Surface Adsorption of Chlorine Oxyanion Species to the Air-water Interface

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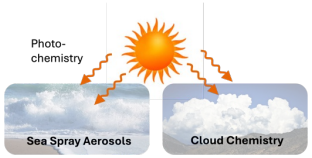
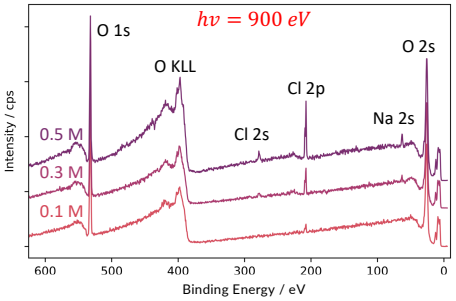
Motivation



The adsorption of select ions to the liquid water interface has profound effects on important environmental processes, such as evaporation rates, aerosol chemistry, accelerated reactions, and more. Despite the overwhelming importance of these molecular details, the underlying physics of ion solvation models used to interpret surface phenomena are still widely debated. Chlorine oxyanions serve as a powerful model system, due to their abundance in seawater and importance in aerosol cloud chemistry. Here, to better understand how size, charge density, and hydration enthalpy, among other factors, influence surface adsorption, we compare the bulk and surface speciation of chlorine oxyanion species (ClO_4^- and ClO_3^-) in liquid water. Using Ambient Pressure X-ray Photoelectron Spectroscopy (APXPS) on planar liquid jets, we are able to track individual ionic species at various depths away from the interface.

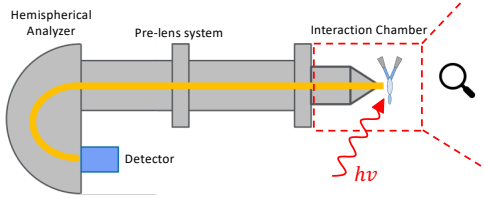
Survey Spectra

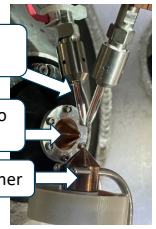
$NaClO_4$ Concentration Series



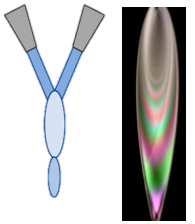
- Contamination tree spectra
- All relevant species identified: O, Cl, and Na
- Highly sensitive to concentration, even with short acquisition times

Ambient Pressure X-ray Photoelectron Spectroscopy of Liquid Flat Jets





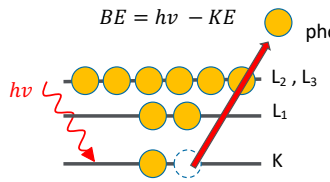
Colliding flat jet



Quartz nozzles

Aperture to analyzer

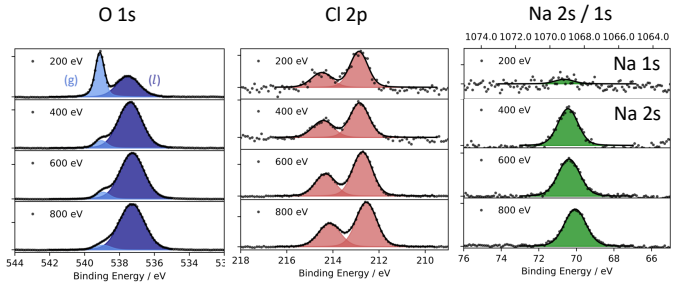
Liquid catcher

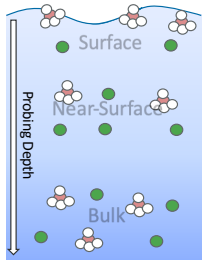


- Temperature control of liquids
- Recirculating solution system
- Inner + outer capillaries for fast mixing and kinetic studies
- Better target for broad X-ray sources, compared to cylindrical jets

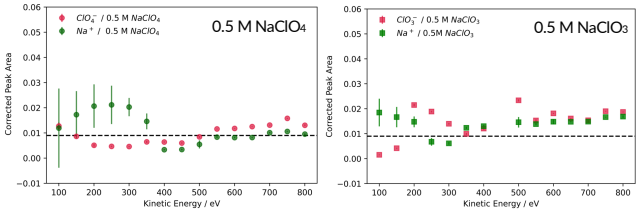
Changing incident photon energy probes chemical species at different depths away from the interface

Surface to Bulk: Ion Depth Profiling of Chlorine Oxyanions



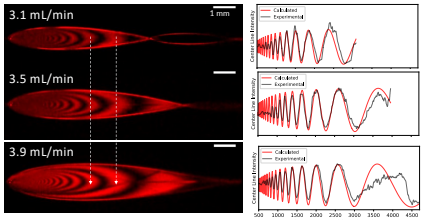


Larger KE probes deeper into the solution

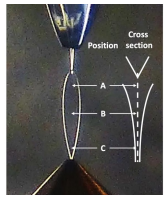


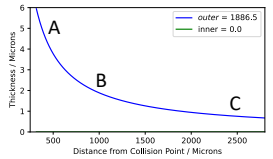
- Surface: ClO_4^- shows stronger preference than ClO_3^-
- Near surface: Trend is reversed

Characterizing Planar Liquid Jets



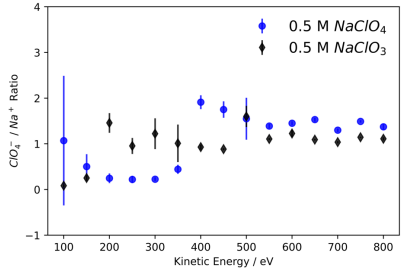
Thin film interference models are used to reliably measure the flat jet thickness





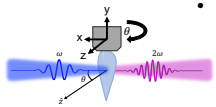
Top of jet: ≈ 5 µm
Bottom of jet: ≈ 800 nm

Conclusions



- 0.5 M $NaClO_4$ and $NaClO_3$ solutions show similar surface speciation

On-going collaborative work: Soft X-ray Second Harmonic Generation at X-ray Free Electron Lasers



- Combining surface selective measurements at XFELs with depth profiling at ALS for a "complete" description of ion distributions at the interface