula $[\text{U}^{\text{V}}\text{O}_2(\text{O}_2\text{CCH}═\text{CH})(\text{H}_2\text{O})]^+$. CID of $[\text{U}^{\text{V}}\text{O}_2(\text{O}_2\text{CCH}═\text{CH})]^+$ generates $[\text{U}^{\text{V}}\text{O}_2(\text{CH}_2═\text{CH})]^+$ via decarboxylation. Isolation of $[\text{U}^{\text{V}}\text{O}_2(\text{CH}_2═\text{CH})]^+$ for up to 1 s hydrolyzes to form $[\text{U}^{\text{V}}\text{O}_2(\text{OH})]^+$. The dissociation reaction chemistry of the positively charged acrylate-containing complexes was identical to that of the analogous acetate precursor used in the previous study [48].

To summarize, ESI, CID, and IMRs were used to make and characterize species derived from precursor complexes composed of the uranyl cation ($\text{U}^{\text{VI}}\text{O}_2^{2+}$) coordinated by propionate or acrylate ligands [38]. Anionic complexes containing $\text{U}^{\text{VI}}\text{O}_2^{2+}$ and propionate or acrylate fragment via elimination of the propionyloxyl or acryloxyl radical and reduction of $\text{U}^{\text{VI}}\text{O}_2^{2+}$ to $\text{U}^{\text{V}}\text{O}_2^{+}$. Subsequent CID generated product ions via numerous reactions including reactions with background $\text{H}_2\text{O}$. Cationic uranyl complexes containing propionate and acrylate first fragment via neutral ligand elimination, loss of $\text{CH}_3\text{CH}_2\text{OH}$. Following the loss of $\text{CH}_3\text{CH}_2\text{OH}$ ligands, decarboxylation or hydrolysis occur to ultimately produce $[\text{U}^{\text{V}}\text{O}_2]^+$.
Differences in fragmentation patterns for propionate or acrylate ligands were observed compared to our previous work with formate and acetate ligands. For example, our previous work showed that with the anionic uranyl complex coordinated to the propionate ligand, we fragment to produce $[\text{U}^{\text{V}}\text{O}_2(\text{CO}_2)]^-$ rather than emitting CO$_2$. With anionic acrylate, we see differences which are suspected to be due to the presence of the C=C double bond.

Future studies will focus on uranyl complexes coordinated to other carboxyl ligands. Additionally, our group hopes to confirm the CO$_2$ ligand present at $m/z$ 314 in the propionate ligand with further FT-ICR observations as well as an LTQ Orbitrap.
Chapter 8

Conclusions and Future Directions

The work summarized in this thesis represents an initial exploration of the reactions and structure of a range of gas-phase uranyl species using tandem (linear) ion trap mass spectrometry and ion-molecule reactions paired with DFT calculations and IRMPD spectroscopy. Through CID and IMRs, the work has shown that lower partial pressure of adventitious H$_2$O in the LIT (compared to the 3-D ion trap used in previous experiments) minimizes adduct formation and allows access to lower uranyl coordination numbers than previously possible as well as elucidates reaction pathways previously obscured by high traces of water. In Chapter 3 and Chapter 4, two previous experiments performed using an older, 3-dimensional ion trap were revisited. These experiments involved an investigation of the dissociation pathways of cationic uranyl nitrate and uranyl perchlorate. Using the linear trap, new dissociation pathways were revealed that allowed the intrinsic fragmentation chemistry of both species to be more accurately reported. For the uranyl nitrate species, the initial proposed reaction was a one-step displacement reaction, the uranyl nitrate species undergoes a reaction with water to generate the hydrated uranyl ion via elimination of the nitrate radical. In the study outlined above, the intrinsic reaction for the uranyl nitrate species, [UO$_2$(NO$_3$)]$^+$, was revised to include the initial formation of a [UO$_2$(O$_2$)]$^+$ which can then undergo a rapid exchange for background H$_2$O to leave the hydrated uranyl ion, [UO$_2$(H$_2$O)]$^+$, observed initially in the previous experiment. A similar pattern was also observed when the dissociation pathway of the cationic uranyl perchlorate species, [UO$_2$(ClO$_4$)]$^+$ was revisited. In the initial experiment the dissociation of the uranyl perchlorate species
ultimately generated the uranyl hydroxide species, [UO$_2$(OH)]$^+$, via the elimination of perchloric acid (HClO$_4$). However, upon reexamination, it was discovered that dissociation of the uranyl perchlorate species initially generated [UO$_2$(Cl)]$^+$ via the elimination of 2O$_2$, then undergoes a rapid exchange with background H$_2$O to leave the uranyl hydroxide species observed in the previous experiment. Through both of these experiments, the established that use of a 2-D linear ion trap has the ability to elucidate dissociation steps not initially observed in a standard quadrupole ion trap, and ultimately revise the current intrinsic reactions for the cationic uranyl nitrate and uranyl perchlorate species.

In Chapter 5, both CID and IMR were used to identify the pathways by which the complexes, with general formula [UO$_2$(R)]$^+$, dissociate by collisional activation or otherwise react when exposed to gas-phase H$_2$O. Additionally, DFT calculations were used to further explain why isolation of [UO$_2$(CH$_3$)]$^+$ and [UO$_2$(CH$_2$CH$_3$)]$^+$ generated the hydrated uranyl ion, and isolation of [UO$_2$(CH=CH$_2$)]$^+$ and [UO$_2$(C$_6$H$_5$)]$^+$ generated the uranyl hydroxide species. The DFT calculations provided transition state structures and energies for the proton transfer steps and explains specific experimental observations with respect to the tendency to eliminate either radicals to furnish the hydrated uranyl ion, [UO$_2$(H$_2$O)]$^+$, as with the methide and ethide complexes, while the vinyl and phenyl species instead generated the uranyl hydroxide species, [UO$_2$(OH)]$^+$ through the elimination of ethane and benzene, respectively. For the methide and ethide precursors, the transition state energy for the proton transfer to generate [UO$_2$(OH)]$^+$ and the associated neutral alkanes is higher than the path involving direct elimination of the organic neutral to form [UO$_2$(H$_2$O)]$^+$. The situation is reversed for the acrylate and
benzoate precursors. The transition state for proton transfer is lower than the energy required for creation of \([\text{UO}_2(\text{H}_2\text{O})]^+\) by elimination of vinyl or phenyl radical. From here, we concluded, that the pathways are thermodynamically controlled. We rationalized competitive pathways based on electron affinities (the electron affinity of each neutral can be used to assess the stability of an anion) of certain ligands demonstrating our ability to use these chemical theories to characterize gas-phase reactions.

These experiments have provided valuable data for the validation of theoretical models through DFT calculations. Lastly, combination of information gained from CID/IMR and DFT calculations has allowed for the comparison to experimental data and corresponding characterization of composition and structure. In Chapter 6, wavelength-selective IRMPD spectroscopy was used to determine ion (geometric) structure, and probe the extent to which halide ligand-binding influences the position of the asymmetric uranyl stretch (it is known that the uranium-oxygen bonds in the uranyl dication, \(\text{UO}_2^{2+}\), are weakened by electron donation to the uranyl metal center by coordinating nucleophiles [53-61]), shedding light on the contribution f-electrons have in bonding.

To further explore the intrinsic reactivity of uranyl species, IMRs can be enhanced to include reagents other than the background \(\text{H}_2\text{O}\) and \(\text{O}_2\) presented in the work here. In January 2020, the inlet to the LIT was modified to allow the intentional introduction of volatile reagent species into the ion trap to allow further exploration of ion molecule reactivity. Specifically, hydride uranyl species (such as the hydride species presented in Chapter 7) and oxide uranyl species (as these are \(\text{U}^+\text{O}_2^+\) species and will readily undergo reactions) with reagents due to the unpaired electron of the f-orbital of the uranium metal center. For example, if the hydride species generated in Chapter 7,
[\text{UO}_2(\text{O}_2\text{CCH}_2\text{CH}_3)(\text{H})]^{-},\text{ underwent an IMR reaction with background methanol, one can expect the generation of } [\text{UO}_2(\text{O}_2\text{CCH}_2\text{CH}_3)(\text{OCH}_3)]^{-}\text{ via the elimination of H}_2.\text{ Reactions such as these would allow for the further investigation of } \text{U}^{\text{V}}\text{O}_2^{+}\text{ species, a species that is difficult or nearly impossible to explore in the condensed phase. In addition, the organometallic species examined in Chapter 5 can be exposed to neutrals such as methyl-, ethyl- or allyl-iodide to probe the tendency for mediation of C-C coupling reactions.}

Throughout this work, one particularly important lesson learned that when the levels of background H}_2\text{O in the ion trap is particularly high, one must exercise caution when making statements about intrinsic reactivity. With low levels of background H}_2\text{O, the tendency for generation of adducts and hydroxide species diminishes, and new species may be generated. Formation of these species allows for the study of their intrinsic reactivity that can be used as a test species for future IMRs and potentially other actinide species, with the help of some collaborators.}

Studies of metal ions and metal ion complexes in the-gas phase are important and necessary because investigation of reactivity in the condensed phase, in a species-specific fashion, is complicated by the presence of solvent molecules and counter ions and complex equilibria between metallic species in different forms. Beyond providing fascinating details about intrinsic metal complex chemistry, the results of these experiments have contributed important details about intrinsic ion behavior for a range of gas-phase uranyl ions. Focus on the intrinsic (dissociation and ion-molecule) reactions and structure of gas-phase uranyl species has supplied the actinide community with
benchmark data to develop and validate theoretical models to describe the nature of bonding within f-element compounds.
References


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