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Impact

- Potential evidence of water splitting on gas-phase lanthanide clusters offers a way to study the intrinsic reactivity of hydrogen-generation materials

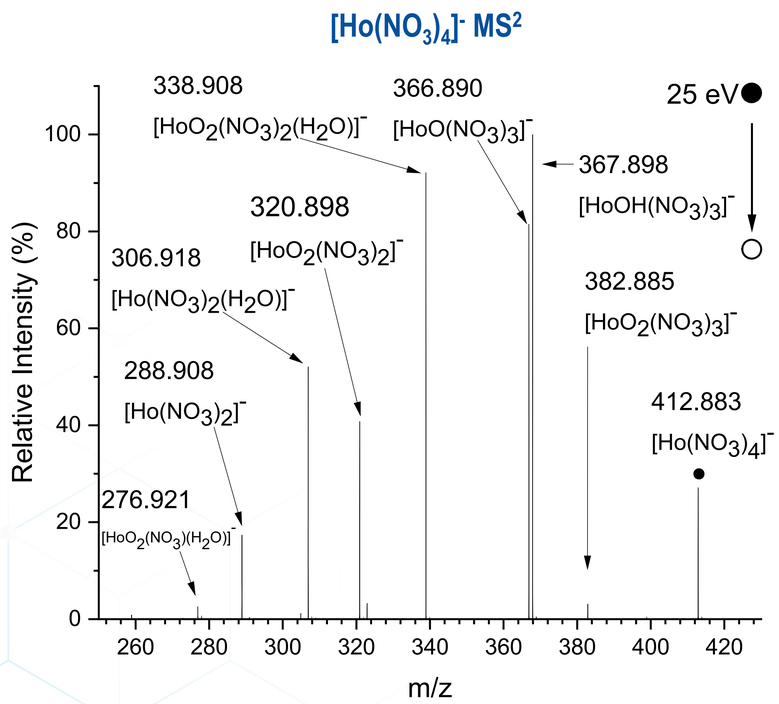
Background

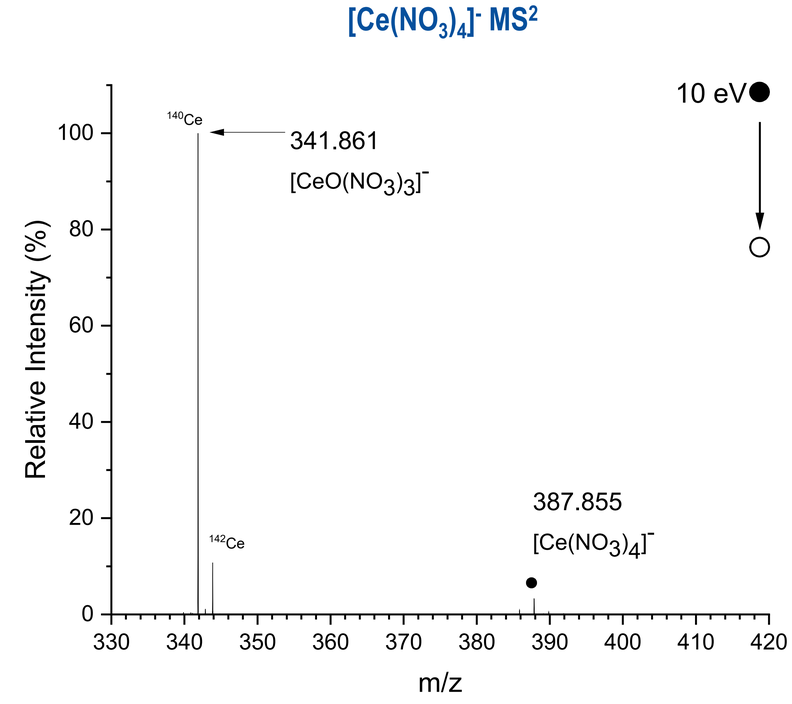
- Molecular hydrogen is a potential energy carrier that could be used to help implement a clean energy economy if it is generated from splitting of water. Studies of the intrinsic reactivity of clusters that are representative of the reactive sites of these materials can increase understanding of the fundamental reaction mechanisms involved in hydrogen production, allowing for more efficient development of new water-splitting materials.

Approach

- Synthesize gas-phase clusters of lanthanide (holmium and cerium) by electrospray of the lanthanide nitrate dissolved in water/acetonitrile mixtures into a Bruker micrOTOF-Q II quadrupole time-of-flight mass spectrometer. The lanthanide tetranitrato anion was isolated and collisionally activated with nitrogen in the collision cell. Activated species were reacted with background water and detected with the time-of-flight mass spectrometer. Species identification is performed using formulas derived from accurate mass measurements.

Results





- Collisional activation of $[Ho(NO_{3)4}]^-$ results in a series of ions formed from elimination of neutral species containing nitrogen and oxygen ($^{\cdot}NO$, $^{\cdot}NO_2$,N_xO_y)
- An additional series is formed from addition of background water to collisionally-produced ions
  - Intensity of hydrated ions are higher than the dehydrated, suggesting water is efficiently added
- Ion at *m/z*=367.898 that has been assigned as $[Ho(NO_3)_3OH]^-$ (theoretical *m/z*=367.897, error=-2.5 ppm)
  - Presence of a hydrogen atom means this ion must have originated from a hydrated species
  - Hypothesize water adds to $[Ho(NO_3)_3]^-$, then splits, eliminating H-radical
  - Process is hypothesized to be rapid and quantitative, as no $[Ho(NO_3)_3]^-$ or $[Ho(NO_3)_3H_2O]^-$ is observed
- Collisional activation of $[Ce(NO_{3)4}]^-$ only results in loss of $^{\cdot}NO_2$
- Difference in behavior must be due to electronic configuration
- Computational electronic structure theory calculations underway to explore mechanisms

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