

Direct Observation of Ion Evaporation from a Triply Charged Nanodroplet

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Supporting Information

General experimental considerations

The ions La^{3+} , Tb^{3+} and Lu^{3+} were chosen for more detailed study because all three are monoisotopic, thus maximizing the sensitivity of the experiment and making spectral interpretation simpler, and for the fact that represent the largest, a medium-sized and the smallest of the lanthanide ions.

Any one of the $[\text{Ln}(\text{H}_2\text{O})_n]^{3+}$ clusters may serve as the starting point for EDESI experiments, though for the purposes of providing useful information, certain criteria had to be met: a large value of n such that the point at which charge reduction occurred (i.e. Eq. 1) was relatively late in the fragmentation process; a high cluster abundance; and no coincidental overlap with other ions with the same nominal m/z value. The ions $[\text{La}(\text{H}_2\text{O})_{48}]^{3+}$, $[\text{Tb}(\text{H}_2\text{O})_{47}]^{3+}$, and $[\text{Lu}(\text{H}_2\text{O})_{48}]^{3+}$ fulfilled all criteria and were therefore chosen to be subjected to a full EDESI analysis.

Calculations of charge density

Charge densities of 3+ and 2+ lanthanide-water clusters were determined using the average cluster volume from 2–4 energy-minimized structures calculated in MOPAC using the lanthanide-specific parameter set SPARKLE/AM1.¹ The starting geometries for the inner coordination sphere were taken from crystal structures in the CSD, and various orientations of water molecules in the outer coordination sphere of the lanthanide clusters were minimized. All starting geometries resulted in energy-minimized structures with similar volumes and charge densities (standard deviation = $4 \times 10^{-5} \text{ \AA}^{-3}$).

Protonated water cluster energy-minimizations were completed using the AM1 method in MOPAC¹ and the HF/6-31+G* basis set in Spartan.² There was < 2% difference between the charge densities calculated by these two methods, and for consistency the charge densities determined using AM1 structures are presented in Table 1.

In Table 1, the charge density of the precursor $[\text{Ln}(\text{H}_2\text{O})_n]^{3+}$ ion is likely overestimated because in Eq. 1 c is probably nonzero. The charge density of the product $[\text{Ln}(\text{OH})(\text{H}_2\text{O})_n]^{2+}$ ions may be slightly underestimated, because other product ions with less water molecules are being simultaneously generated (though possibly simply from the competing water dissociation reaction rather than from Eq. 1).

EDESI-MS/MS maps for $[\text{Tb}(\text{H}_2\text{O})_{47}]^{3+}$ and $[\text{Lu}(\text{H}_2\text{O})_{48}]^{3+}$

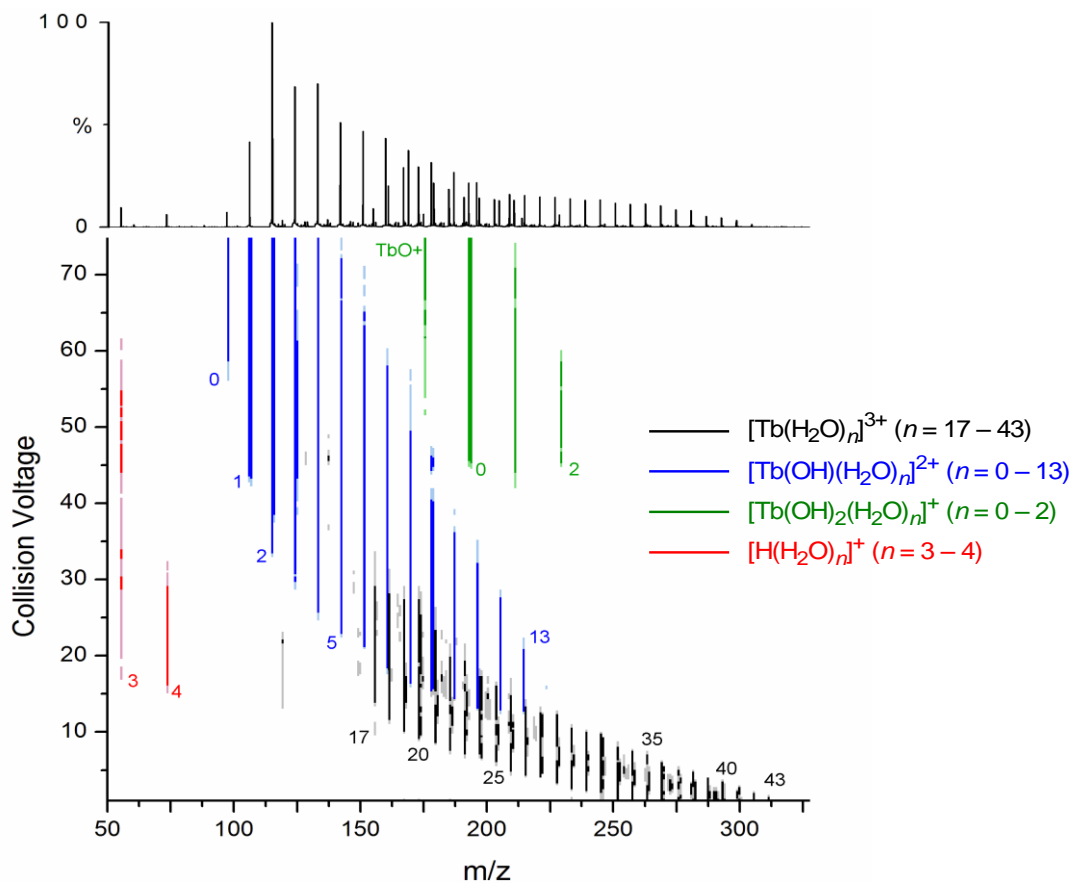


Figure S1. Positive-ion EDESI-MS/MS of $[\text{Tb}(\text{H}_2\text{O})_{47}]^{3+}$. Fragmentation energy increases vertically in the contour map. The top mass spectrum is a summation of all 75 spectra used to generate the contour map.

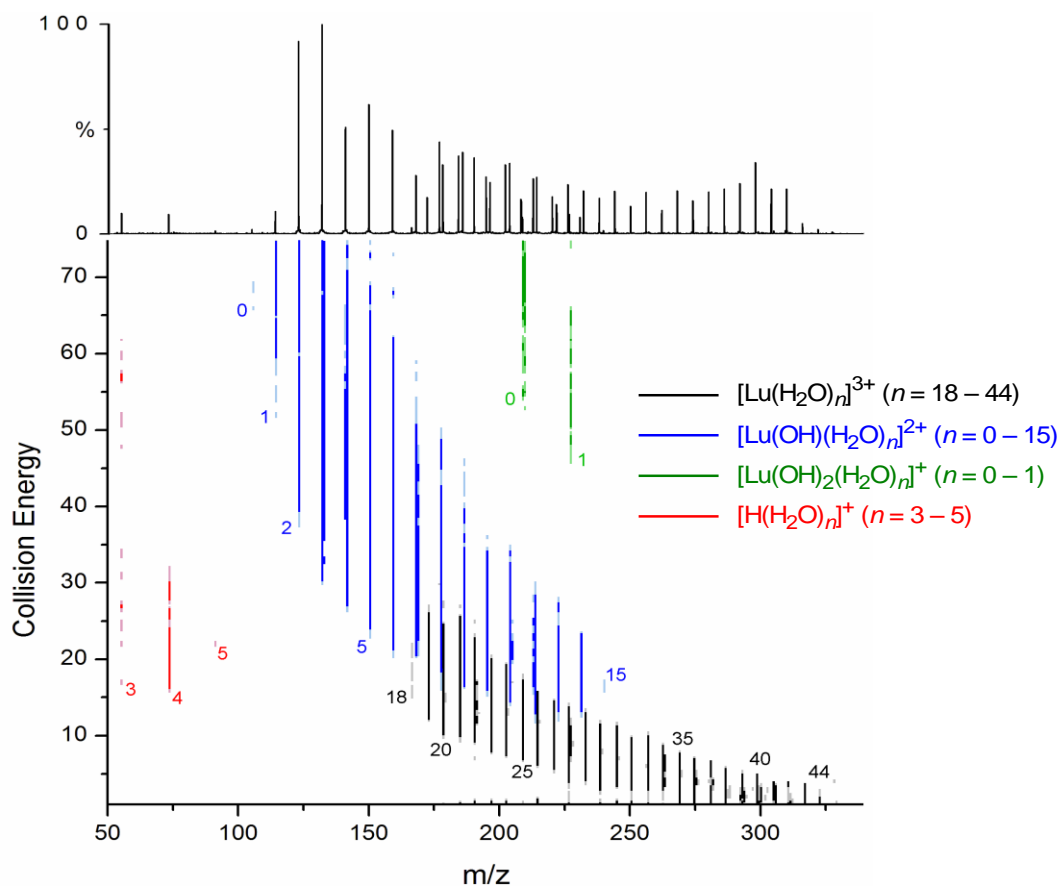


Figure S2. Positive-ion EDESI-MS/MS of $[\text{Lu}(\text{H}_2\text{O})_{48}]^{3+}$. Fragmentation energy increases vertically in the contour map. The top mass spectrum is a summation of all 75 spectra used to generate the contour map.

pH effect

Samples for electrospray analysis were prepared by dissolving LnCl_3 salts (5 mM) in deionized water without adjusting the pH. While decreasing the pH should have the effect of suppressing the hydrolysis of the lanthanide aquo ions, in practice we found that it had a deleterious effect on the observed intensity of ALL of the lanthanide-containing ions, i.e. the $[\text{Ln}(\text{H}_2\text{O})_n]^{3+}$ series was suppressed along with the $[\text{Ln}(\text{OH})(\text{H}_2\text{O})_n]^{2+}$ and $[\text{Ln}(\text{OH})_2(\text{H}_2\text{O})_n]^+$ ions (see Figure S3), leaving the $[\text{H}(\text{H}_2\text{O})_n]^{3+}$ ions as only species.

LaCl_3 in deionized water: measured pH = 6.12

LaCl_3 in 0.05% trifluoroacetic acid: measured pH = 2.36

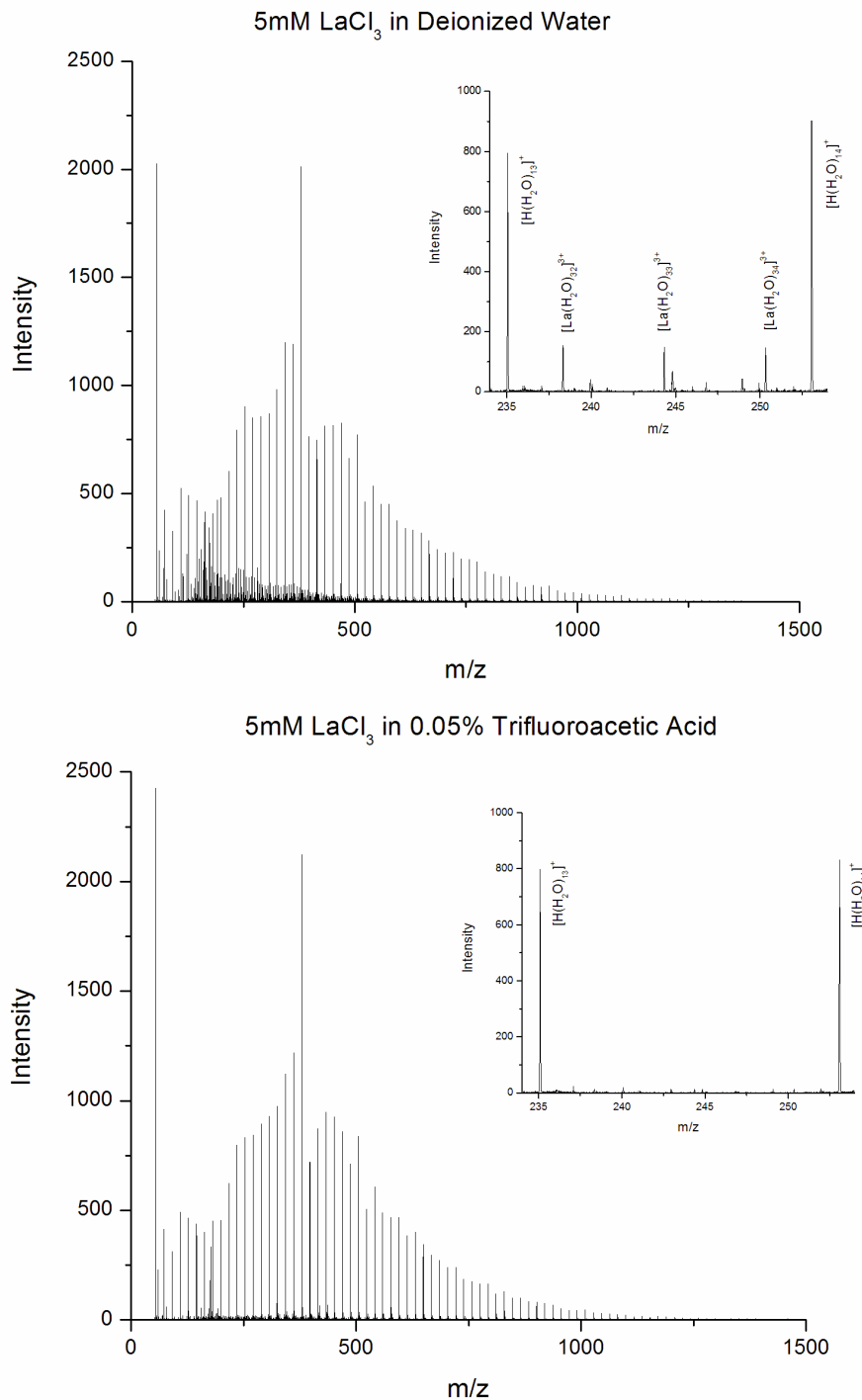


Figure S3. Positive-ion ESI-MS of LaCl₃ in pure water (top) and in 0.05% aqueous F₃CCOOH (bottom). Note the complete suppression of peaks due to the La³⁺-centred clusters at low pH.

References

- 1 MOPAC2007, Colorado Springs, CO, USA, 2007.
- 2 Spartan '06, Wavefunction, Inc., Irvine, CA, USA, 2006.