



The hydrogen bonding structure of adsorbed water on silver iodide and feldspar minerals

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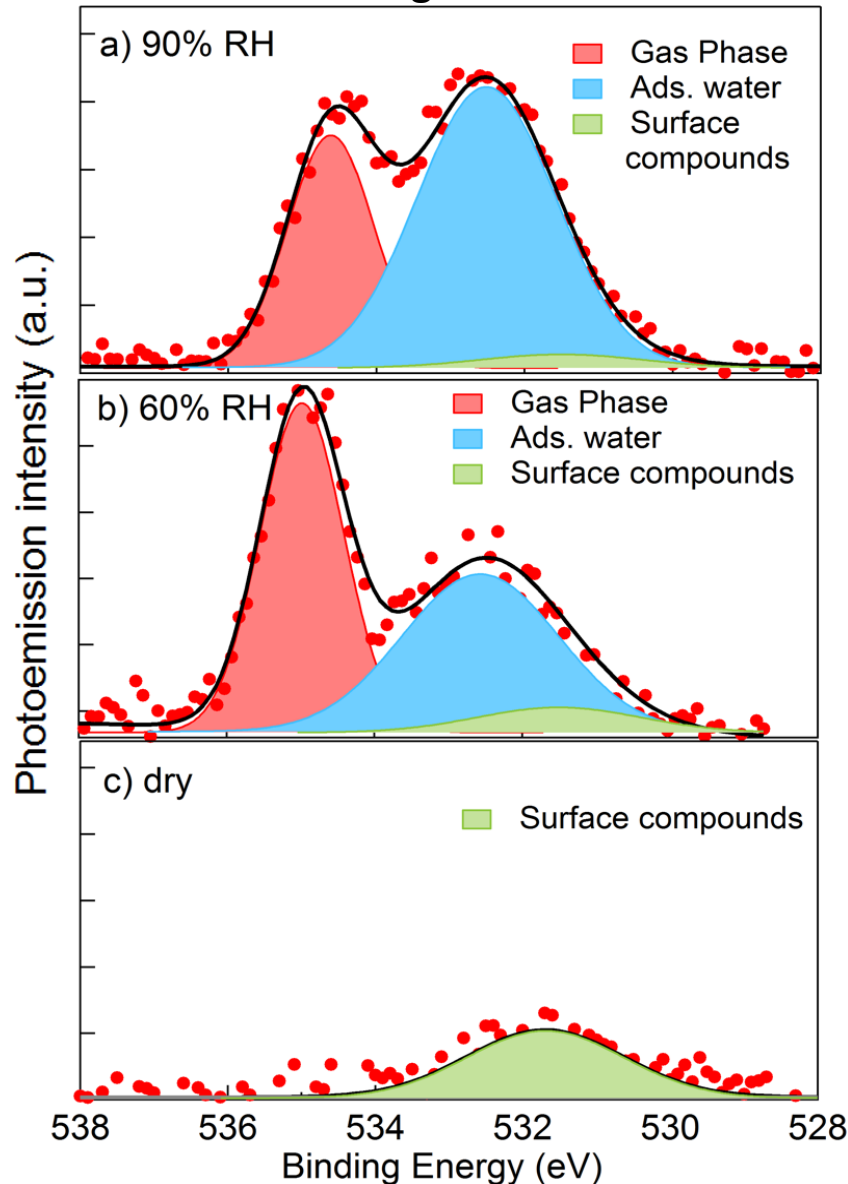
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X-ray photoemission of adsorbed water on AgI

XPS of O1s on AgI surface.

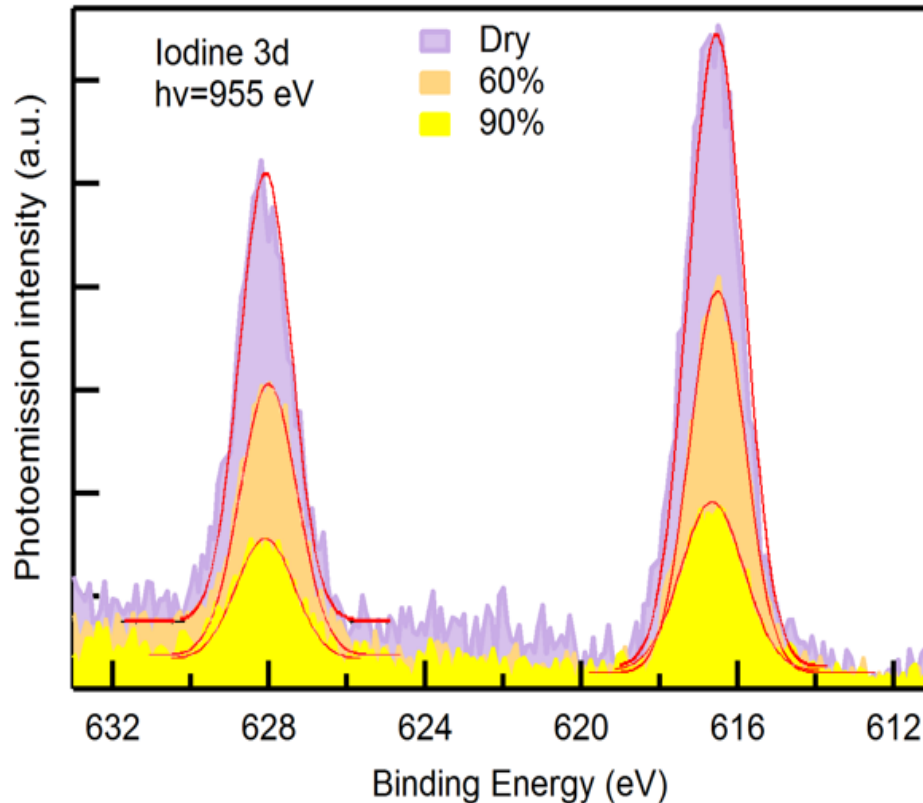


AgI particles in the atmosphere show exceptionally good ice nucleation ability.

We investigate the amount of adsorbed water (by XPS) and its hydrogen bonding structure (by NEXAFS) on AgI particles.

The thickness of the water on the AgI surface at 90% RH is determined to be 13ML, with islands of adventitious carbon. This is consistent with AgI being hydrophilic (but not very hygroscopic).

Iodine 3d signal from surface confirm low solubility of AgI

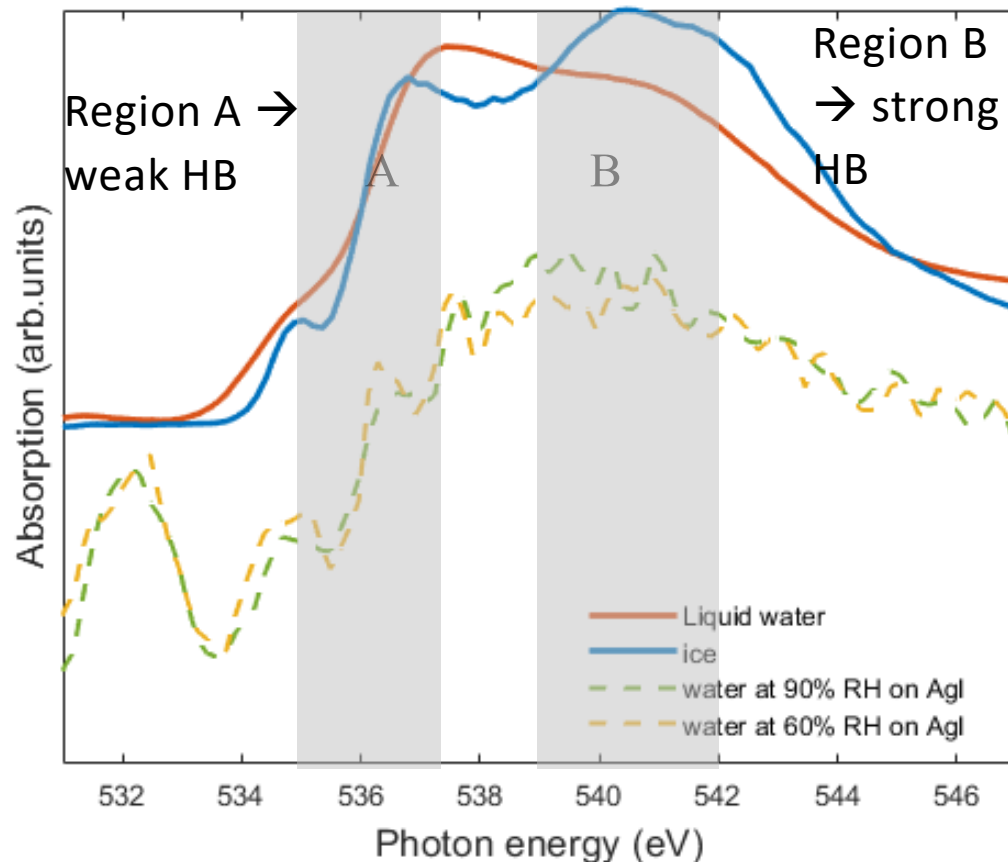


Left: Plot of measured I 3d XPS spectra at dry (purple), 60% RH (orange) and 90% (yellow) at kinetic energy of 340 eV. As the relative humidity increases, the adsorption of water on the AgI surface attenuates the signal of I3d from the bulk.

Corresponding spectra of Iodine 3d show only one single species for AgI, thus, within uncertainty, no dissolved iodide is present at the surface.

This mirrors the low solubility of AgI, no iodide ion is dissolving and migrating into the adsorbed water.

O K edge NEXAFS: Hydrogen bonding structure of water molecules on AgI particle surface

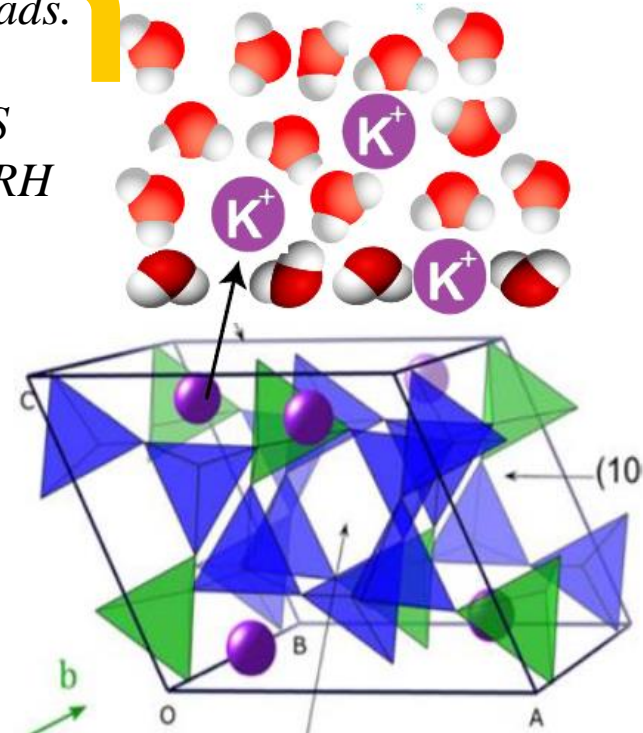
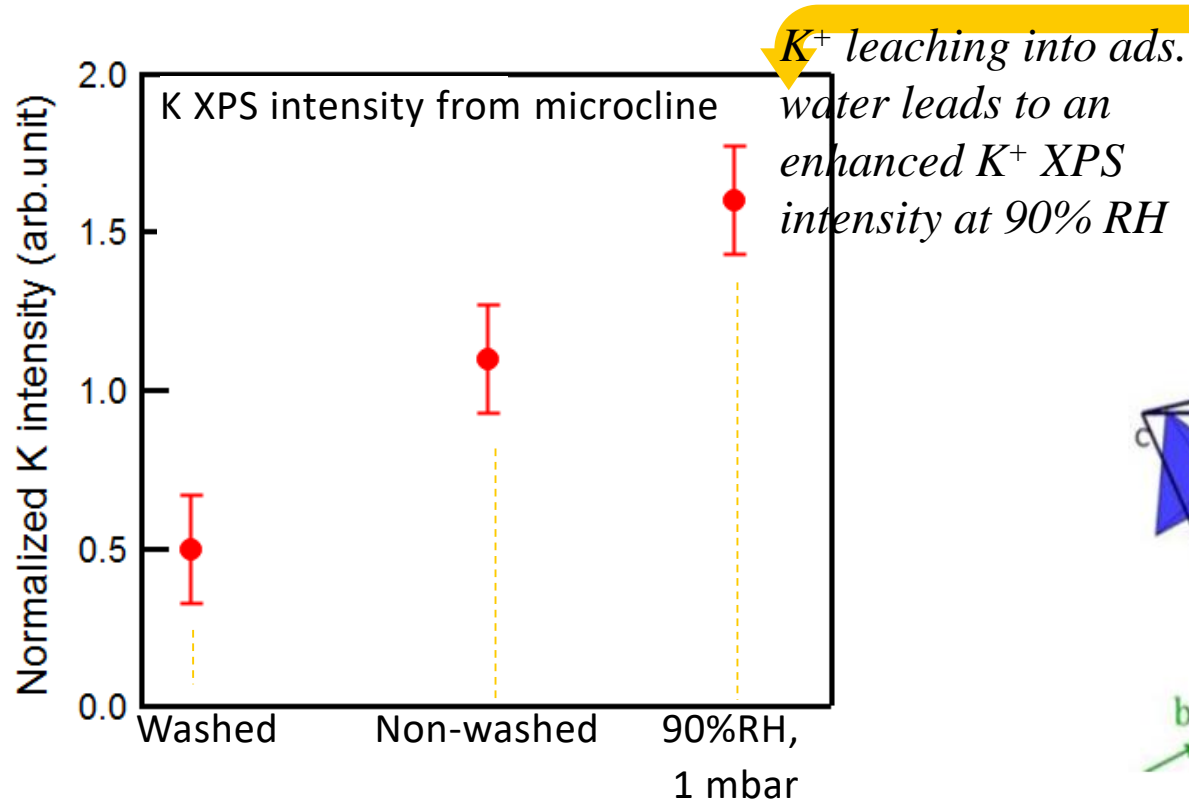


The O K edge NEXAFS of adsorbed water on AgI at 60% RH (-22.3 °C, dashed yellow) and 90%RH(-26.4 °C, dashed green), compared with liquid water (red) and ice spectra (blue).

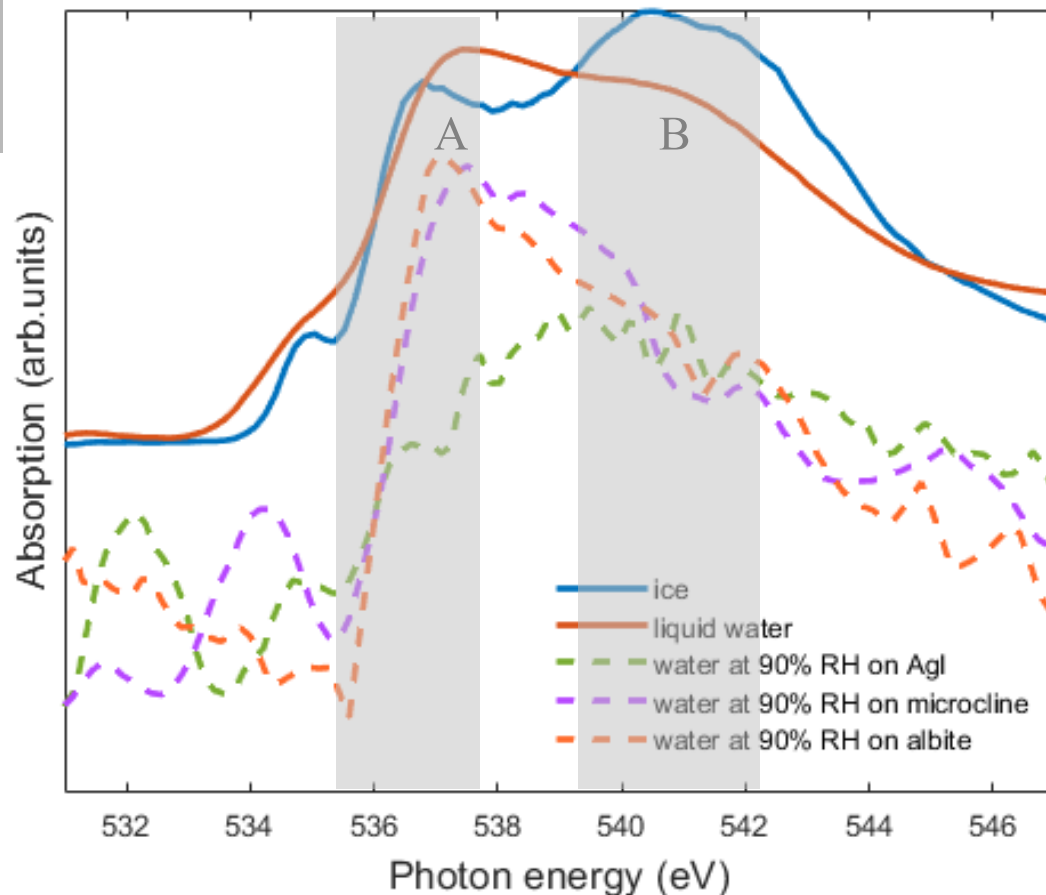
- Adsorbed water molecules on AgI surface exhibit higher portion of tetrahedrally coordinated water molecules, i.e, stronger hydrogen bonding structure.
- The unit cell of ice and silver iodide are both of hexagonal structure, their lattice constant shows a similarity of 98%. This may help to stabilize adsorbed water in a hexagonal ice-like structure.
- The low charge density of Ag and I ions has only a small influence on the coordination of water molecules, so that they can attain the preferred coordination (tetrahedral) at this temperature.

Contrast case: Potassium leaching from microcline

Microcline suspended in water may leach K^+ ion, (Kumar, Marcolli et al. 2018). This eventually influences the hydrogen bonding structure, when a fresh sample is directly exposed to water vapor, due to the relatively large concentration of K^+ ions in the just few layers of adsorbed water. Our sample after washing in water shows a decreased K level, this further confirms the K leaching of the microcline.



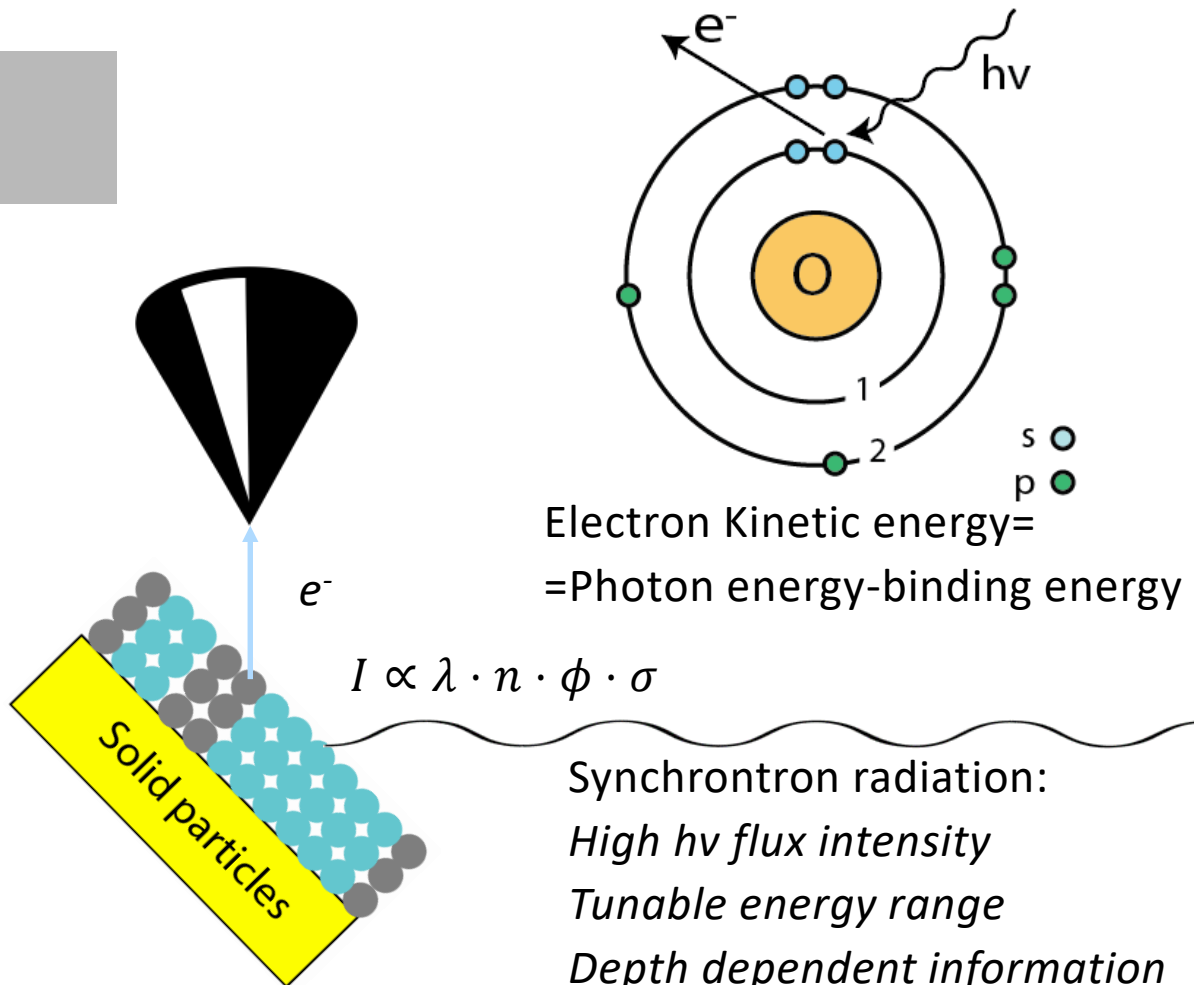
Adsorbed water on albeit and microcline



The O K edge NEXAFS of adsorbed water of adsorbed water at 90% RH for AgI (dashed blue), albite (dashed red) and microcline (dashed purple) surface, compared with liquid water (red) and ice spectra (blue).

- O K edge NEXAFS of adsorbed water on albite particles (dashed red) shows the highest relative contribution for weak hydrogen bonding (region A), thus exhibits rather liquid-like character.
- This is in contrast to AgI, where the maximum is indicating a predominance of tetrahedrally coordinated water molecules.
- Literature suggests that microcline is a better INP than albite. However, their adsorbed water spectra are similar, the small difference (between dashed purple and red) is probably not beyond uncertainty. The spectrum of adsorbed water is liquid-like for both, probably dominated by the ion-leaching. Analysis of washed samples are ongoing.

Methodology: X-ray Photoemission Spectroscopy and O K edge NEXAFS



Method 1 → XPS:

Surface sensitive (1-5nm)

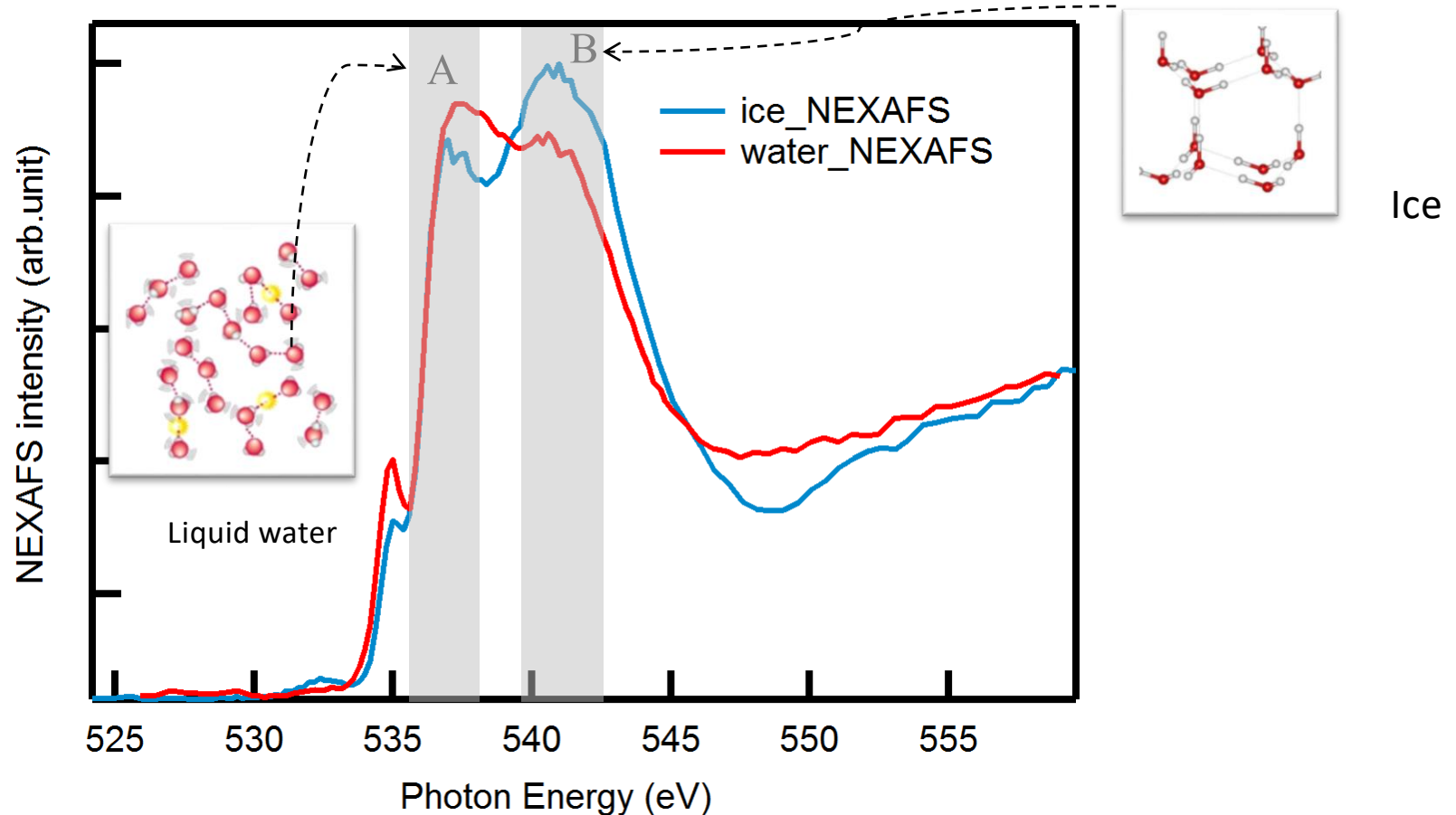
Quantitative elemental
ratio analysis

Method 2 → O K edge

NEXAFS:

Probes the lowest
unoccupied molecular
orbital (LUMO) → Sensitive
to the local hydrogen
bonding between water
molecules

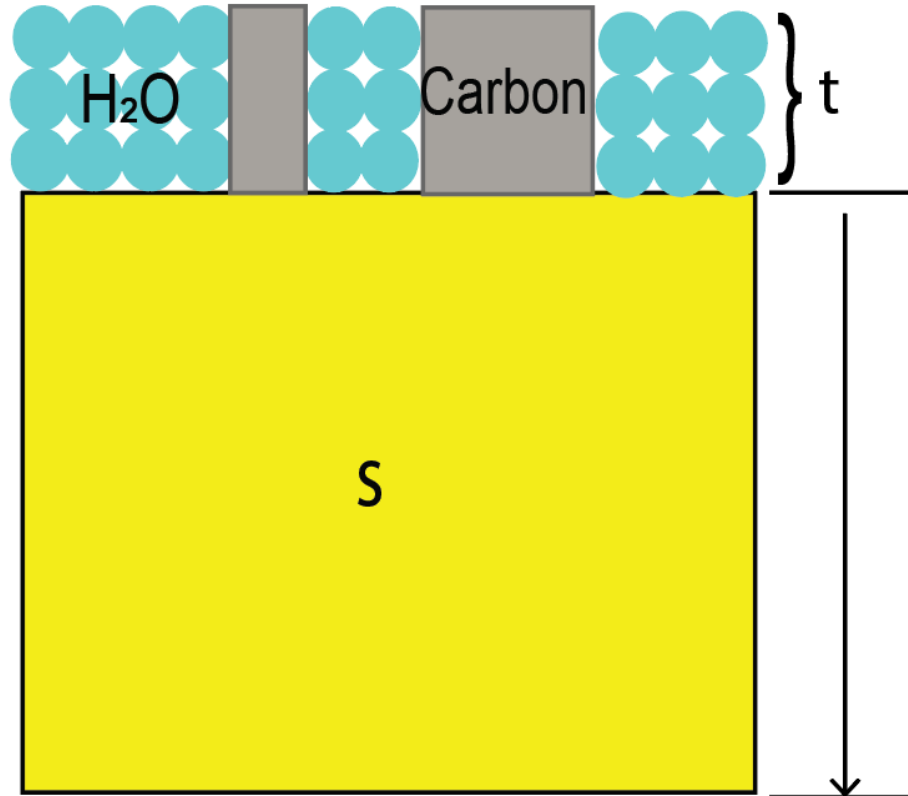
O K edge NEXAFS reference: Liquid water and Ice



- The absorption edge at the **region A** (537-538 eV) is dominated by the weak hydrogen bonds, this feature is very pronounced in **liquid water**.
- The strong hydrogen bond between two water molecules appear at **region B** (540-541 eV) peak, this feature is more pronounced in **ice**.

Patched carbon model

- Adventitious carbon is inevitable for solids material.



On the surface of solid substrate, the adsorbed water increase the thickness by t , mixed with adventitious carbon generated in situ (same height with water).

$\gamma \rightarrow$ percentage of carbon as islands on the solid surface

N_c : carbon photoemission intensity

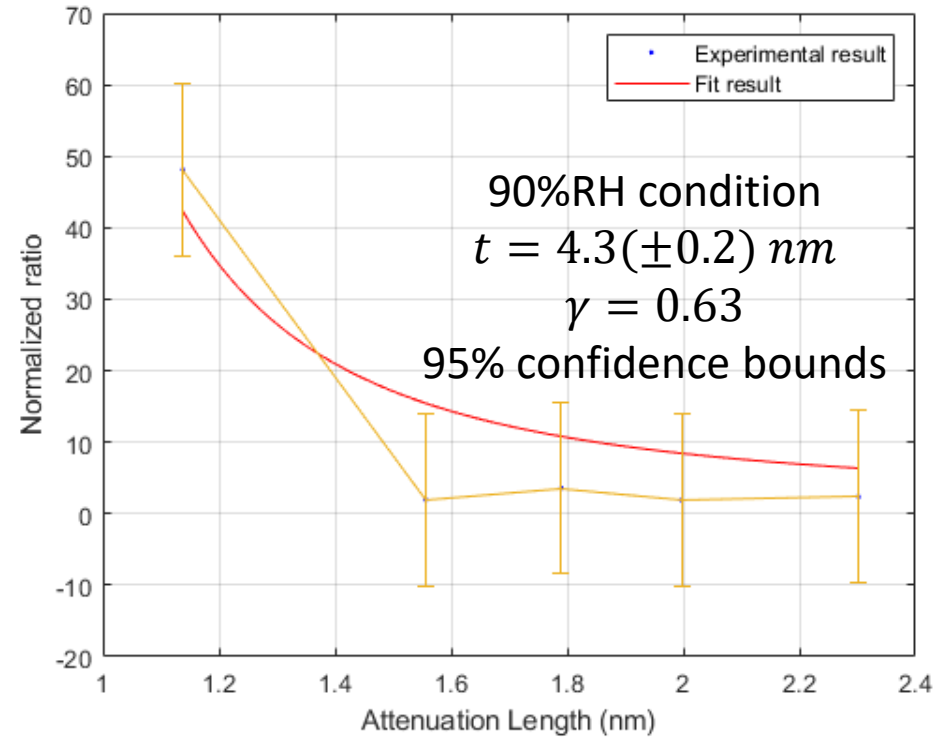
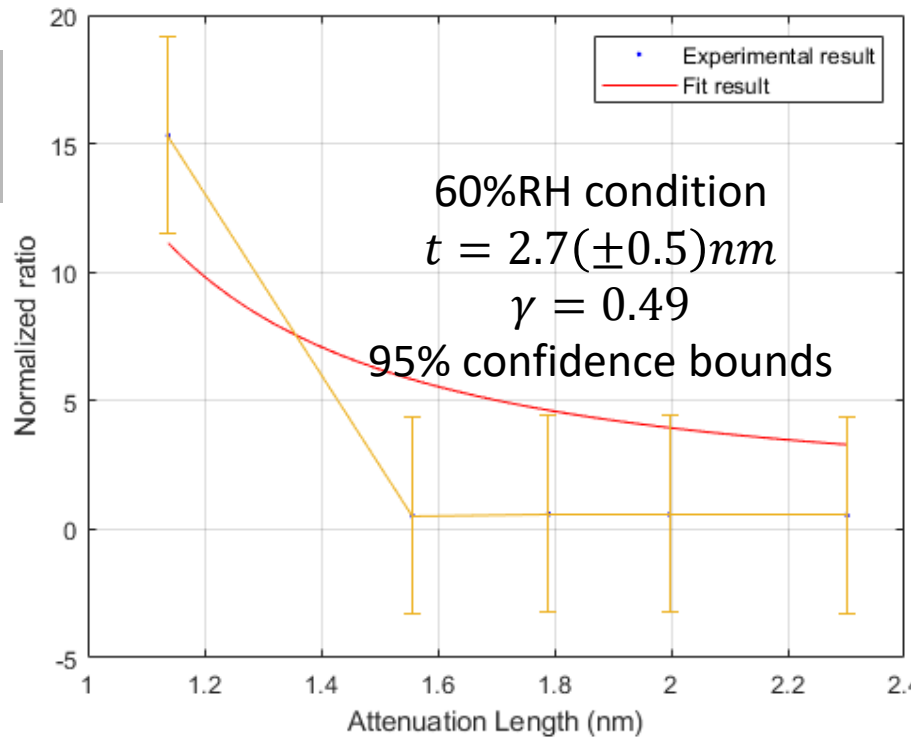
N_s : photoemission intensity from the substrate

$\lambda_a \cdot \cos \theta$: attenuation length

photoemission intensity ratio between carbon on surface and any element from substrate

$$\frac{N_{\text{carbon_patched}}}{N_{\text{Substrate_patched}}} = \frac{N_c}{N_s} \frac{1 - \exp\left(-\frac{t}{\lambda_a \cdot \cos \theta}\right)}{\frac{(1 - \gamma)}{\gamma} + \exp\left(-\frac{t}{\lambda_a \cdot \cos \theta}\right)}$$

Depth profile of adsorbed water on AgI → Water molecules thickness



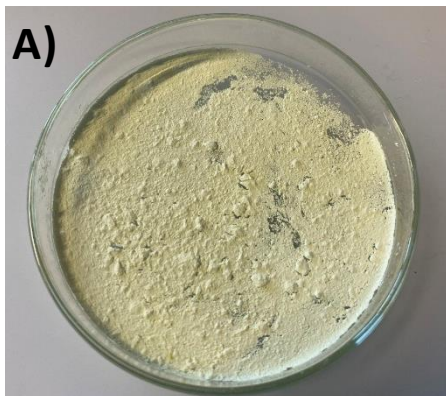
Normalized ratio between the photoemission intensity of O1s from adsorbed water and I3d ($O1s_{ads}/I3d$), measured with 5 different probing depths is monitored by XPS.

Using the overlayer attenuation model, coupled with the patched carbon model. We have determined the thickness of adsorbed water and the carbon portion on the surface.

Sample material preparation

Agl

1. 10ml of KI+ 10ml AgNO₃ +80ml H₂O
2. Precipitates forms, wash with water and centrifugate after ~15h
3. Dry in 150 °C for about 3h and then cool down at 0.3 K/min to room temperature. (Maximize the formation of β phase AgI).



A): AgI, Bright yellow solid
Highly photosensitive



Feldspar

Feldspar sample are purchased from the Bureau of analysed sample Ltd.

The original sample is a finely divided sand-like material passing a nominal 250 micron aperture sieve.

In order to obtain a powder sample that is suitable for our experiment, the feldspar sample was milled using a ball milling machine for 5 minutes and then sieved through a mesh with 64 μ m aperture.

B) *The powder sample of microcline (white circular part) on our photoelectron spectroscopy sample holder, prepared by droplet of feldspar milled powder in isopropanol suspension.*

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