INL/CON-24-76413-Revision-1

ASMS 2024 Investigation of Uranyl Perchlorate Anion Complexes in the Gas Phase via Infrared Multiphoton Dissociation and Collision Induced Dissociation

June 2024

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Idaho National Laboratory
Idaho Falls, Idaho 83415

http://www.inl.gov

Prepared for the
U.S. Department of Energy
Under DOE Idaho Operations Office
Contract DE-AC07-05ID14517

Investigation of Uranyl Perchlorate Anion Complexes in the Gas Phase via Infrared Multiphoton Dissociation and Collision Induced Dissociation

Brittany D.M. Hodges[1]

Research Scientist, Idaho National Laboratory

JungSoo Kim[1], Christopher A. Zarzana[1], Jonathan K. Martens[2], Giel WCM Berden[2], Jos Oomens[2]

1 Idaho National Laboratory, Idaho Falls, Idaho, United States

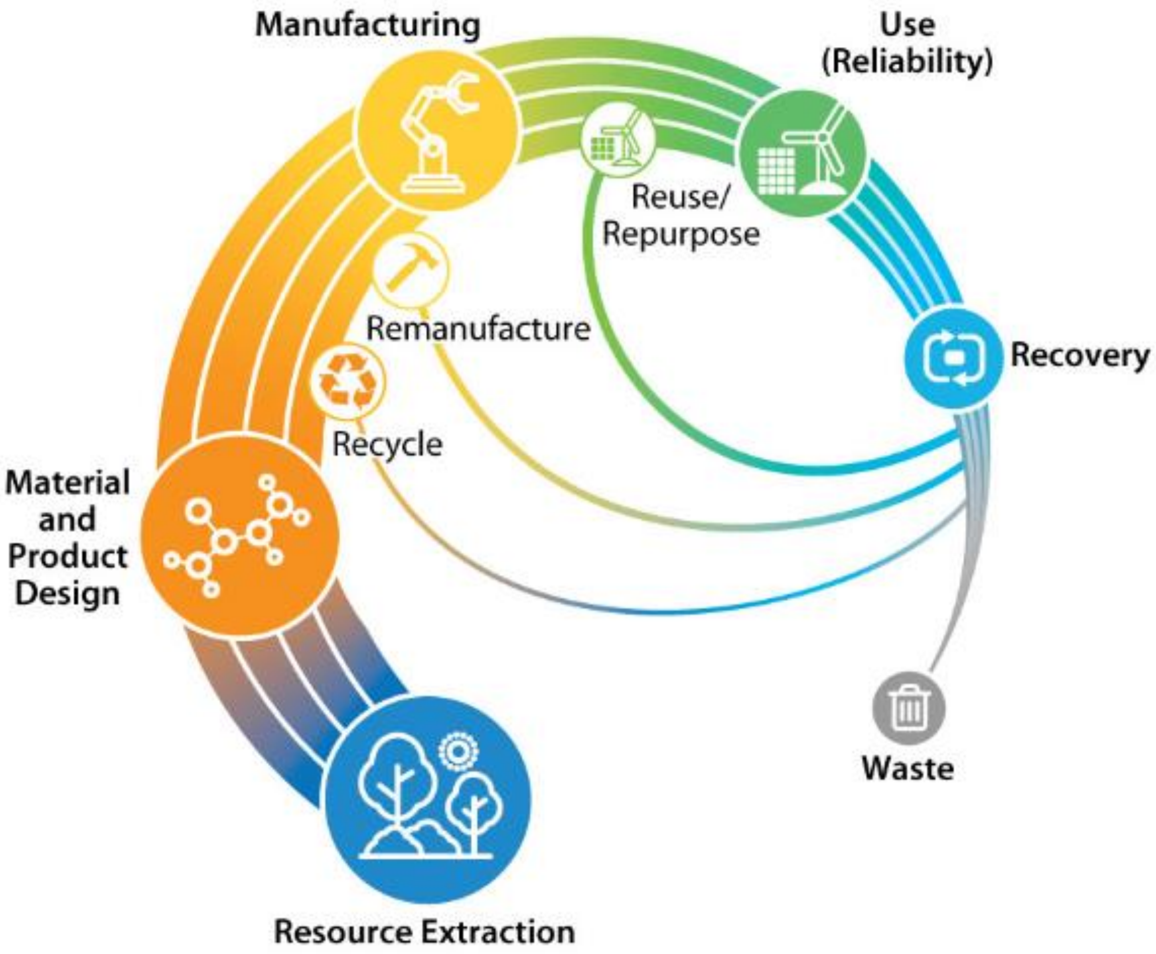
2 Free-Electron Lasers for Infrared eXperiment (FELIX) Facility Radboud University, Nijmegen, Netherlands

June 4, 2024 TOC PM. ***72nd Conference on Mass Spectrometry and Allied Topics American Society For Mass Spectrometry, Anaheim, CA***

The authors declare no competing financial interest.

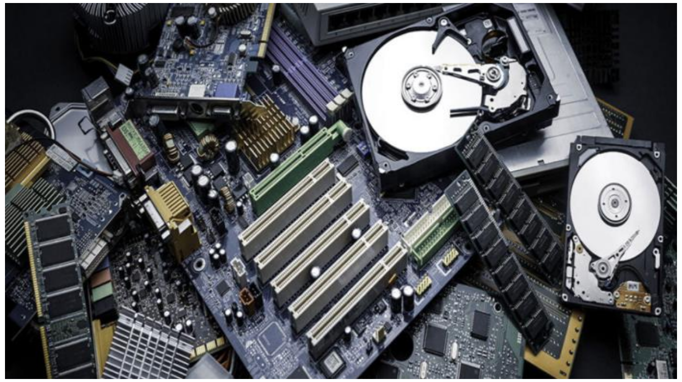
INL/CON-24-76413

Circular Economy for Critical Materials



https://www.nrel.gov/about/circular-economy.html

Understanding Metal-Ligand Interactions: Recycling and Recovery of Critical Materials and Rare Earth Elements



MAGAZINE · RARE EARTH METAL

Recycling Efforts May Undermine China's Rare-Earth Monopoly

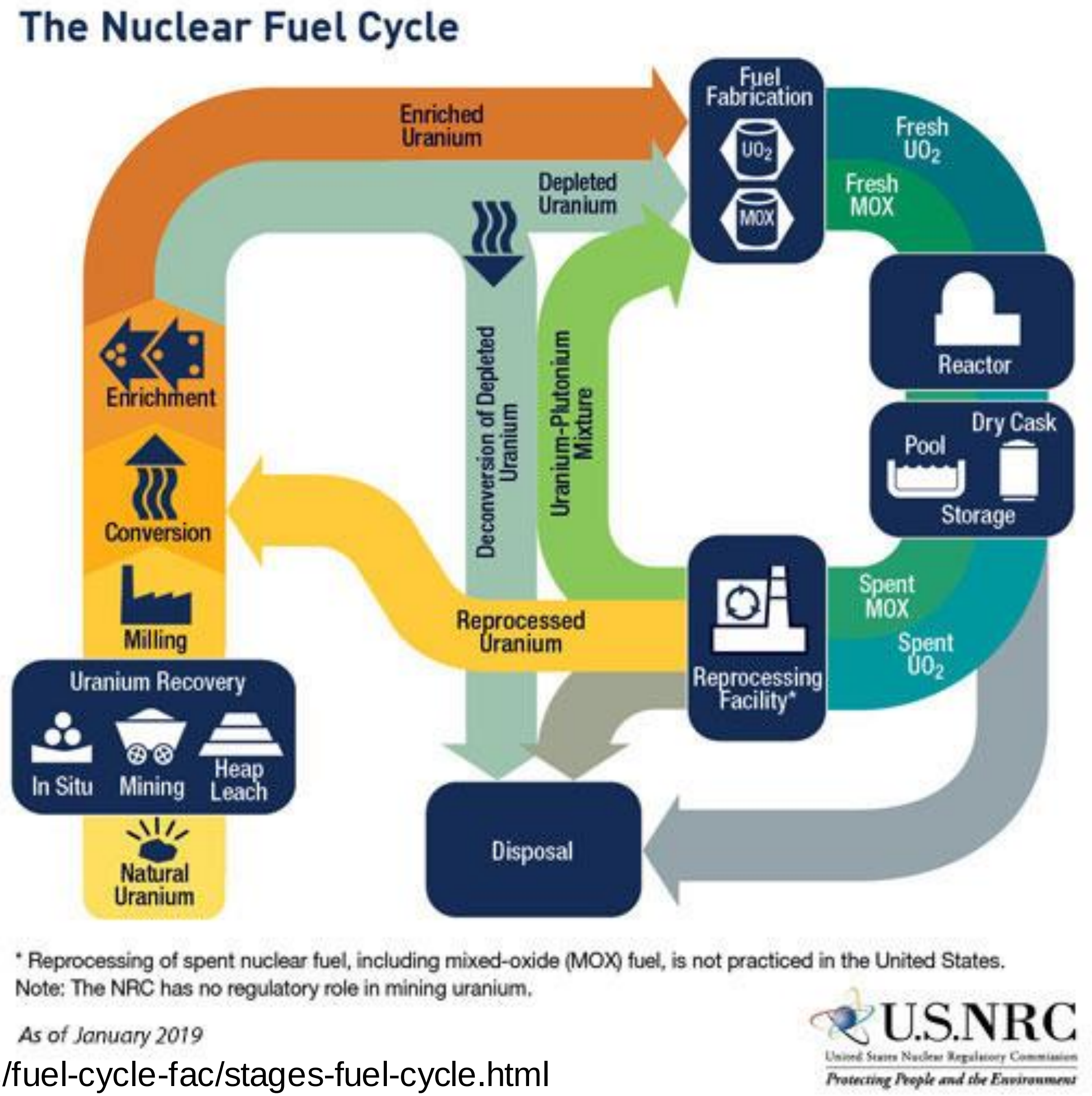
BY EAMON BARRETT

July 27, 2019 at 8:00 AM MDT

https://www.snexplores.org/article/recycling-rare-earth-elements-hard-reuse-greener-technology

https://fortune.com/2019/07/27/rare-earth-metals-recycling-us-china/

Understanding Metal-Ligand Interactions: Nuclear Fuel Cycle


The Nuclear Fuel Cycle

* Reprocessing of spent nuclear fuel, including mixed-oxide (MOX) fuel, is not practiced in the United States.
Note: The NRC has no regulatory role in mining uranium.

As of January 2019

https://www.nrc.gov/materials/fuel-cycle-fac/stages-fuel-cycle.html

Understanding Metal-Ligand Interactions: Environmental Management of Waste

TIME

SPOTLIGHT WHY PENCE LAUNCHED HIS PRESIDENTIAL BID IN IOWA

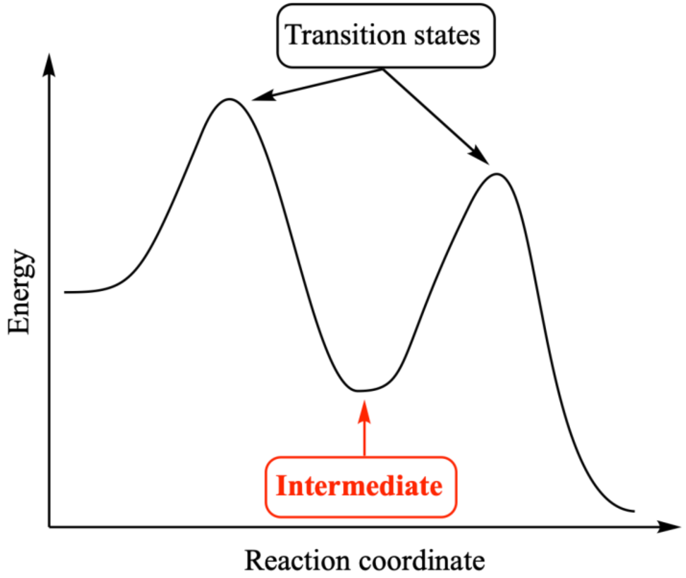
SIGN IN

How the Atomic Age Left Us a Half-Century of Radioactive Waste

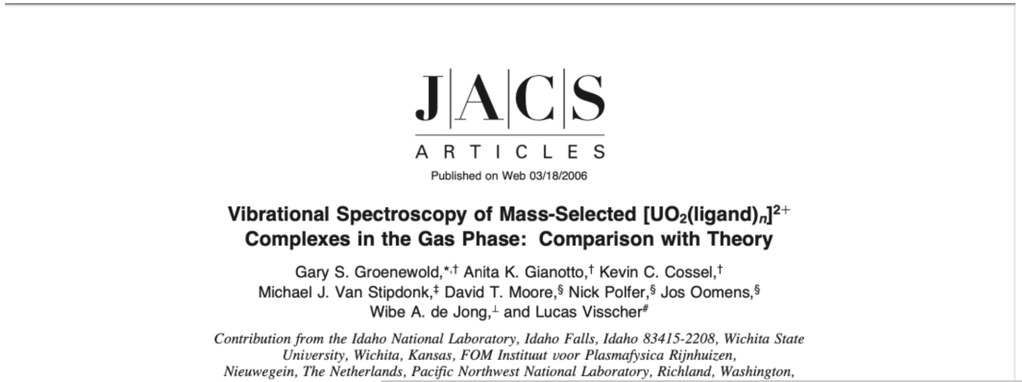
https://www.pbs.org/newshour/science/nuclear-waste-tunnel-collapses-hanford-site-washington-state
https://www.pbs.org/newshour/science/nuclear-waste-tunnel-collapses-hanford-site-washington-state
https://time.com/3672177/hanford-radioactive-waste-history/
https://www.researchgate.net/figure/Aerial-view-of-the-Radioactive-Waste-Management-Complex-The-yellow-area-shows-the_fig2_250129611

Why should we care about any of this?

- Transport of metal ions across boundary of aqueous to organic phases (and vice versa) is a critical step in nuclear fuel reprocessing and critical material recovery
- Initial metal coordination environment may be significantly different from the final one
  - metal transitions through a series of transient species as it passes from one phase to another.
- ***Thus, we need to understand the role of metal ligand interactions and the roles of transition states and intermediates***



Previous Studies


J|A|C|S
ARTICLES

Published on Web 03/18/2006

Vibrational Spectroscopy of Mass-Selected $[UO_2(ligand)_n]^{2+}$ Complexes in the Gas Phase: Comparison with Theory

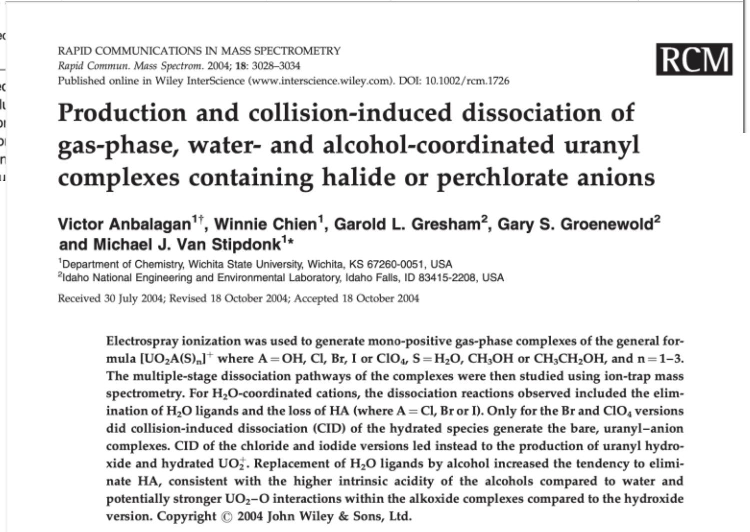
Gary S. Groenewold,[*,†] Anita K. Gianotto,[†] Kevin C. Cossel,[†]
Michael J. Van Stipdonk,[‡] David T. Moore,[§] Nick Polfer,[§] Jos Oomens,[§]
Wibe A. de Jong,[⊥] and Lucas Visscher[#]

Contribution from the Idaho National Laboratory, Idaho Falls, Idaho 83415-2208, Wichita State University, Wichita, Kansas, FOM Instituut voor Plasmafysica Rijnhuizen, Nieuwegein, The Netherlands, Pacific Northwest National Laboratory, Richland, Washington, and

Receivec

Abstract: The gas-phase infrarec
or acetonitrile were used to evalu
and to enable rigorous compariso
in a Fourier transform ion cyclotro
dissociation using a free electron
stretching frequency was measu

6, 2023 at 18:08:26 (UTC).
mately share published articles.


RAPID COMMUNICATIONS IN MASS SPECTROMETRY
Rapid Commun. Mass Spectrom. 2004; **18**: 3028–3034
Published online in Wiley InterScience (www.interscience.wiley.com). DOI: 10.1002/rcm.1726

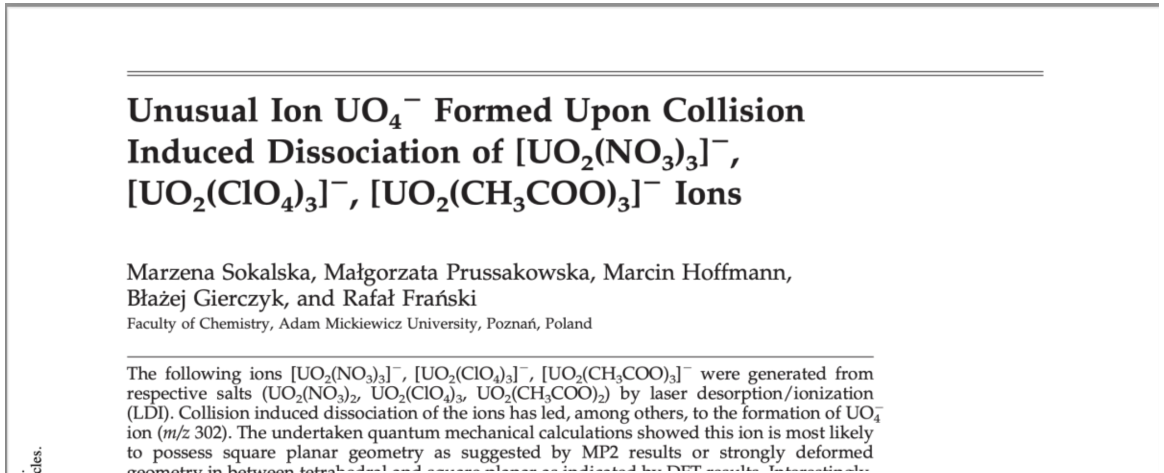
RCM

Production and collision-induced dissociation of gas-phase, water- and alcohol-coordinated uranyl complexes containing halide or perchlorate anions

Victor Anbalagan[1†], Winnie Chien[1], Garold L. Gresham[2], Gary S. Groenewold[2] and Michael J. Van Stipdonk[1*]
[1]Department of Chemistry, Wichita State University, Wichita, KS 67260-0051, USA
[2]Idaho National Engineering and Environmental Laboratory, Idaho Falls, ID 83415-2208, USA

Received 30 July 2004; Revised 18 October 2004; Accepted 18 October 2004

Electrospray ionization was used to generate mono-positive gas-phase complexes of the general formula $[UO_2A(S)_n]^+$ where A = OH, Cl, Br, I or ClO_4, S = H_2O, CH_3OH or CH_3CH_2OH, and n = 1–3. The multiple-stage dissociation pathways of the complexes were then studied using ion-trap mass spectrometry. For H_2O-coordinated cations, the dissociation reactions observed included the elimination of H_2O ligands and the loss of HA (where A = Cl, Br or I). Only for the Br and ClO_4 versions did collision-induced dissociation (CID) of the hydrated species generate the bare, uranyl–anion complexes. CID of the chloride and iodide versions led instead to the production of uranyl hydroxide and hydrated UO_2^+. Replacement of H_2O ligands by alcohol increased the tendency to eliminate HA, consistent with the higher intrinsic acidity of the alcohols compared to water and potentially stronger UO_2–O interactions within the alkoxide complexes compared to the hydroxide version. Copyright © 2004 John Wiley & Sons, Ltd.


Unusual Ion UO_4^- Formed Upon Collision Induced Dissociation of $[UO_2(NO_3)_3]^-$, $[UO_2(ClO_4)_3]^-$, $[UO_2(CH_3COO)_3]^-$ Ions

Marzena Sokalska, Małgorzata Prussakowska, Marcin Hoffmann,
Błażej Gierczyk, and Rafał Frański
Faculty of Chemistry, Adam Mickiewicz University, Poznań, Poland

The following ions $[UO_2(NO_3)_3]^-$, $[UO_2(ClO_4)_3]^-$, $[UO_2(CH_3COO)_3]^-$ were generated from respective salts ($UO_2(NO_3)_2$, $UO_2(ClO_4)_3$, $UO_2(CH_3COO)_2$) by laser desorption/ionization (LDI). Collision induced dissociation of the ions has led, among others, to the formation of UO_4^- ion (*m/z* 302). The undertaken quantum mechanical calculations showed this ion is most likely to possess square planar geometry as suggested by MP2 results or strongly deformed geometry in between tetra
geometrical parameters ar
which oxygen atoms bear
2010, 21, 1789–1794) © 20

Uranium can occur
III, IV, V, and VI [
most common. For
abundant uranium comp
considered as consisting
oxide) and two molecule

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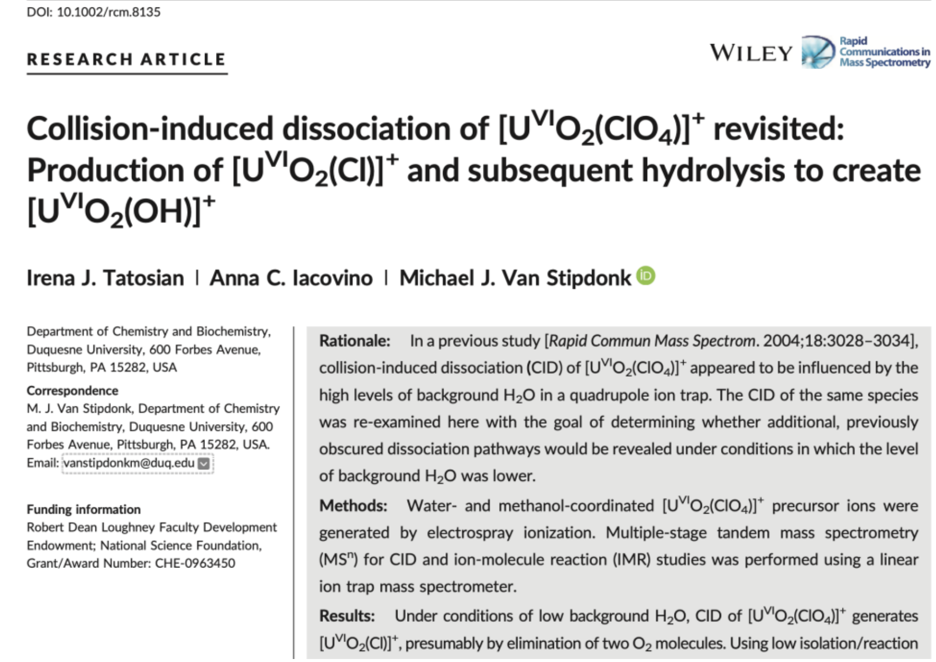

Received: 7 March 2018 | Revised: 23 March 2018 | Accepted: 26 March 2018
DOI: 10.1002/rcm.8135

WILEY Rapid Communications in Mass Spectrometry

RESEARCH ARTICLE

Collision-induced dissociation of $[U^{VI}O_2(ClO_4)]^+$ revisited: Production of $[U^{VI}O_2(Cl)]^+$ and subsequent hydrolysis to create $[U^{VI}O_2(OH)]^+$

Irena J. Tatosian | Anna C. Iacovino | Michael J. Van Stipdonk

Department of Chemistry and Biochemistry, Duquesne University, 600 Forbes Avenue, Pittsburgh, PA 15282, USA

Correspondence
M. J. Van Stipdonk, Department of Chemistry and Biochemistry, Duquesne University, 600 Forbes Avenue, Pittsburgh, PA 15282, USA.
Email: vanstipdonkm@duq.edu

Funding information
Robert Dean Loughney Faculty Development Endowment; National Science Foundation, Grant/Award Number: CHE-0963450

Rationale: In a previous study [*Rapid Commun Mass Spectrom*. 2004;18:3028–3034], collision-induced dissociation (CID) of $[U^{VI}O_2(ClO_4)]^+$ appeared to be influenced by the high levels of background H_2O in a quadrupole ion trap. The CID of the same species was re-examined here with the goal of determining whether additional, previously obscured dissociation pathways would be revealed under conditions in which the level of background H_2O was lower.

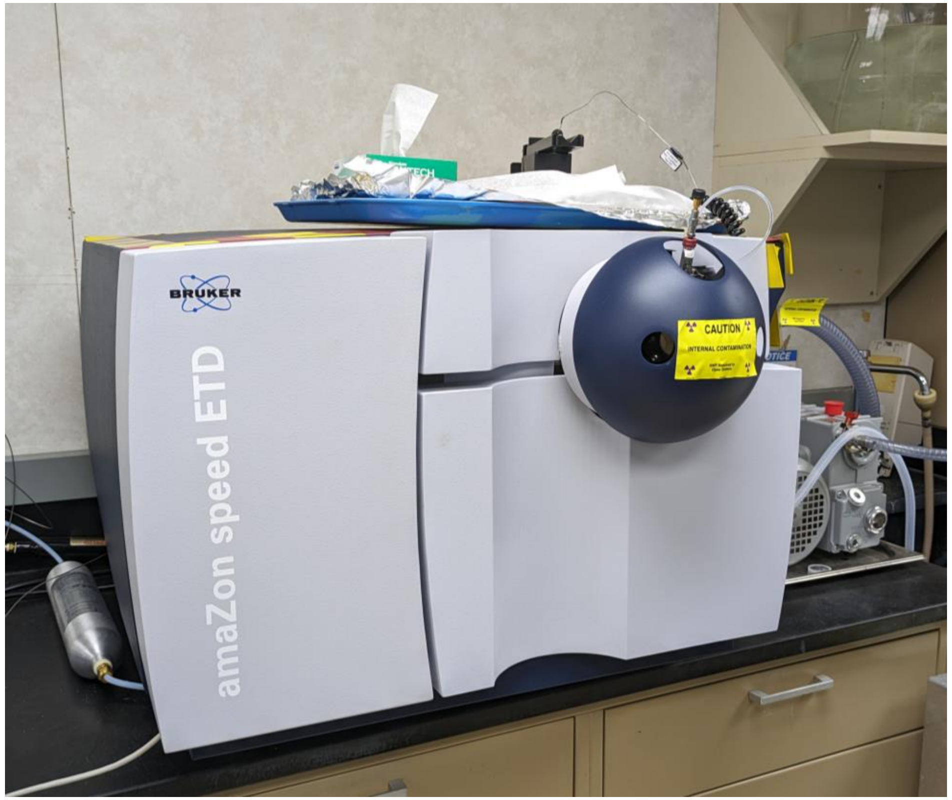
Methods: Water- and methanol-coordinated $[U^{VI}O_2(ClO_4)]^+$ precursor ions were generated by electrospray ionization. Multiple-stage tandem mass spectrometry (MS^n) for CID and ion-molecule reaction (IMR) studies was performed using a linear ion trap mass spectrometer.

Results: Under conditions of low background H_2O, CID of $[U^{VI}O_2(ClO_4)]^+$ generates $[U^{VI}O_2(Cl)]^+$, presumably by elimination of two O_2 molecules. Using low isolation/reaction

Groenewold 2006 Journal of The American Chemical Society
Sokalska 2010 JASMS 21, 1789–1794 https://doi.org/10.1016/j.jasms.2010.06.018
Anbalagan 2004 Rapid Communications in Mass Spectrometry 18 3028-3034
Tatosian 2018 Rapid Communications in Mass Spectrometry, 32, 1085-1091 DOI: 10.1002/rcm8135

Gas-Phase Intrinsic Reactivity and Bonding of Actinide Metal Ligand Complexes

Hood Suitable For Working With Radioactive Materials



Bruker AmaZon Speed ETD Ion Trap Mass Spectrometer With Electrospray Ionization

Trained Personnel

Idaho National Laboratory Center for Radiation Chemistry Research

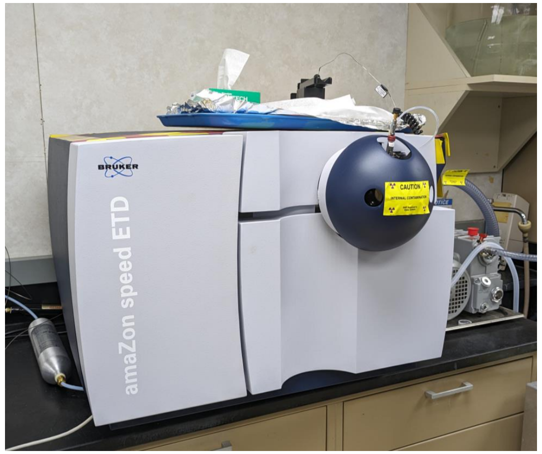
- Actinide Studies of Gas Phase Intrinsic Bonding and Reactivity
- New instrument and laboratory suitable for Actinide Metal Ligand Complex Gas-Phase Studies.
- This laboratory is one of only a few instruments with the capability to perform mass spectrometry gas-phase bonding and reactivity studies of chemistry and interactions with ligands in gas phase experiments
- *https://cr2.inl.gov*

TP 151 Comparison of Gas Phase Fragmentation Behaviors of Nuclear Fuel Cycle Ligands in Lanthanide and Americium Metal Ligand Complexes JungSoo Kim

ThP 308 Gas Phase Coordination of Phosphine-Chalcogenides to Uranyl Cation Christopher Zarzana

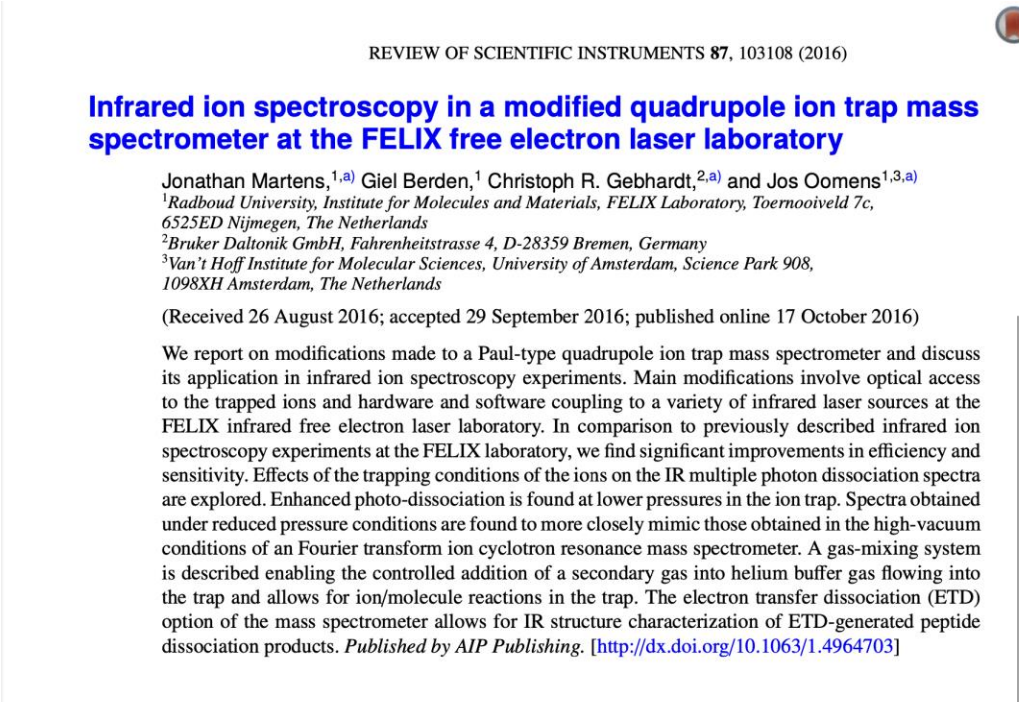
Methods

- Metal cluster ions of uranyl perchlorate ligands were formed via electrospray on the commercial Bruker ESI ion source
- Metal-ligand clusters formed from uranyl perchlorate solutions in acetonitrile
  - Concentrations for optimal cluster formation were experimentally derived, and ranged from 10-100µM
- Uranyl-perchlorate complexes formed via electrospray ionization were isolated and fragmented by collisionally induced dissociation (CID) or Infrared Multiphoton Dissociation (IRMPD).
- All experiments shown here were performed on Bruker AmaZon Ion Traps or MicroTOF-II
  - CID was performed on an unmodified instrument
  - IRMPD was performed at FELIX at Radboud University on a modified instrument (Martens, 2016, Rev. Sci. Inst. 87, 103108 (2016). DOI: 10.1063/1.4964703).



Infrared Multiphoton Dissociation

- FELIX instrument is based on the Bruker AmaZon Speed ETD instrument described by Martens Rev. Sci. Instrum. **87**, 103108 (2016); https://doi.org/10.1063/1.4964703



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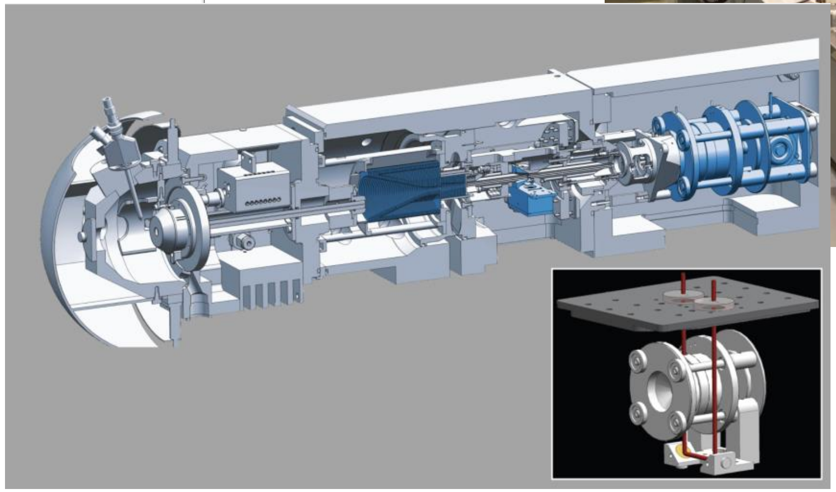
REVIEW OF SCIENTIFIC INSTRUMENTS **87**, 103108 (2016)

Infrared ion spectroscopy in a modified quadrupole ion trap mass spectrometer at the FELIX free electron laser laboratory

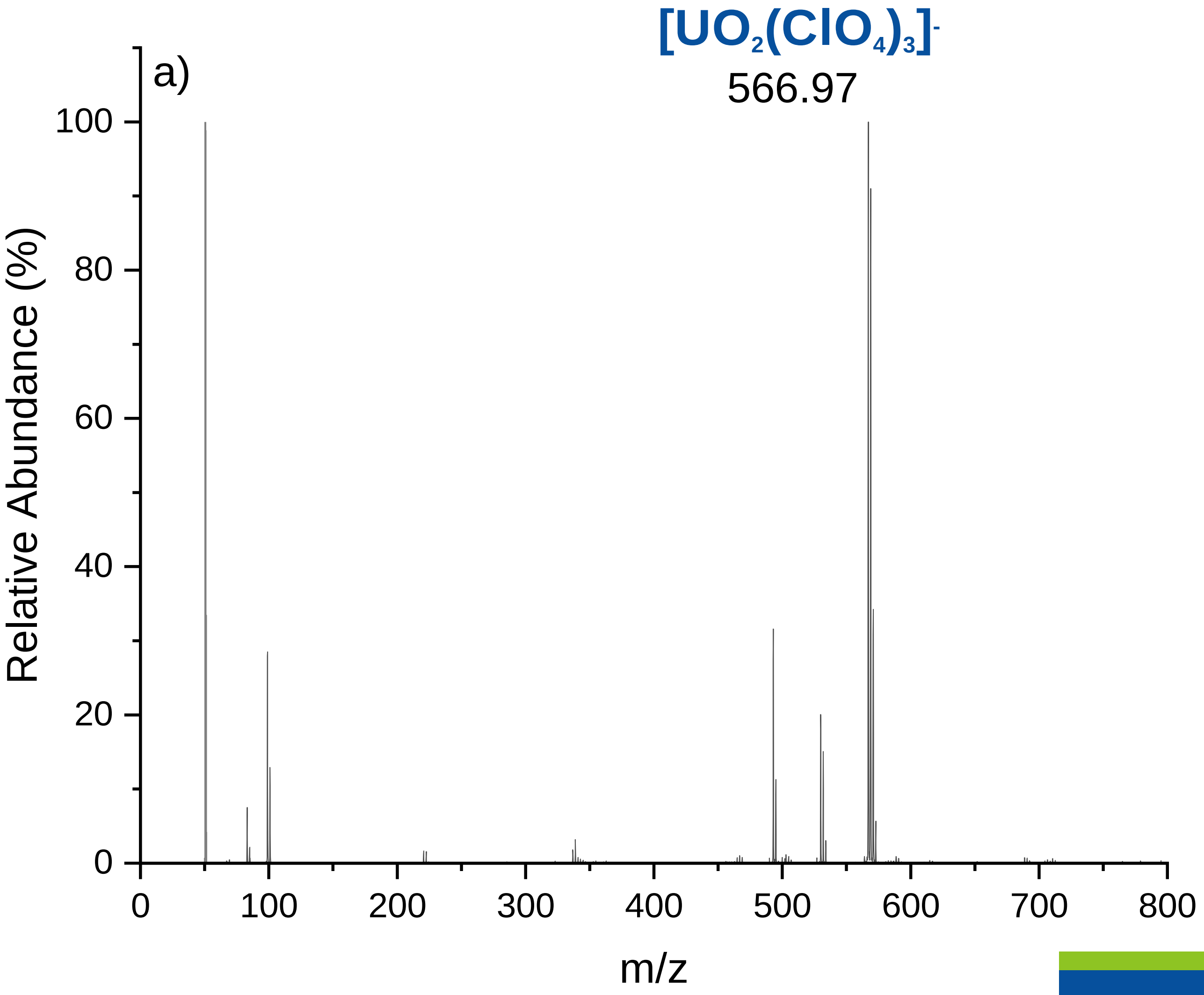
Jonathan Martens,[1,a)] Giel Berden,[1] Christoph R. Gebhardt,[2,a)] and Jos Oomens[1,3,a)]
[1]*Radboud University, Institute for Molecules and Materials, FELIX Laboratory, Toernooiveld 7c, 6525ED Nijmegen, The Netherlands*
[2]*Bruker Daltonik GmbH, Fahrenheitstrasse 4, D-28359 Bremen, Germany*
[3]*Van't Hoff Institute for Molecular Sciences, University of Amsterdam, Science Park 908, 1098XH Amsterdam, The Netherlands*

(Received 26 August 2016; accepted 29 September 2016; published online 17 October 2016)

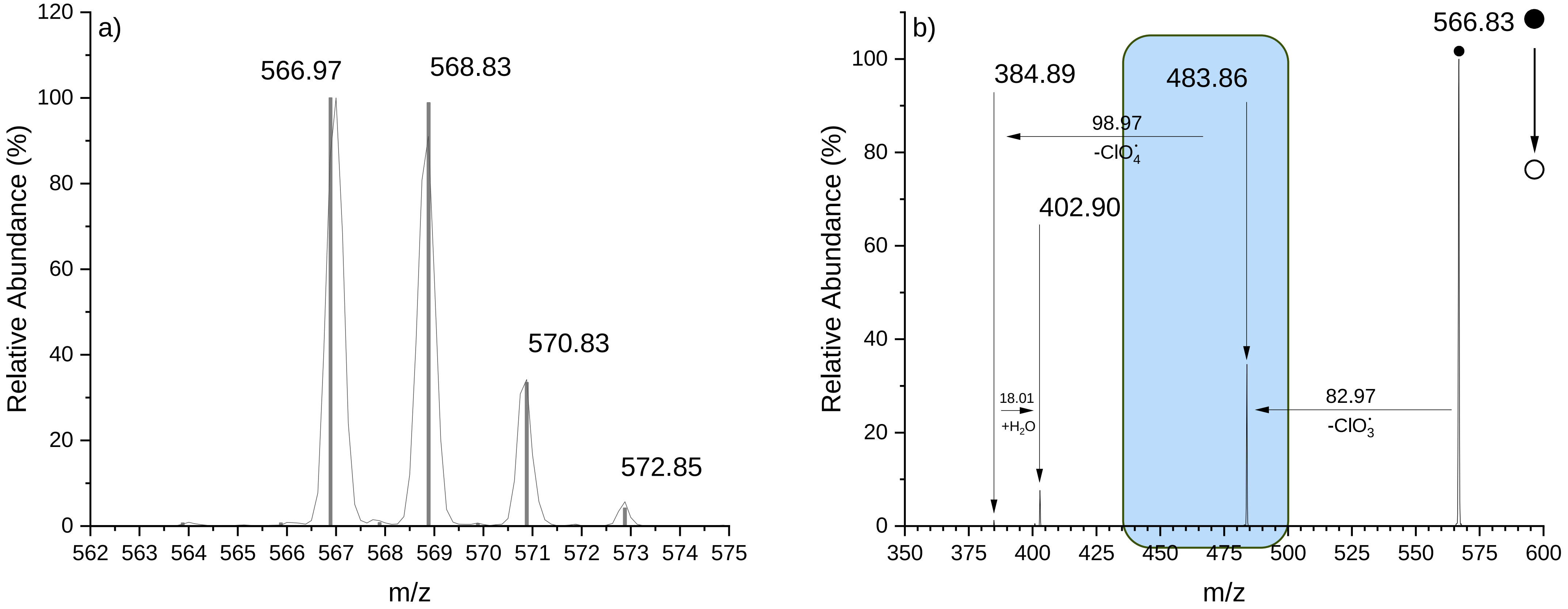
We report on modifications made to a Paul-type quadrupole ion trap mass spectrometer and discuss its application in infrared ion spectroscopy experiments. Main modifications involve optical access to the trapped ions and hardware and software coupling to a variety of infrared laser sources at the FELIX infrared free electron laser laboratory. In comparison to previously described infrared ion spectroscopy experiments at the FELIX laboratory, we find significant improvements in efficiency and sensitivity. Effects of the trapping conditions of the ions on the IR multiple photon dissociation spectra are explored. Enhanced photo-dissociation is found at lower pressures in the ion trap. Spectra obtained under reduced pressure conditions are found to more closely mimic those obtained in the high-vacuum conditions of an Fourier transform ion cyclotron resonance mass spectrometer. A gas-mixing system is described enabling the controlled addition of a secondary gas into helium buffer gas flowing into the trap and allows for ion/molecule reactions in the trap. The electron transfer dissociation (ETD) option of the mass spectrometer allows for IR structure characterization of ETD-generated peptide dissociation products. *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4964703]



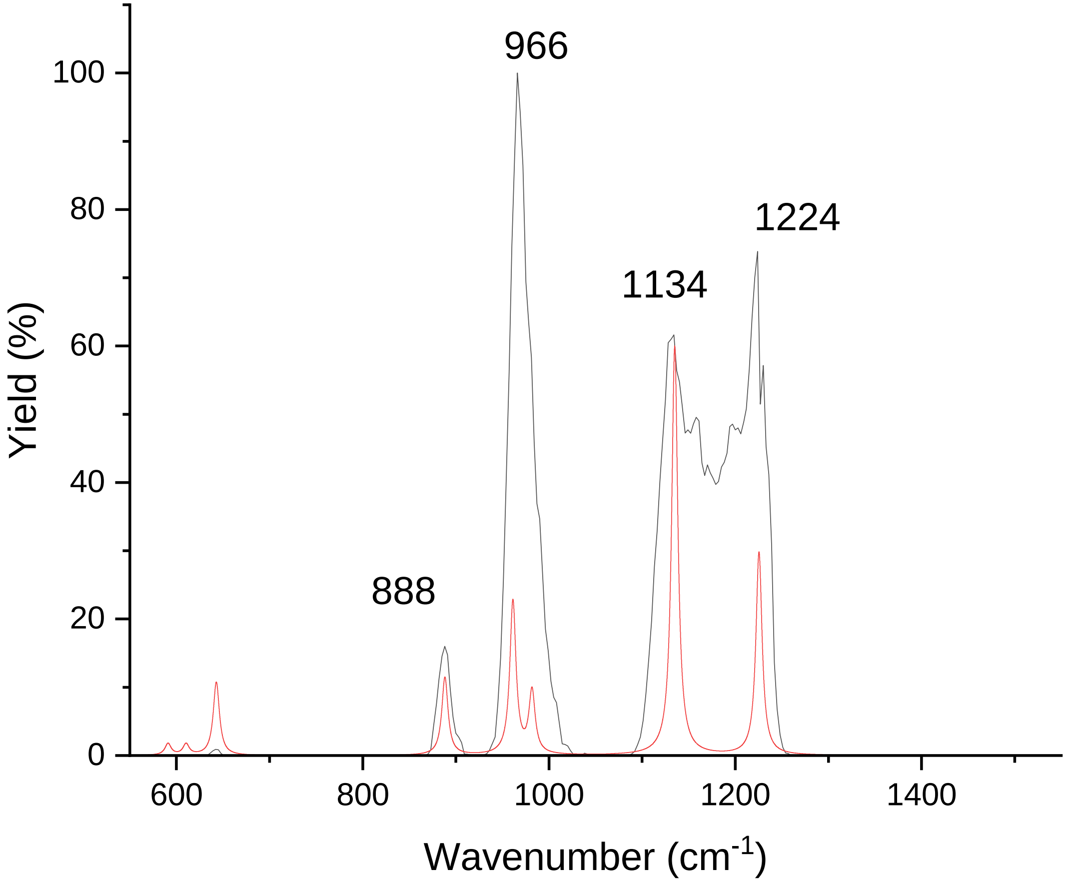
Collision Induced Dissociation MS1 Spectrum showing $[UO_2(ClO_4)_3]^-$ *m/z* 567 on Quadrupole Ion Trap



Collision Induced Dissociation Spectrum $[UO_2(ClO_4)_3]^-$ *m/z* 567 from Ion Trap

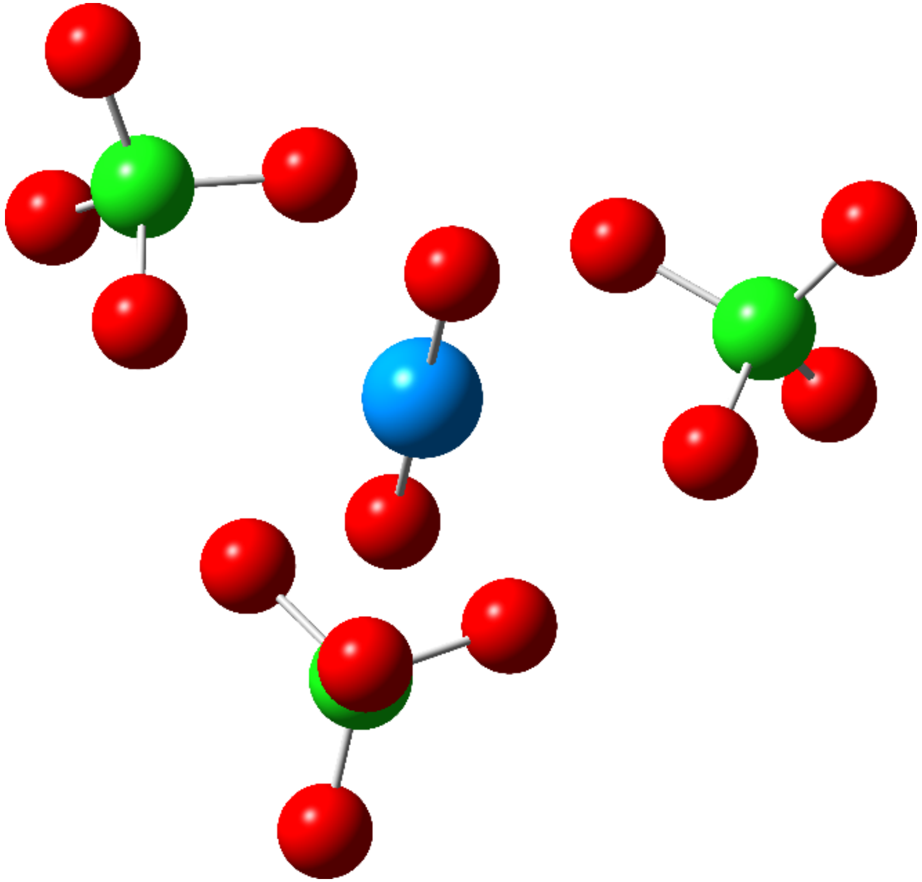


IRMPD of Uranyl tris-Perchlorate $[UO_2(ClO_4)_3]^-$



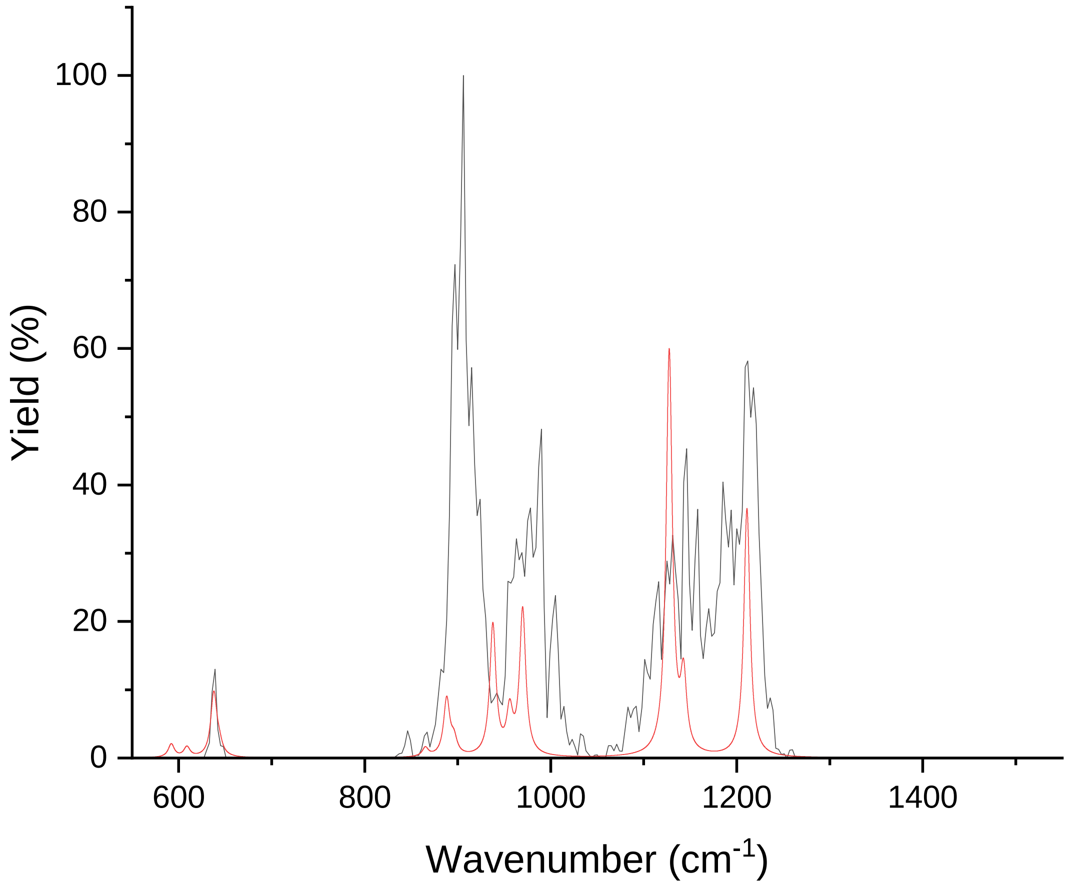
- Solid black trace: IRMPD spectrum of *m/z* 567 from negative-mode electrospray of uranyl tris-perchlorate, identified as $[UO_2(ClO_4)_3]^-$
- Solid red trace: predicted infrared spectrum of $[UO_2(ClO_4)_3]^-$ calculated at the B3LYP level of theory using the ECP60MDF basis set and relativistic effective core potential for uranium, and the Def2-TZVP basis set for Cl and O. Theoretical frequencies scaled by 0.995
- Peak at 966 is likely composed of two modes: one from perchlorate and one from uranyl asymmetric stretch. Based on calculation the U-O stretch is likely near 990 cm^{-1}

Uranyl tris-Perchlorate Anion Calculated Structure



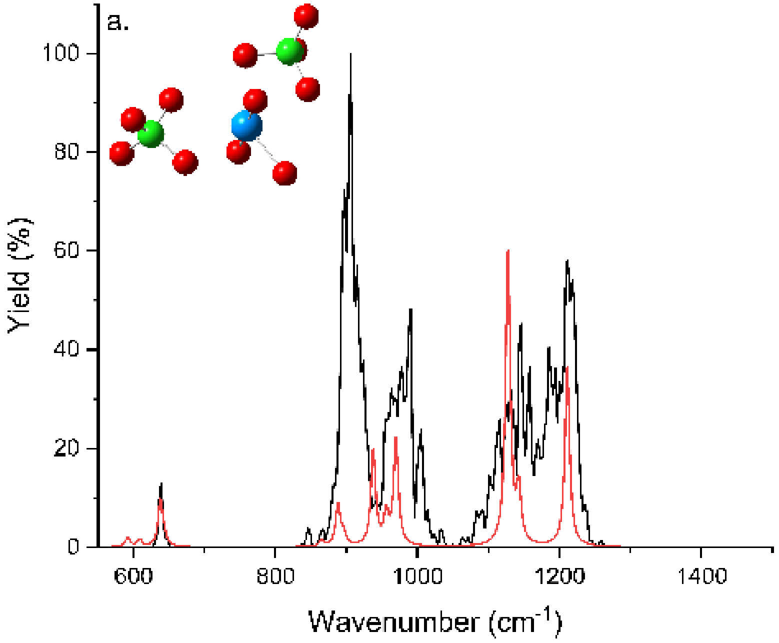
- Structure of $[UO_2(ClO_4)_3]^-$ *m/z* 567 optimized at the B3LYP level of theory
- Axial U—O bond lengths are calculated at 1.76 Å
- U—O bond lengths to the oxygens in the perchlorate ligands are calculated at 2.54 Å

IRMPD of Uranyl Perchlorate Anion fragment *m/z* 484

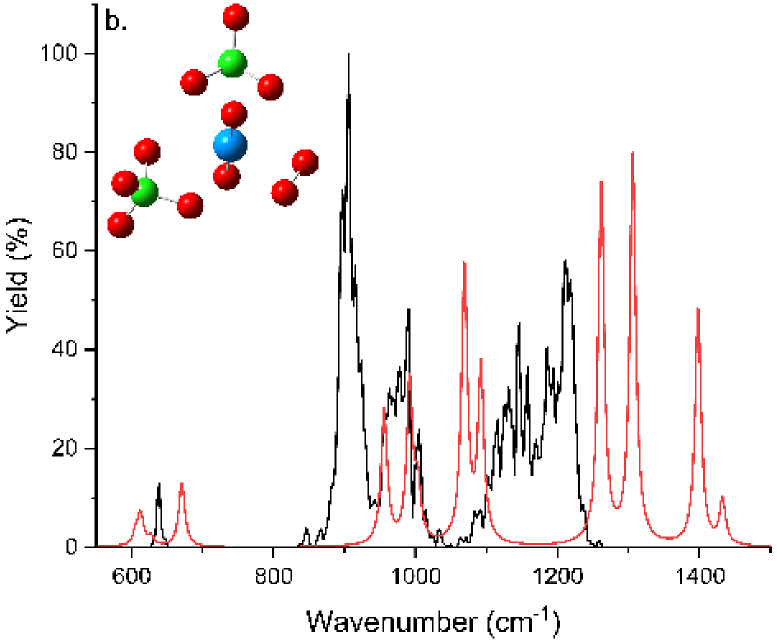


- Solid black trace: IRMPD spectrum of *m/z* 484 $[UO_3(ClO_4)_2]^-$ produced from CID of *m/z*=567 ($[UO_2(ClO_4)_3]^-$
- Solid red trace: predicted infrared spectrum of $[UO_3(ClO_4)_2]^-$
- Calculated at the B3LYP level of theory using the ECP60MDF basis set and relativistic effective core potential for uranium, and the Def2-TZVP basis set for Cl and O. Theoretical frequencies scaled by 0.995

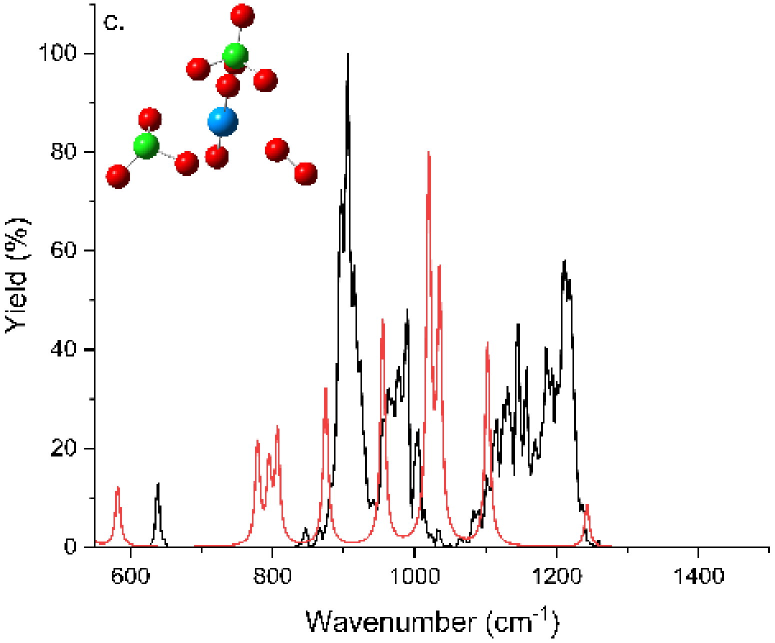
Comparing Measured IRMPD Spectra with Varied Theoretical Structures of *m/z 484 from CID of* $[UO_2(ClO_4)_3]^-$ *m/z 567*



a. Uranyl with an oxo ligand and two perchlorate anion ligands

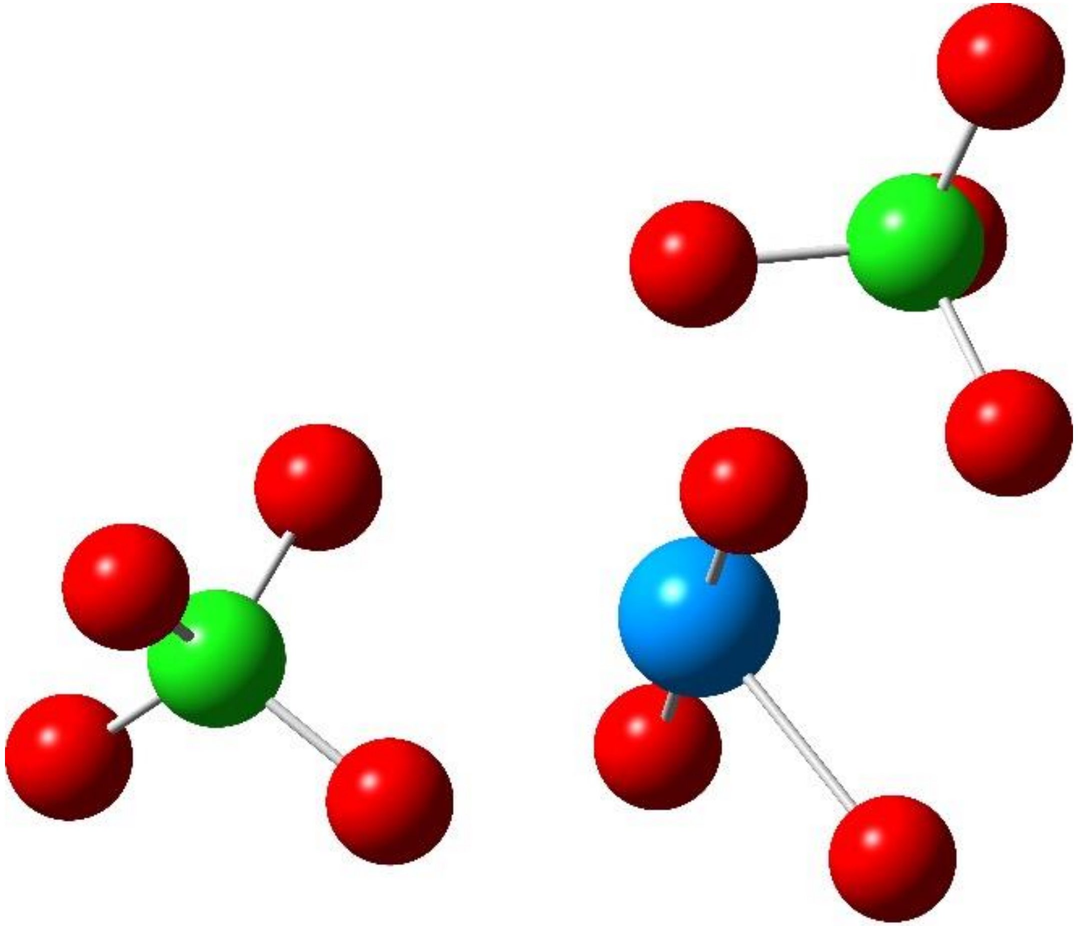


b. uranyl with a bidentate superoxide ligand, a chlorate radical anion ligand, and a perchlorate anion ligand



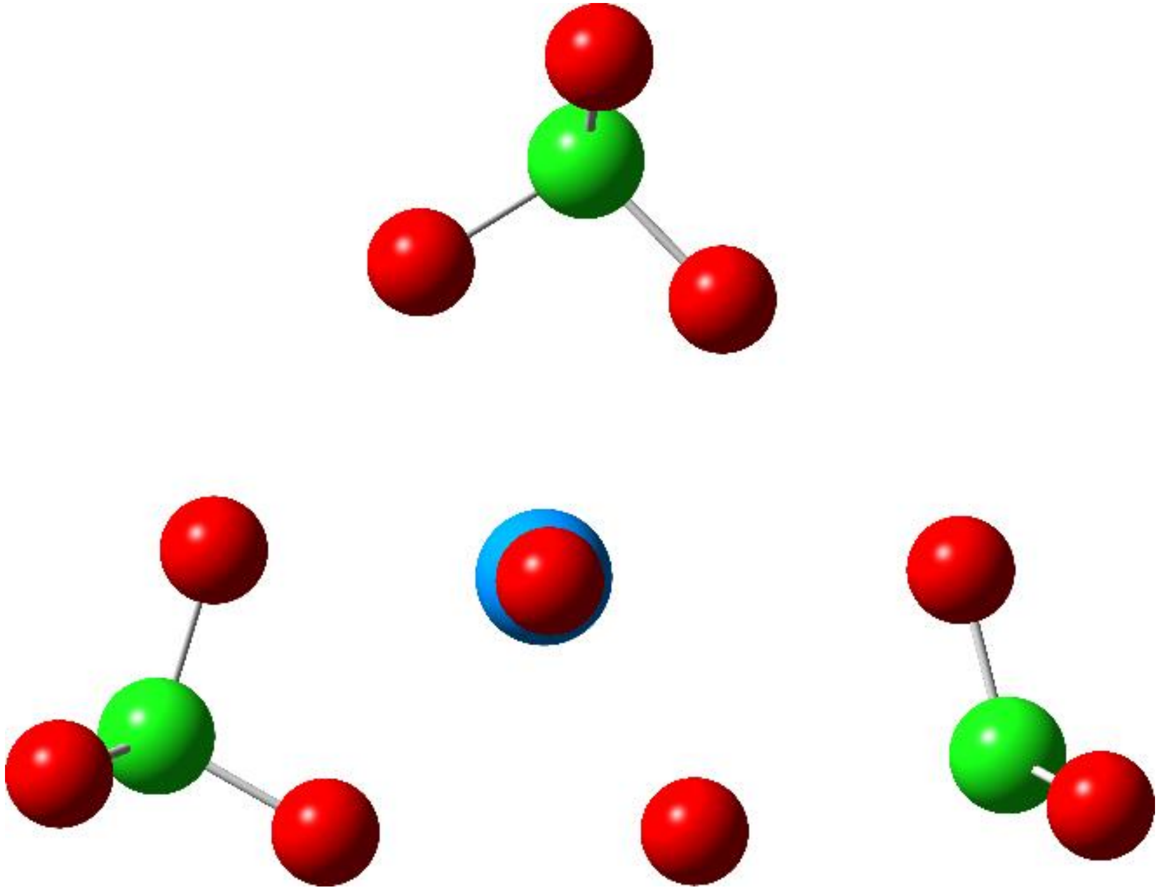
c) uranyl with monodentate superoxide ligand, a chlorate radical anion ligand, and a perchlorate anion ligand

Optimized $[UO_3(ClO_4)_2]^-$ Structure



- Structure of $[UO_3(ClO_4)_2]^-$ optimized at the B3LYP level of theory
- Axial U—O bond lengths are calculated at 1.78 Å
- U—O bond length to the third oxygen in the central UO_3 moiety is calculated at 2.11 Å

Proposed Transition State



- Transition state structure for the fragmentation of *m/z 567* $[UO_2(ClO_4)_3]^-$ to the product at *m/z* 484
- Axial U—O bond lengths are calculated at 1.77 Å
- U—O bond length to the oxygen that will become the third oxygen in the central UO_3 moiety is calculated at 2.26 Å

Conclusions

- Uranyl perchlorate forms metal ligand complexes via electrospray in the gas phase that can be investigated by a number of fragmentation mechanisms
- Initial look at the IRMPD spectra of $[UO_3(ClO_4)_2]^-$ and $[UO_2(ClO_4)_3]^-$, and a proposed calculated transition states using B3LYP level of theory in Gaussian
- In these structures, we identified an overlap between each of these uranyl stretches resulting in their largely being obscured by a perchlorate mode
- Upon collision induced dissociation, we observed a CID product
  - CID product geometry appears to agree with similar structure reported previously for uranyl nitrate (Groenewold 2006 DOI: 10.1021/ja058106n)
- Idaho National Laboratory's new capability for analysis of metal-ligand gas phase complexes enables gas-phase metal-ligand complex studies of radioactive species

Acknowledgements


Christopher A. Zarzana


Brittany D.M. Hodges


JungSoo Kim


Jonathan Martens


Giel Berden


Jos Oomens


Free-Electron Lasers for Infrared eXperiment (FELIX) Facility Radboud University, Nijmegen, Netherlands


Collaborative Computing Center Idaho National Laboratory

Funding: This work was supported by the U.S. Department of Energy through the INL Laboratory Directed Research & Development (**LDRD**) Program under DOE Idaho Operations Office Contract 22A1059-125.

Calculations: High Performance Computing (**HPC**) was performed using the Idaho National Laboratory computing resources which are supported by the Office of Nuclear Energy of the U.S. Department of Energy and the Nuclear Science User Facilities under Contract No. DE-AC07-05ID14517.
https://hpc.inl.gov/SitePages/Home.aspx

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