INL/CON-21-63443-Revision-1

Investigating Covalent Bonding in f-elements using Gas-phase Ion Chemistry

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Idaho National Laboratory

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

Gas-Phase Stability of Large Lanthanide:Ligand Clusters Evaluated Using Collision-Induced Dissociation

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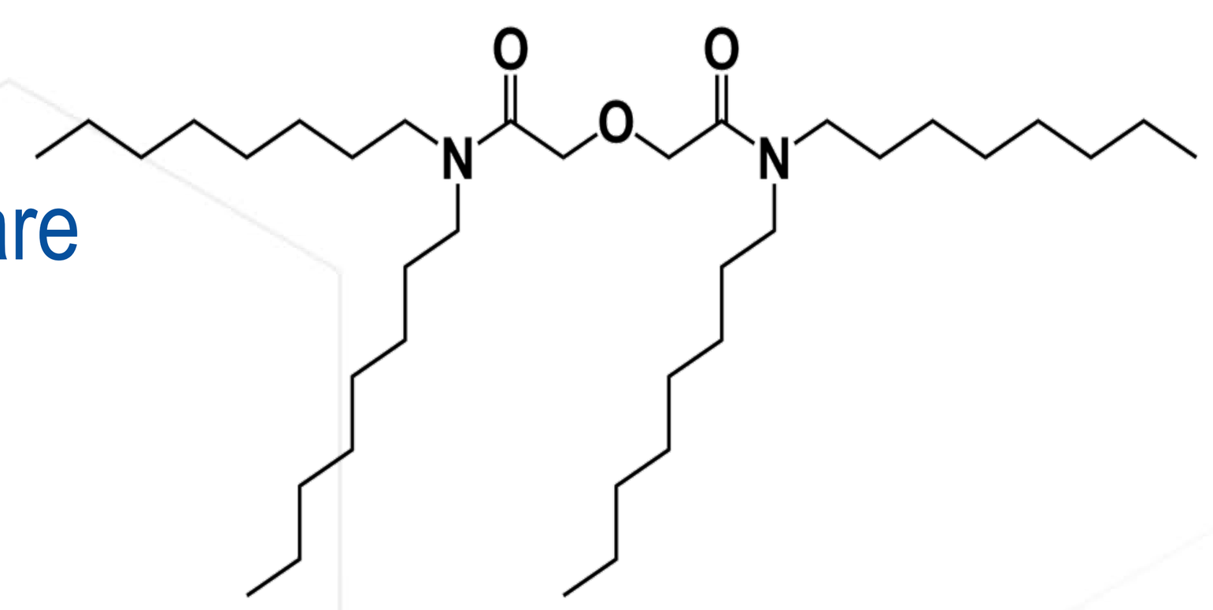
Impact

- Improve biphasic organic-aqueous separation of actinides and lanthanides in used nuclear fuels by elucidating intrinsic differences in lanthanide-ligand covalent behaviors

Objective

- Improve understanding of covalent interactions in *f*-element reprocessing systems absent from solvent effects by investigating lanthanide:N,N,N',N'-tetraoctyl diglycolamide (TODGA) gas-phase metal ion clusters

Background



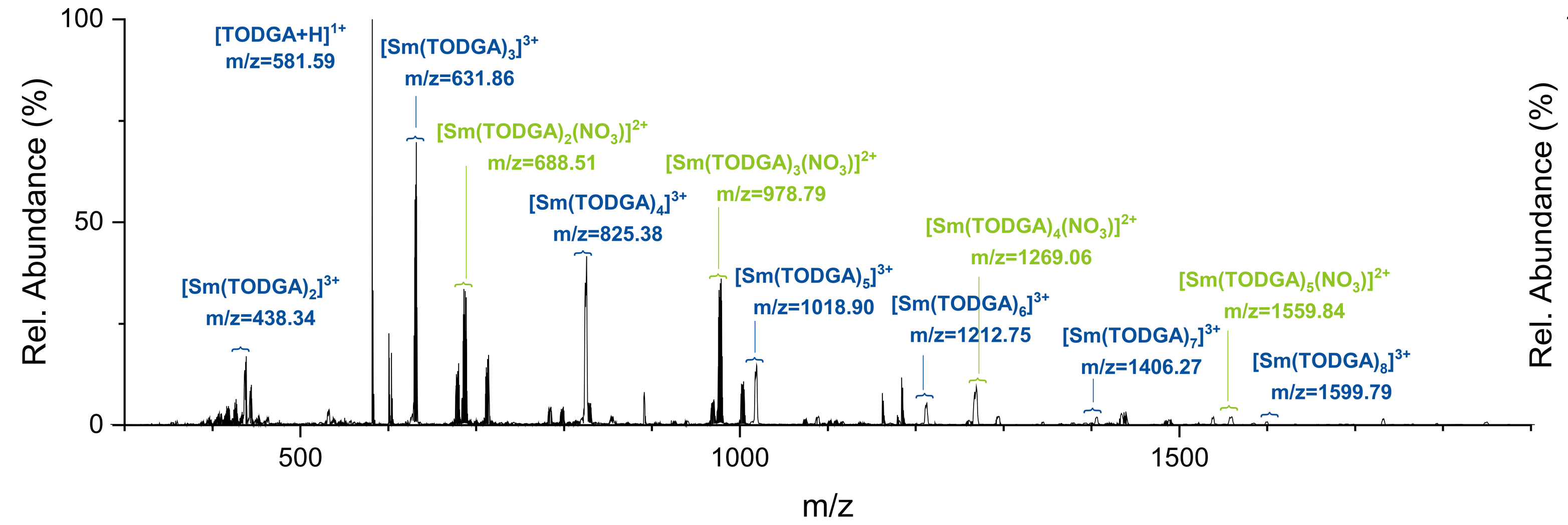
- Diglycolamides (DGAs) are utilized by the Actinide Lanthanide Separation (ALSEP) process, a promising single-process separation
- Tandem mass spectrometry (MS[2]) isolates and collisionally induces fragmentation of gas-phase molecular ions formed during ionization, enabling relative determination of covalent bond strength

Approach

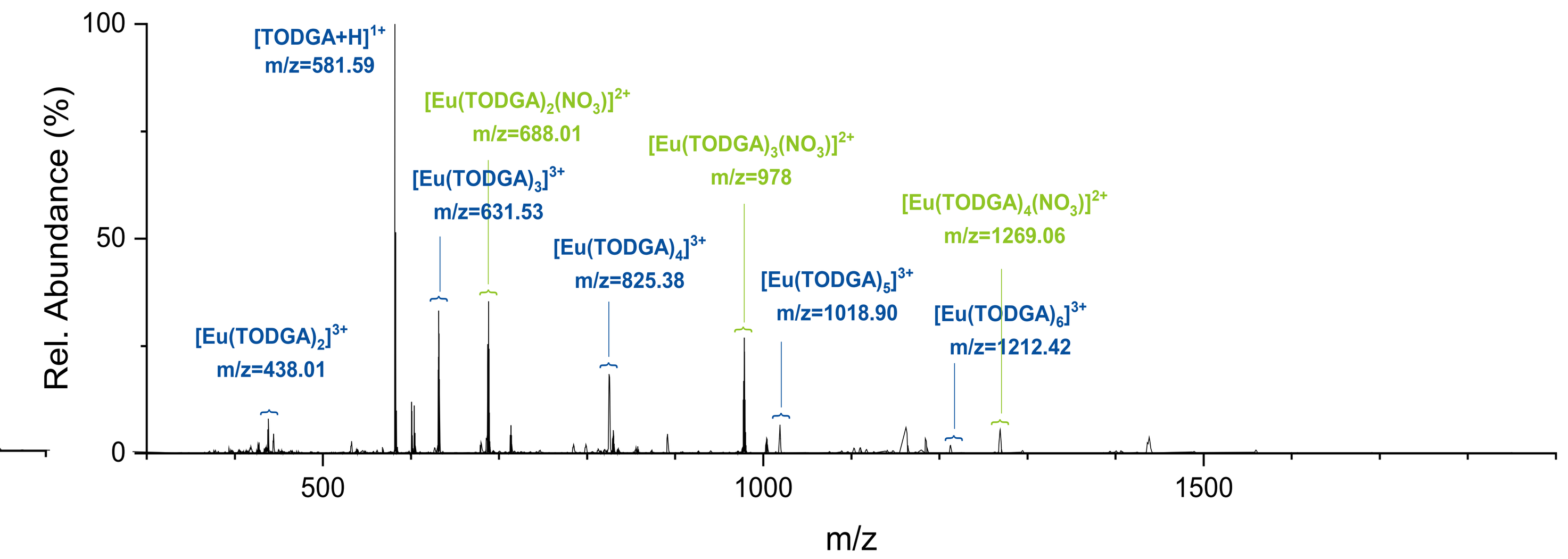
- Synthesize lanthanide:TODGA gas phase ion clusters containing samarium (Sm) or europium (Eu) using nanospray ionization and a quadrupole time-of-flight mass spectrometer.
- Identify metal ion clusters using exact mass measurements and tandem mass spectrometry experiments
- Compare relative covalent bond strength of metal ion clusters by varying applied collision voltage and determining collisional fragments

Results

30 µM $Sm(NO_3)_3$ 3 µM TODGA

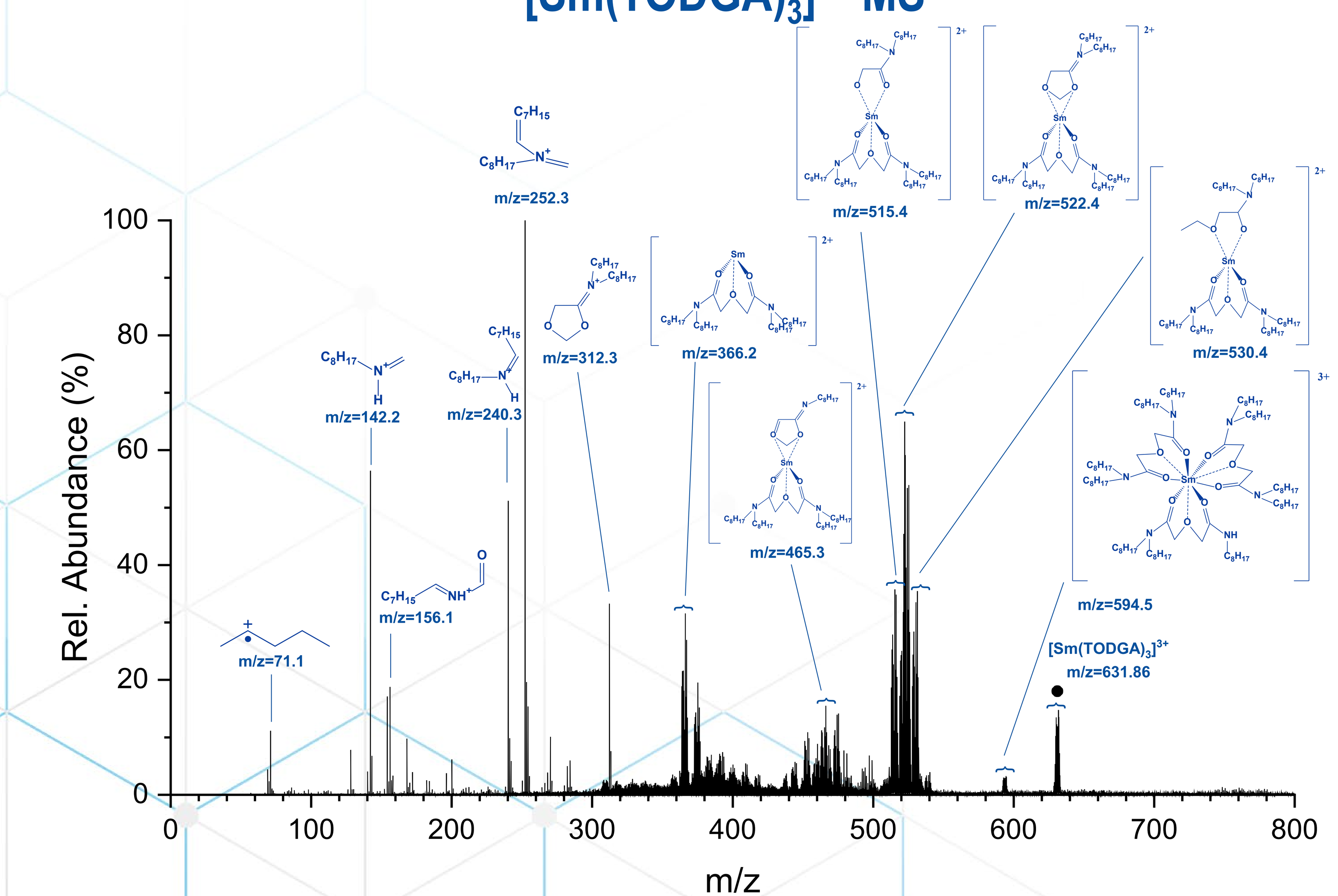


30 µM $Eu(NO_3)_3$ 3 µM TODGA

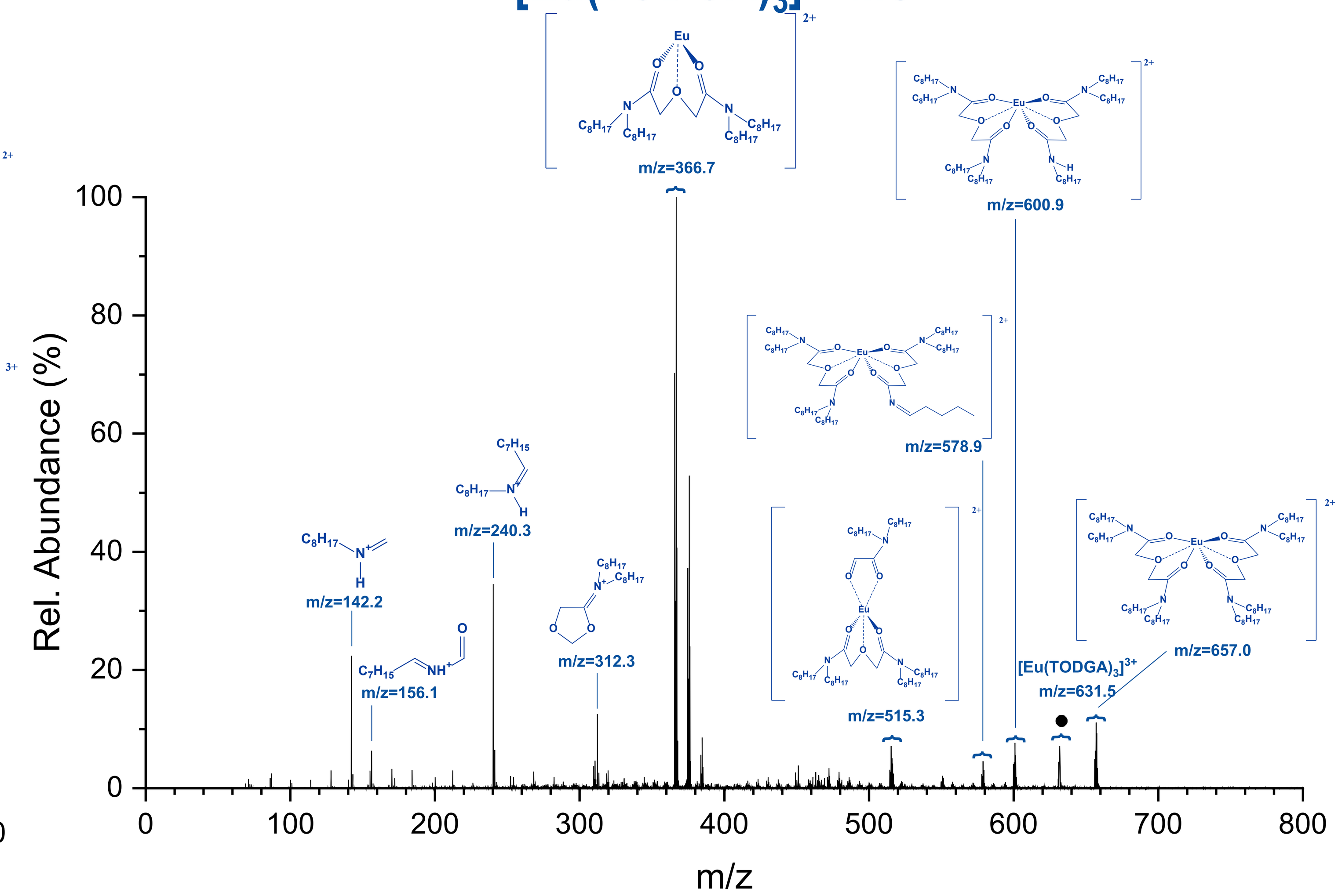


- Surprisingly large clusters were detected: up to $[Sm(TODGA)_{10}]^{3+}$ and $[Eu(TODGA)_8]^{3+}$
- Large clusters containing nitrate were also identified: up to $[Sm(TODGA)_8(NO_3)]^{2+}$ and $[Eu(TODGA)_6(NO_3)]^{2+}$
- MS[2] experiments show that $[Ln(TODGA)_3]^{3+}$ clusters produce complex fragmentation spectra, while $[Ln(TODGA)_n]^{3+}$ ($n \geq 4$) fragment through elimination of intact TODGA molecules
- MS[2] also shows that less collision energy is required to remove a neutral ligand with increasing cluster size
- This suggests that the metal coordination sphere is saturated by three TODGA ligands, so additional ligands are weakly bound

$[Sm(TODGA)_3]^{3+}$ MS[2]



$[Eu(TODGA)_3]^{3+}$ MS[2]



- The product of the loss of a TODGA cation, $[Ln(TODGA)_2]^{2+}$, is not observed for samarium and is not particularly abundant for europium; however, there is evidence of serial fragmentation of this cluster due to other metallic species present

Acknowledgements

This work was also supported by the U.S. Department of Energy, Office of Science, Office of Workforce Development for Teachers and Scientists (WDTS) under the Science Undergraduate Laboratory Internships Program (SULI) and through the INL Laboratory Directed Research& Development (LDRD) Program under DOE Idaho Operations Office Contract DE-AC07-05ID14517 .

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INL/CON-21-63443