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**Soft X-Ray Absorption Spectra of Aqueous Salt Solutions with Highly Charged
Cations**

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Abstract

X-ray absorption spectra of 1M aqueous solutions of indium (III) chloride, yttrium (III) bromide, lanthanum (III) chloride, tin (IV) chloride and chromium (III) chloride have been measured at the oxygen K-edge. Relatively minor changes are observed in the spectra compared to that of pure water. SnCl_4 and CrCl_3 exhibit a new onset feature which is attributed to formation of hydroxide or other complex molecules in the solution. At higher energy, only relatively minor, but salt-specific changes in the spectra occur. The small magnitude of the observed spectral changes is ascribed to offsetting perturbations by the cations and anions.

Introduction

Highly charged cations can have a large restructuring effect on the hydrogen bond network of water.(1) Here we study this effect via the perturbations on the near edge X-ray absorption fine structure (NEXAFS) spectrum of water. NEXAFS is a spectroscopic technique in which the core electrons of selected atoms in a molecule are excited to high energy anti-bonding and continuum states.(2) These unoccupied orbitals are highly sensitive to their local environments due to their large spatial extent, which make them excellent probes of changes in the local water structure.(3)

Until recently, it was prohibitive to apply the inherently high vacuum technique of soft X-ray spectroscopy to high vapor pressure liquids (such as water, octane, methanol etc.). Following the approach Faubel and coworkers' developed for UV photoelectron spectra of such volatile species,(4) in 2001 we incorporated liquid microjet technology into a synchrotron X-ray experiment, thereby opening many new systems to study by this powerful technology.(3) Dramatic changes were observed in NEXAFS spectra for strongly interacting molecules, e.g. methanol and water, as a function of state (gas, solid, liquid).(3,5) Liquid water exhibits a spectrum with none of the well-resolved peaks that are prevalent in the gas phase spectrum and which is also quite different from that of the solid; these prominent spectral changes have been interpreted with the aid of theoretical calculations to help elucidate the liquid state of water and have engendered much recent controversy.(6-8)

Previous NEXAFS studies of aqueous salt solutions have shown that halide ions perturb the vacant electronic orbitals of water in a manner specifically dependent upon the identity of the halide.(9) This was in contrast to monovalent cations, which exhibited relatively small effect on the oxygen K-edge spectra of water, independent of their identity.(10,11) Interestingly, doubly

charged cations produce spectral changes that were specific to the identity of the cation. Highly charged cations have previously been investigated in the soft X-ray region, but only in the spectral region preceding the onset of the water pre-edge (energy < 534 eV), where an increase in intensity was observed for transitions of Cr^{3+} and Fe^{3+} but not Al^{3+} ; this was attributed to d-shell mixing between metals and water,(12) although it was later argued that these features could instead be due to the formation of hydroxide ions, which also absorb in that energy range.(13) We note that there have been many previous studies of aqueous salt solutions (reviewed previously)(14) and that structural and coordination information can be gathered by diffraction methods (X-ray and neutron) as well as nuclear magnetic resonance (NMR) and extended X-ray absorption fine structure (EXAFS) experiments in the hard X-ray region.(14) Simulations are becoming increasingly reliable for determining coordination numbers for solvated ions.(15) Raman spectrometry can determine the symmetry and stability of certain ion complexes.(16) Mass spectroscopy studies of small ion-containing water clusters have been performed, but are not definitively related to the liquid because these small clusters lack counterions.(17) Herein, we investigate the possible restructuring of the aqueous hydrogen bond network by highly charged cations via the effects observed on the oxygen K-edge NEXAFS spectra of water upon the addition of halide (chloride, except for one case) salts which contain highly charged cations.

2. Experimental

2.1 Samples - Samples purchased from Sigma-Aldrich (>97% purity, in certain cases the hydrate was purchased) and used without further purification were dissolved in 18 M Ω water. Concentrations of up to 1M were used for all salts. CrCl_3 was dissolved in water, and allowed to age for approximately 6 hours before measurements were taken. Under these conditions, the dominant species would be $[\text{CrCl}(\text{H}_2\text{O})_5]^{2+}$ with smaller amounts of $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ and

$[\text{CrCl}_2(\text{H}_2\text{O})_4]^+$ also present.(18-20) This was previously determined by a combination of EXAFS, X-ray scattering and NMR with a high degree of certainty. In the case of YBr_3 , yttrium will largely be in the +3 charge state coordinated by 8 waters, but there will also be significant direct ion pairing between yttrium and the counter ion, as determined recently by EXAFS, neutron scattering and Raman spectroscopy.(21-23) InCl_3 will predominantly be found in water as $[\text{InCl}_2(\text{H}_2\text{O})_5]^+$, as determined by EXAFS, Raman spectroscopy and X-ray scattering.(24) For LaCl_3 , lanthanum will be in the +3 state at all concentrations studied here and solvated by 9 waters (although eightfold hydration has been invoked in the past).(25) Lanthanum salts have been studied extensively by techniques including EXAFS, X-ray diffraction and Raman spectroscopy. Based on NMR and Raman data, the dominant tin species at 1.0 molar will be $[\text{SnCl}_3(\text{H}_2\text{O})_3]^{+3}$ and Sn^{+4} but there will still be significant (>5%) amounts of $[\text{SnCl}_3(\text{H}_2\text{O})_3]^+$, $[\text{SnCl}_4(\text{H}_2\text{O})_2]$, $[\text{SnCl}_2(\text{H}_2\text{O})_4]^{+2}$, $[\text{SnCl}_3(\text{H}_2\text{O})_3]^{+3}$, $[\text{SnCl}_5(\text{H}_2\text{O})_1]^{-1}$, $[\text{SnCl}_3(\text{H}_2\text{O})_3]^+$ and $[\text{SnCl}_4(\text{H}_2\text{O})_2]$.(26)

2.2 Absorption Measurements - Total electron yield (TEY) X-ray absorption spectra were recorded at the oxygen K-edge (~550 eV) for each sample, as detailed previously,(3) using Beamline 8.0.1 at the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory in Berkeley, CA. A detailed description of the experimental system has been previously published.(27)(28) Briefly, an intense ($< 10^{11}$ photons/sec), high resolution ($E/\Delta E > 4000$), and tunable X-ray beam is focused (~50 μm spot size) onto a small liquid jet (~30 μm diameter). The jet is produced by using a syringe pump (Teledyne-Isco) to pressurize the liquid behind a fused silica capillary tip. Almost immediately (~1mm and ~30 μs) after leaving the tip orifice, the liquid is intersected by the intense X-ray beam, wherein the sample is close to room temperature ($> 15^\circ\text{C}$).(29) The signal is normalized to that from a gold mesh located ~3 meters

up beam of the chamber. The energy is calibrated to the water vapor NEXAFS spectrum. To allow for comparison between spectra, all spectra have been area normalized.

3. Results and Discussion

Area-normalized TEY spectra of water and 1M aqueous solutions are shown in Figure 1A for halide solutions containing several highly charged cations. When lower concentrations were investigated, similar effects were observed, but the changes from the pure water spectrum were less pronounced. The water spectrum is typically in terms of the pre-edge (~535 eV), the main-edge (~538 eV) and the post-edge (~542 eV).(6,7) The solution spectra show small but salt-specific shifts in spectral intensity compared to pure water, or compared to a comparable concentration of chloride from sodium chloride. This is in contrast to what was found when monovalent cation salts were used, wherein spectral changes were shown to be independent of the cation identity. Cation-specific changes were observed for divalent cations, however, and ascribed to charge exchange interactions.(10,11) Due to the small magnitude of the spectral change apparent in the present data, a theoretical analysis of sufficient accuracy (i.e. using the recently developed XCH approach)(8) to be reliable was deemed not possible at this current time. This problem is especially acute due to the difficulty in accurately simulating both the dynamics of the system and describing the electronic structure of the excitation within experimental accuracy.(8,30,31) The combined error on both of these calculations coupled with the small magnitude of observed experimental changes makes accurately simulating the experimental spectra beyond the current scope of theoretical calculations.

Interestingly, and as previously found for CrCl_3 ,⁽¹²⁾ dissolution of certain salts (CrCl_3 and SnCl_4) leads to the observation of relatively strong features at an energy below the water pre-edge (Figure 1B). The observation of peaks before the pre-edge was previously attributed to

d-orbital mixing of the cation with the neighboring water molecules.(12) Later, it was noted that these features could actually be due to hydroxide and hydroxide-ion complexes, as hydroxide also absorbs strongly in this region.(13) The data presented here support the conclusion that it is likely due to formation of hydroxide, as other species which contain d-orbitals, viz. InCl_3 , LaCl_3 and YBr_3 , do not exhibit this feature in the present data set. Therefore, d-orbital mixing appears unlikely to be the cause of this spectral feature; hydroxide-containing species in CrCl_3 and SnCl_4 appears a more likely explanation. We note that both SnCl_4 and CrCl_3 are very reactive species. (18-20,26)

In the pre-edge region, all the salt solutions show a decrease in intensity relative to pure water. Previously, a decrease in pre-edge intensity has been interpreted as indicating the existence of fewer broken hydrogen bonds,(7) but this type of qualitative analysis can no longer be justified.(32) Furthermore, this analysis is not appropriate when the spectral features are due to several chemical species, such as hydroxide in addition to the water. Where the pre-edge evolves into the main-edge, the addition of salts leads to an increase in intensity relative to water at ~ 536 eV for all cases except LaCl_3 . We note that some other species other than bulk water must cause this feature, so as the number of ion-paired species that are present in water increase, the likelihood there is some species that will strongly absorb at ~ 536 eV should increase. We note that LaCl_3 will be predominantly solvated without chloride in its first shell, minimizing the variety of ion pairs compared to the other salts considered in this study. Chromium, indium, yttrium and tin will form a large variety of complexes, as noted in the samples section, which have previously been characterized by techniques other than NEXAFS.(18-24,26)

The main-edge and post-edge regions exhibit salt-specific perturbations to the water spectrum. InCl_3 produces a small increase in intensity at the main-edge, with a post-edge similar

to that of water, whereas YBr_3 produces an increase in intensity at the main-edge and decrease at the post-edge relative to water. These spectra are noticeably different from those of LaCl_3 solutions, which show a similar intensity to pure water at the main-edge, but greater intensity at the post-edge. Both SnCl_4 and CrCl_3 produce slight decreases in intensity at the main-edge and post-edge relative to that of pure water. This may be a function of normalization, as for these species there is increased intensity below the pre-edge in there must correspondingly be less intensity elsewhere in the spectrum. This region of the spectrum is especially difficult to interpret as it will have competing effects induced by both the cation and the anion which may to some extent offset, explaining the relatively small degree of spectral changes observed. It is known that anions can effect large perturbations,(9) and given the relatively high concentration of anions in this study (3M or greater) and the small degree of spectral change, it is likely that the perturbations to the water electronic structure by the highly charged cations are offsetting much of the spectral changes induced by the anions.(9) Overall, the spectral changes induced by these salts are surprisingly small.

4. Conclusions

X-ray absorption spectra of aqueous solutions of InCl_3 , YBr_3 , LaCl_3 , SnCl_4 and CrCl_3 have been measured at the oxygen K-edge, using liquid microjet technology. The spectra of the aqueous solutions differ only slightly from that of pure water, although the observed differences do depend on the identity of the salt. Due to the relatively minor effects apparent in the main-edge and post-edge regions, as compared to similar solutions of concentrated alkali halide salts, it is probable that the spectral perturbations effected by a highly charged cation offset much of the spectral effect of the anion. More detailed analysis must await further developments in theoretical methods for calculating XAS spectra of ionic solutions.

Acknowledgements

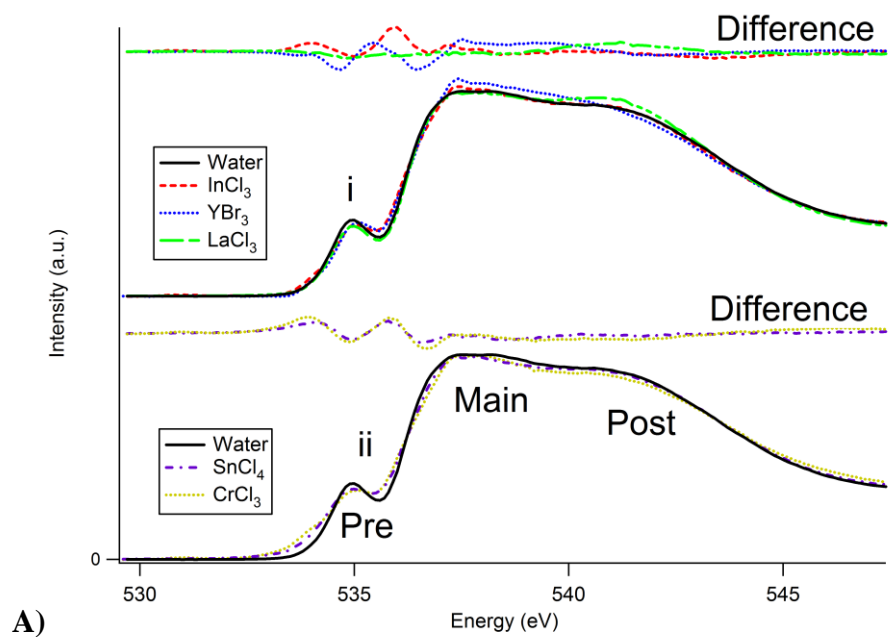
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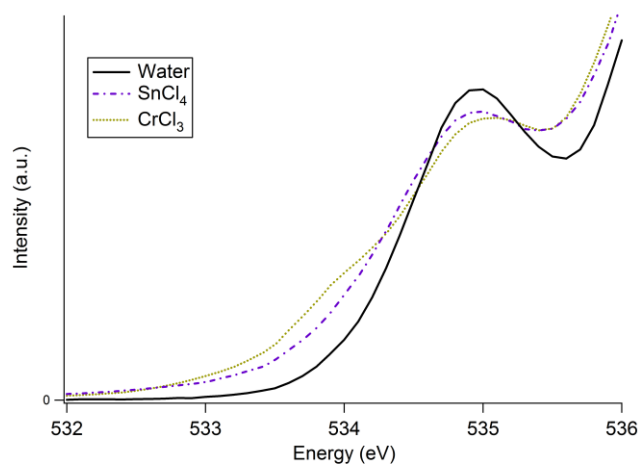
Figure Captions

Figure 1. Oxygen NEXAFS K-edge spectra of water and several salt solutions with a concentration of 1M. Part A - section i shows the spectrum of bulk water (black, solid) and 1M solutions of InCl_3 (red, - - -), YBr_3 (blue, $\cdot\cdot\cdot$) and LaCl_3 (green, - - -); the difference spectra between the salt containing spectra and the spectra of bulk water are shown above the main spectra. Section ii shows the spectrum of bulk water (black, solid) and 1M solutions of SnCl_4 (purple, - \cdot - \cdot) and CrCl_3 (yellow, $\cdot\cdot\cdot$); the difference spectra between the salt containing spectra and the spectra of bulk water are shown above the main spectra. The approximate locations of the pre-edge, main-edge and post-edge are labeled. Part B - an expansion of Figure 1 section ii in the pre-edge region. The spectrum of bulk water (black, solid) and 1M solutions of SnCl_4 (purple, - \cdot - \cdot) and CrCl_3 (yellow, $\cdot\cdot\cdot$).

Figures



A)



B)

Figure 1

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Figure 1a
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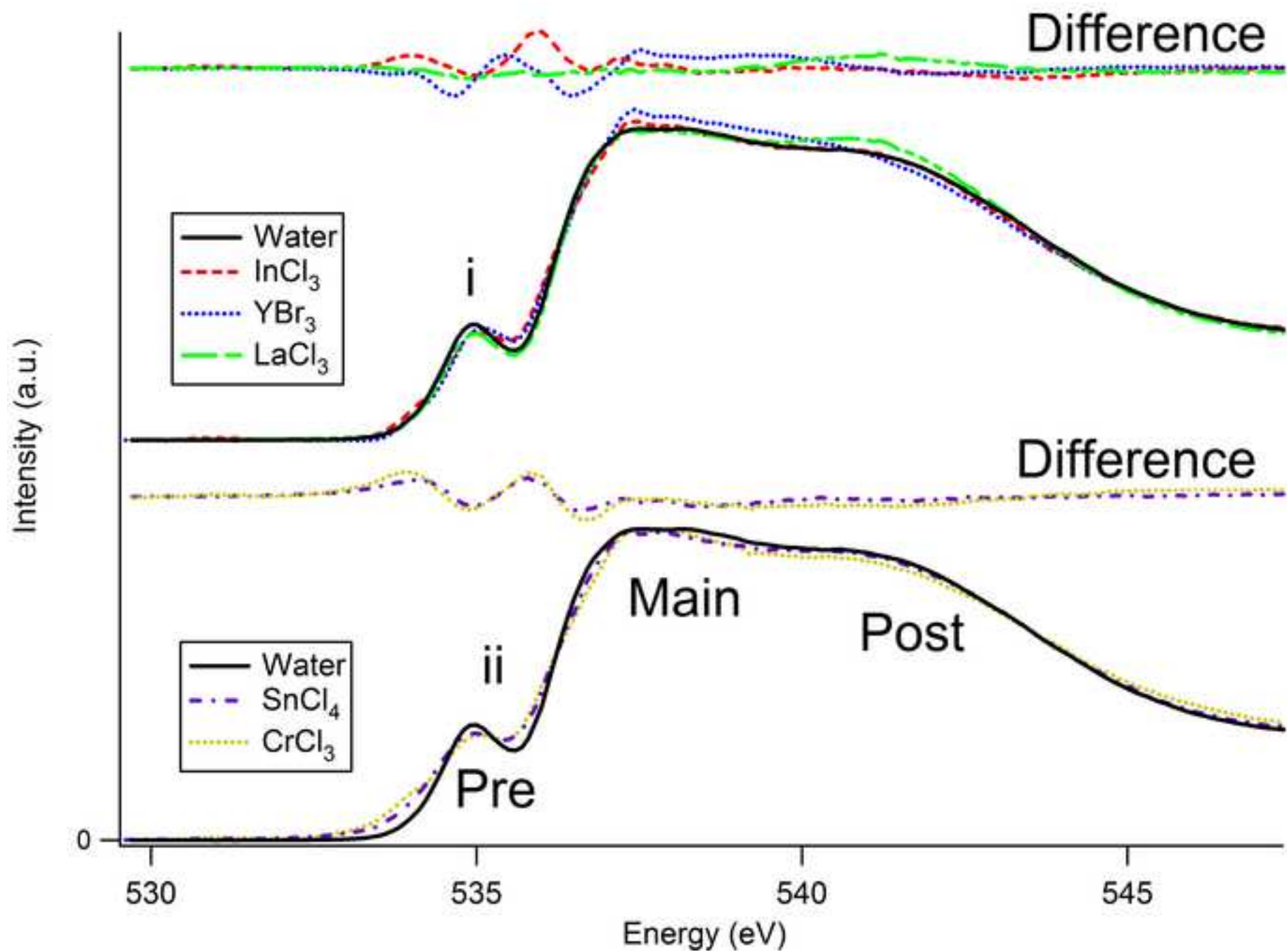
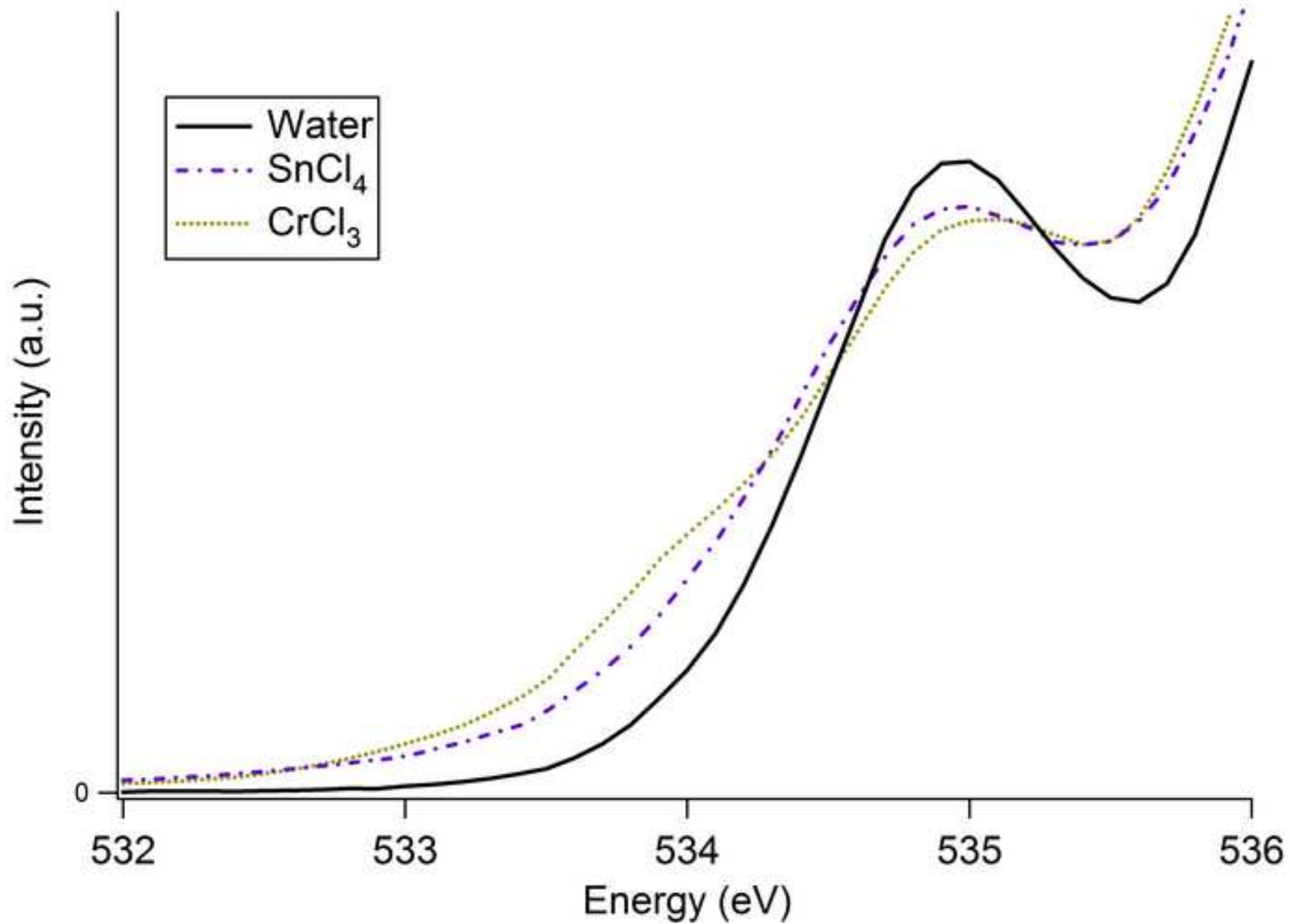
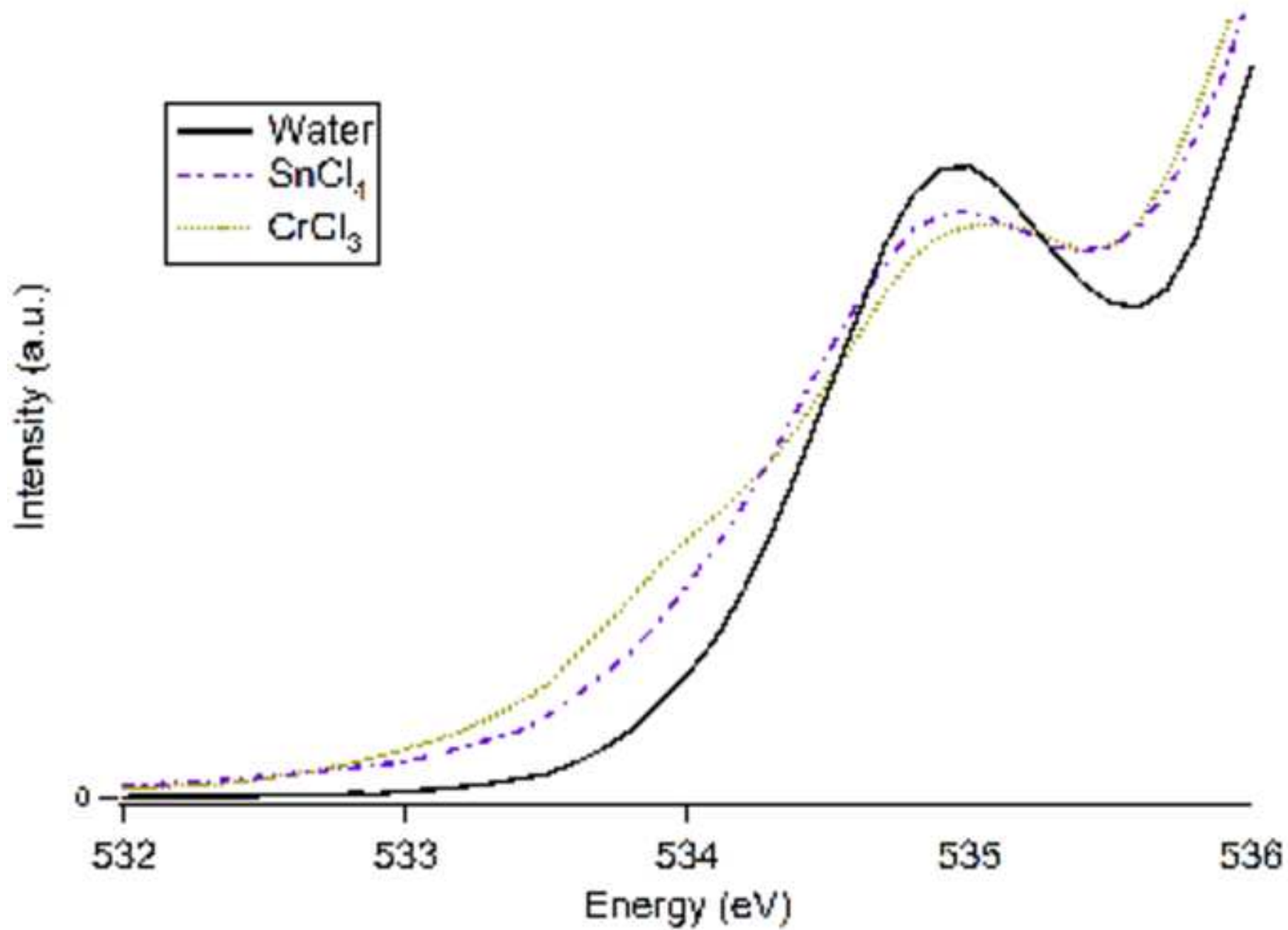


Figure 1b
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*Research Highlights

- NEXAFS Spectra of Aqueous Salt Solutions including CrCl_3 , SnCl_4 , YBr_3 , InCl_3 , LaCl_3
- Salt Specific Spectral Changes are observed
- Provides Evidence Showing a Low Energy Feature is Due to Hydroxide Formation