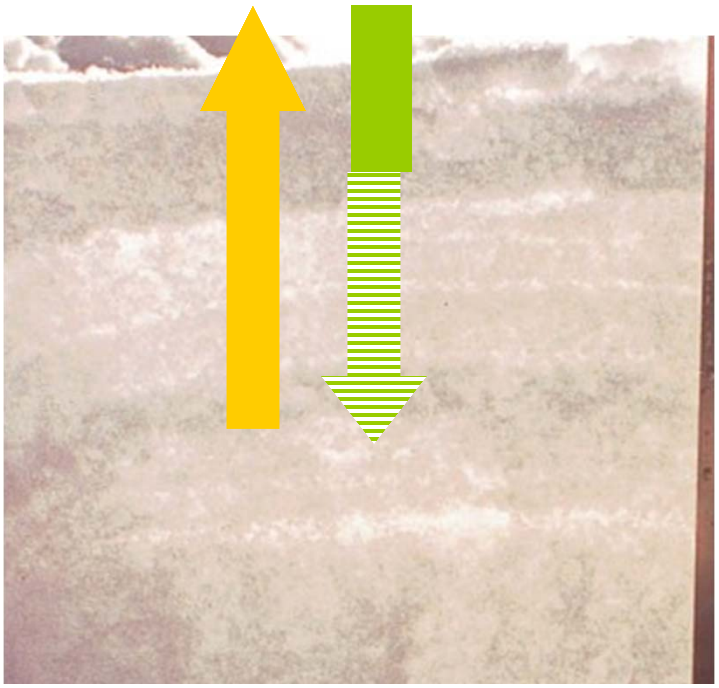
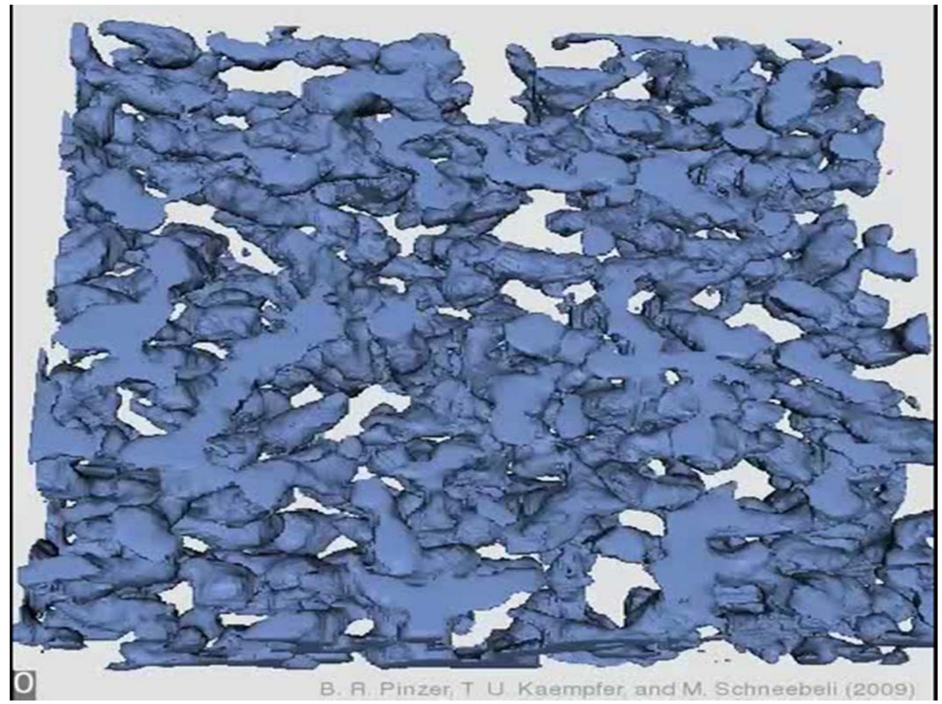
Wir schaffen Wissen – heute für morgen

Paul Scherrer Institut
Markus Ammann

The ice - air interface in snow - the molecular to micron scale perspective



Transport processes in and out of snow: Thorsten on wednesday



Snow metamorphism: Thomas Kaempfer will dicuss this wednesday

Foto: www.powderguide.com

(Q)L(L) are

…. called like that for lack of better term (Paul)

Projection of unknown unknowns

Medium to assist modelling snowpack chemistry as aqueous phase chemistry in a ‚well defined‘ solution reservoir.

Remaining liquid after precipitation of ice upon freezing a solution

Reasonably well understood as surface premelting for pure ice

Several models suggested for thermodynamics of solute affected QLL

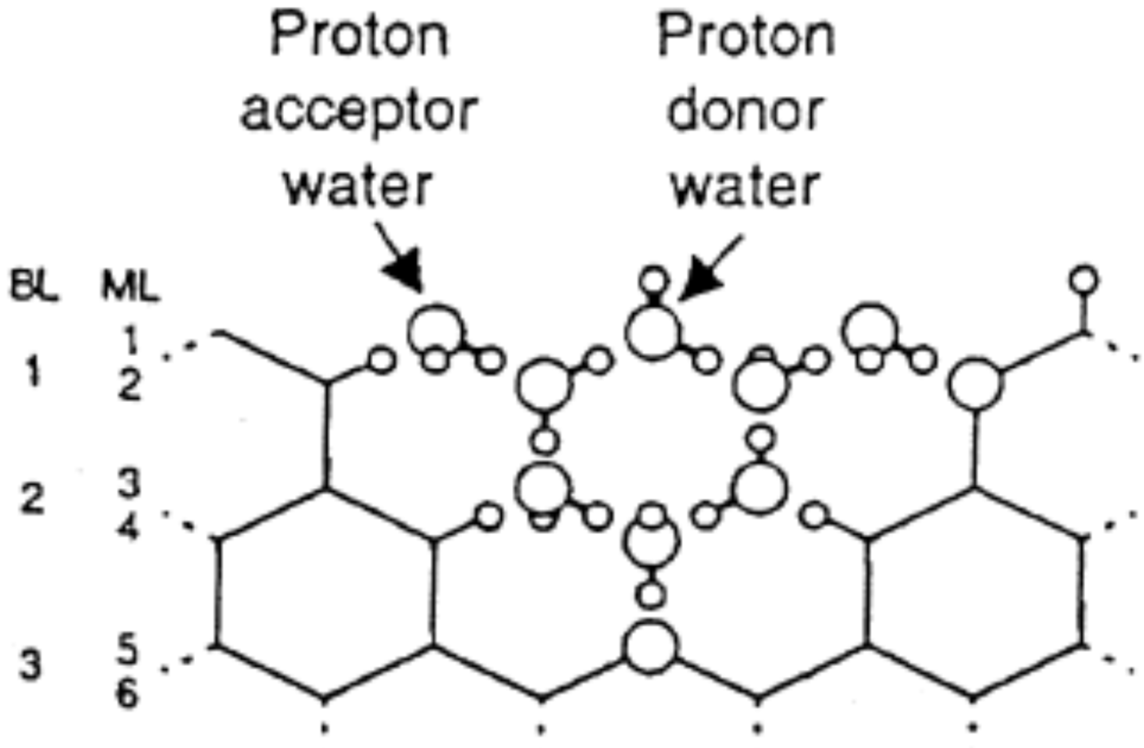
Significant body of literature of freeze/concentration experiments

Is there liquid beyond that expected as pure ice QLL plus stable (thermodynamic) solutions of solutes ?

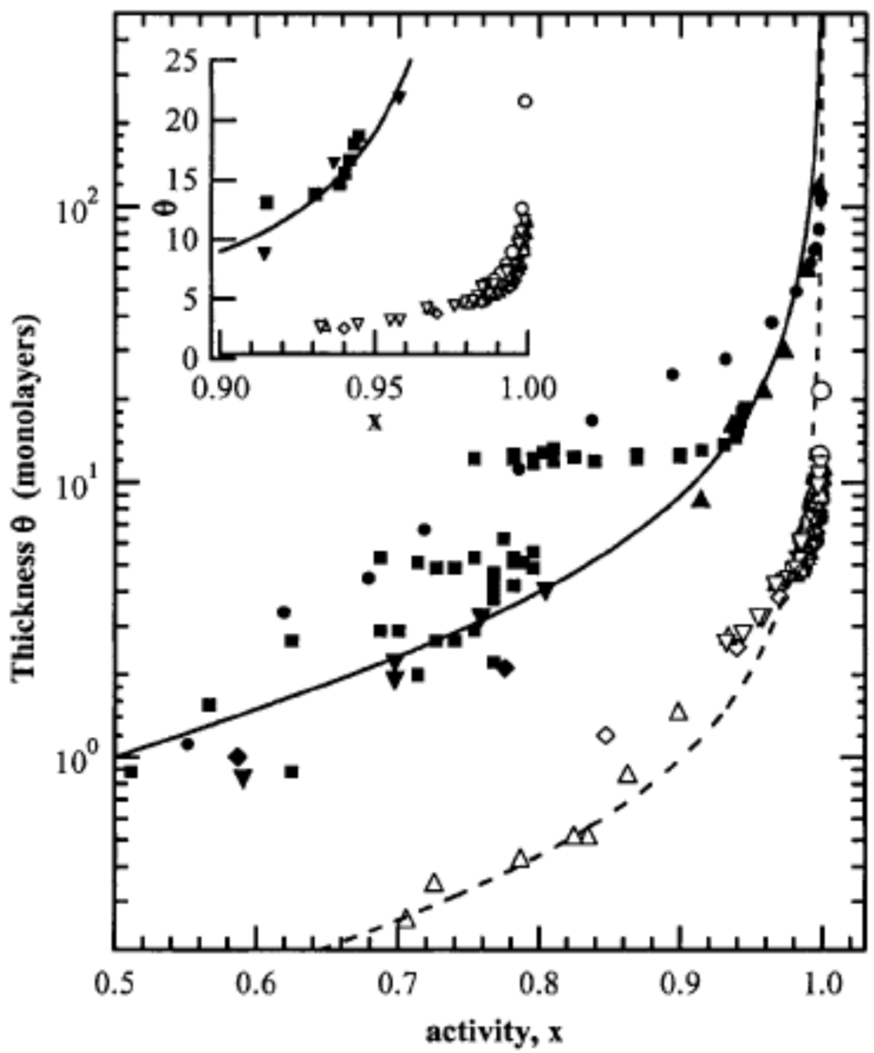
Is there chemistry in the presumed QL that is not due to the purely ‚physical concentration‘ effect?

How important is differentiating between surface and bulk?

Ice surface



General view of surface premelting

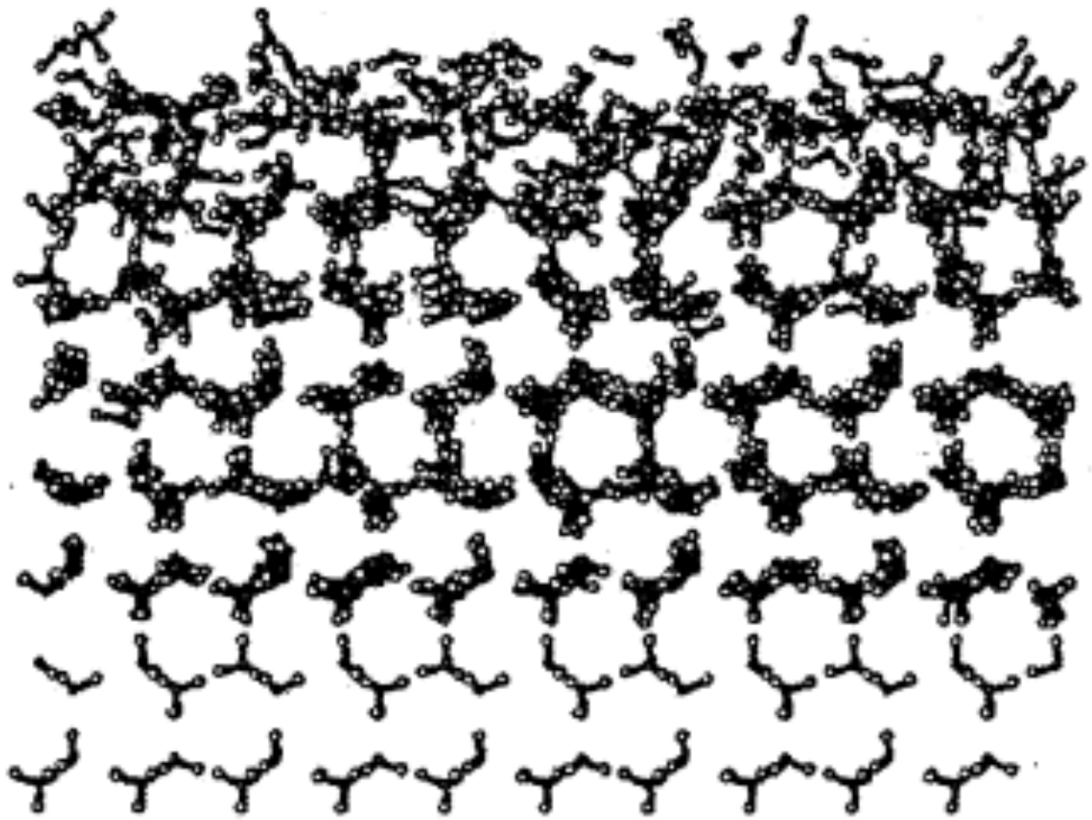


$$x = \frac{P_{sol}}{P_{liq}} = \exp\left[-\frac{\Delta H_{fus}}{R}\left(\frac{1}{T} - \frac{1}{T_t}\right)\right].$$

- General relation between thermodynamic activity and thickness of QLL
- Knowing the triple point temperature and the enthalpy of fusion allows predicting the QLL thickness
- Different behaviour of atomic solids (e.g., Ar, Al, Pb,…) as compared to molecular materials (O_2, organics…)

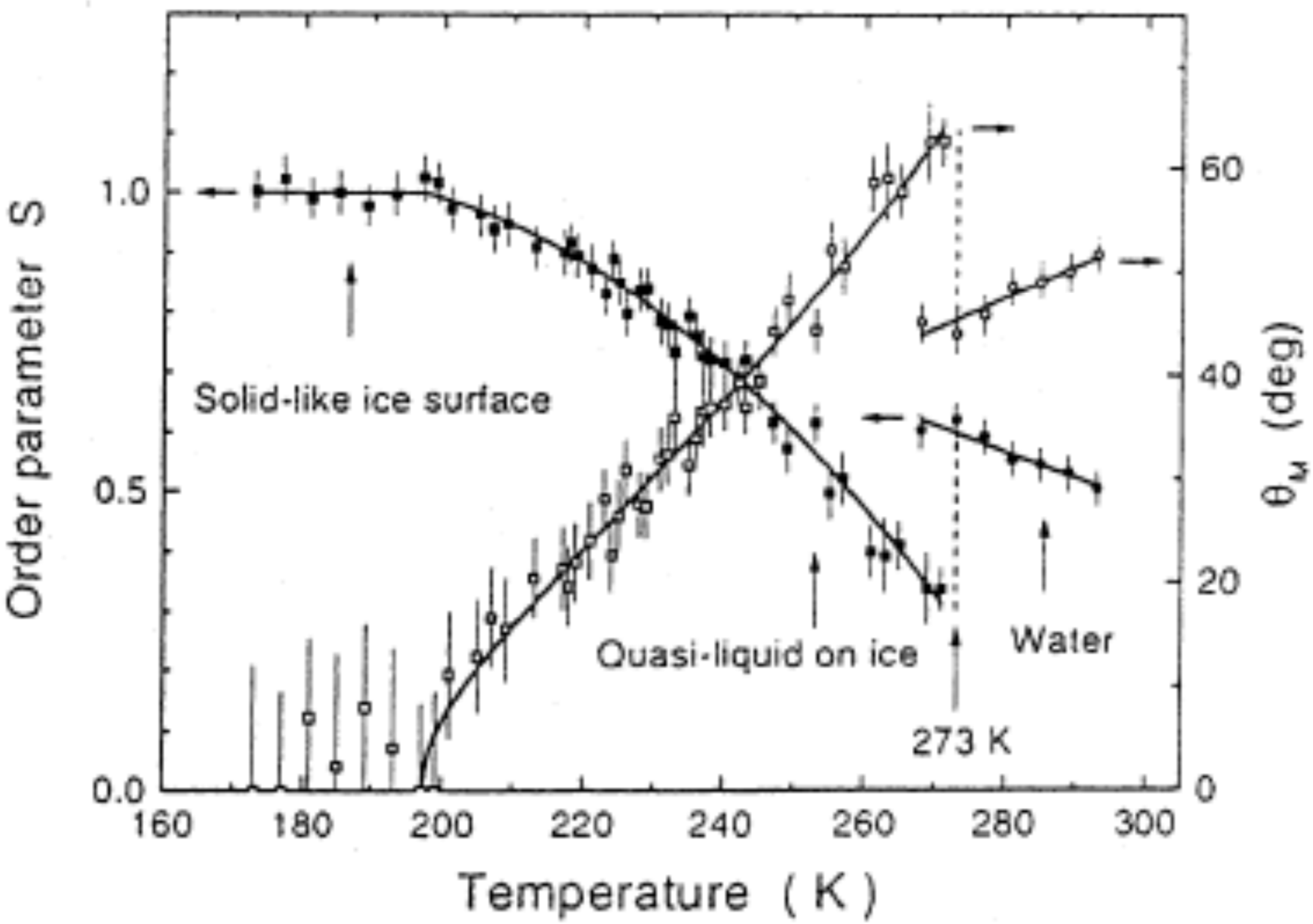
Henson et al., 2004

Molecular dynamic simulation of ice at 235 K



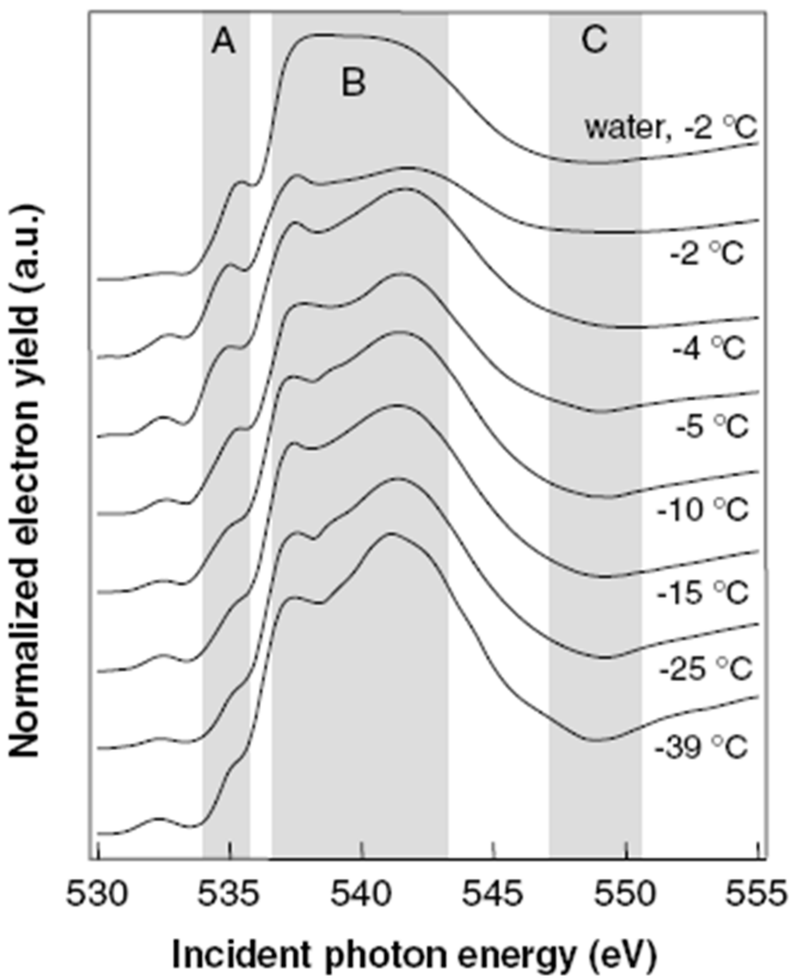
Girardet and Toubin, 2001

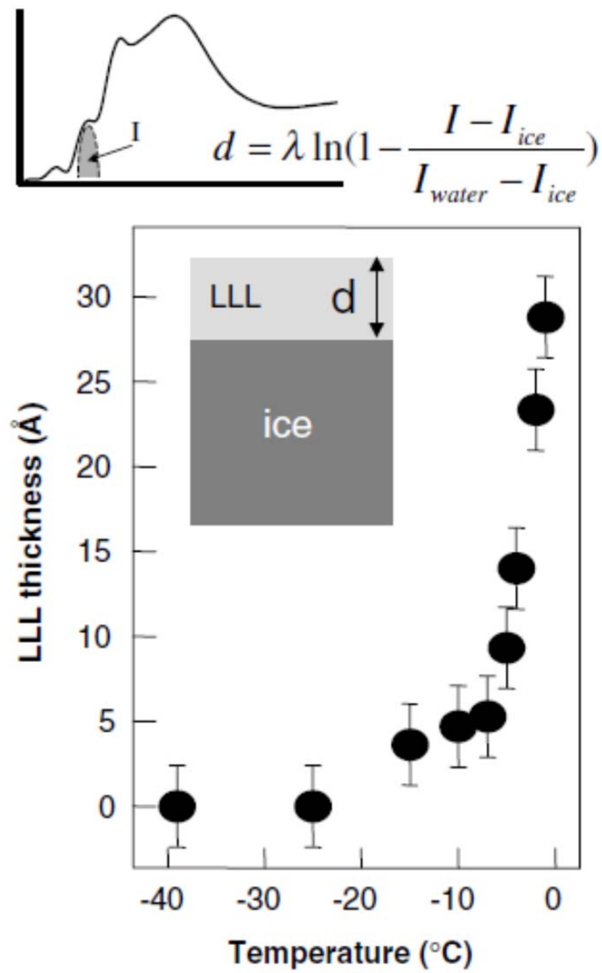
The QLL is a surface phenomenon



Wei et al., 2001

The ice QLL as seen from electron yield NEXAFS

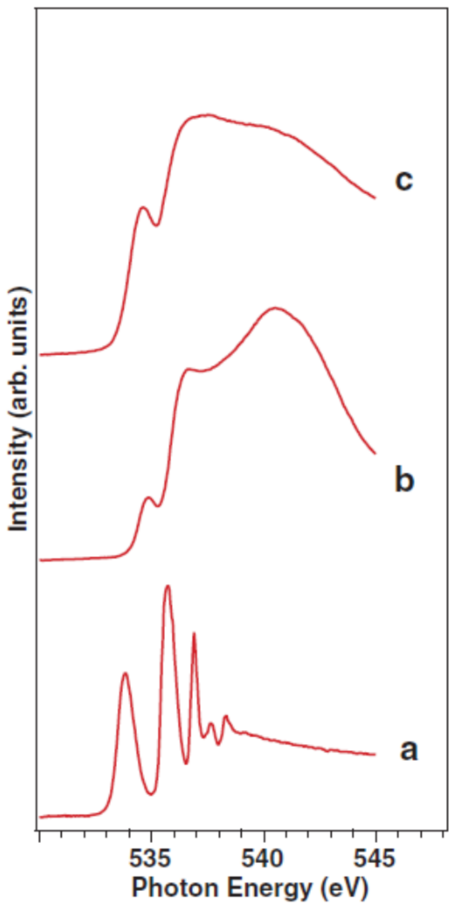




Bluhm et al.: J. Phys.: Condens. Matter **14**, L227 (2002).

NEXAFS

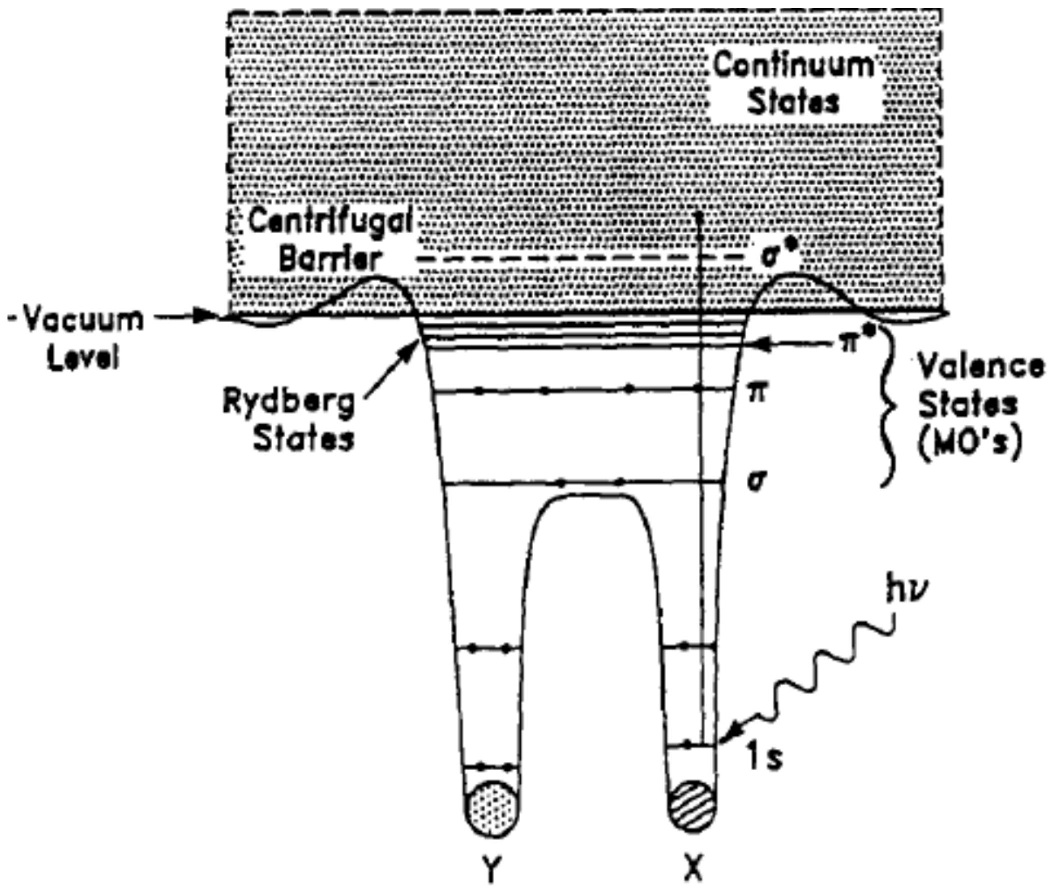
- XANES/NEXAFS (X-ray absorption near edge structure) probes density and orientation of unoccupied valence levels, thus sensitive to electronic and structural properties



Liquid water

Ice

Gas phase water

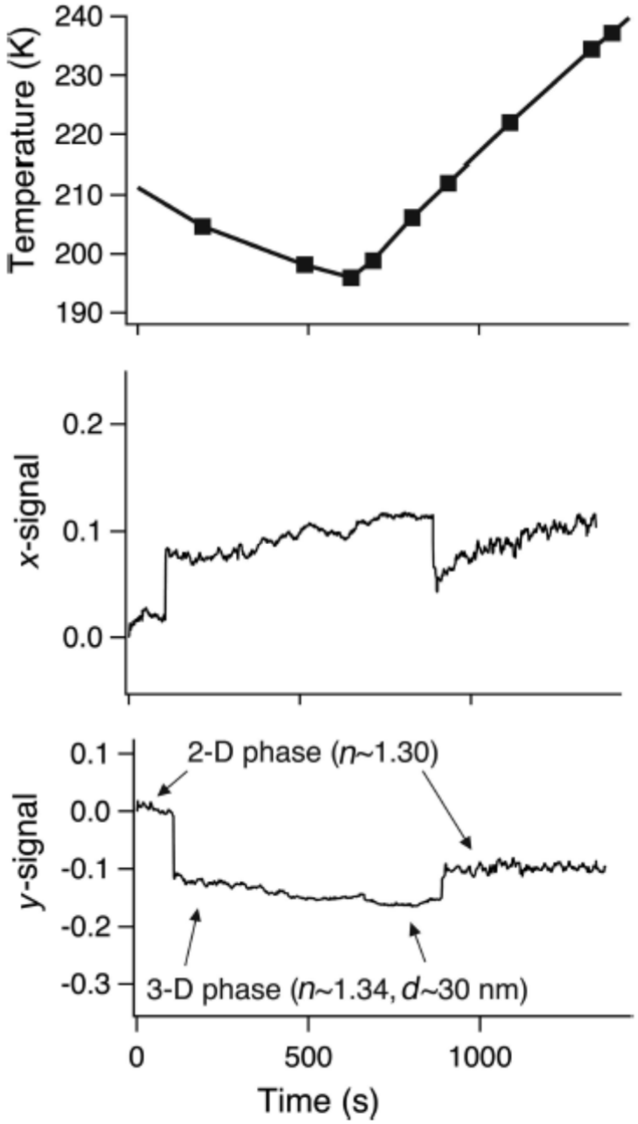


Myneni et al. (2002)

J.G. Chen: Surf. Sci. Rep. 30, 10 (1997).

PAUL SCHERRER INSTITUT PSI

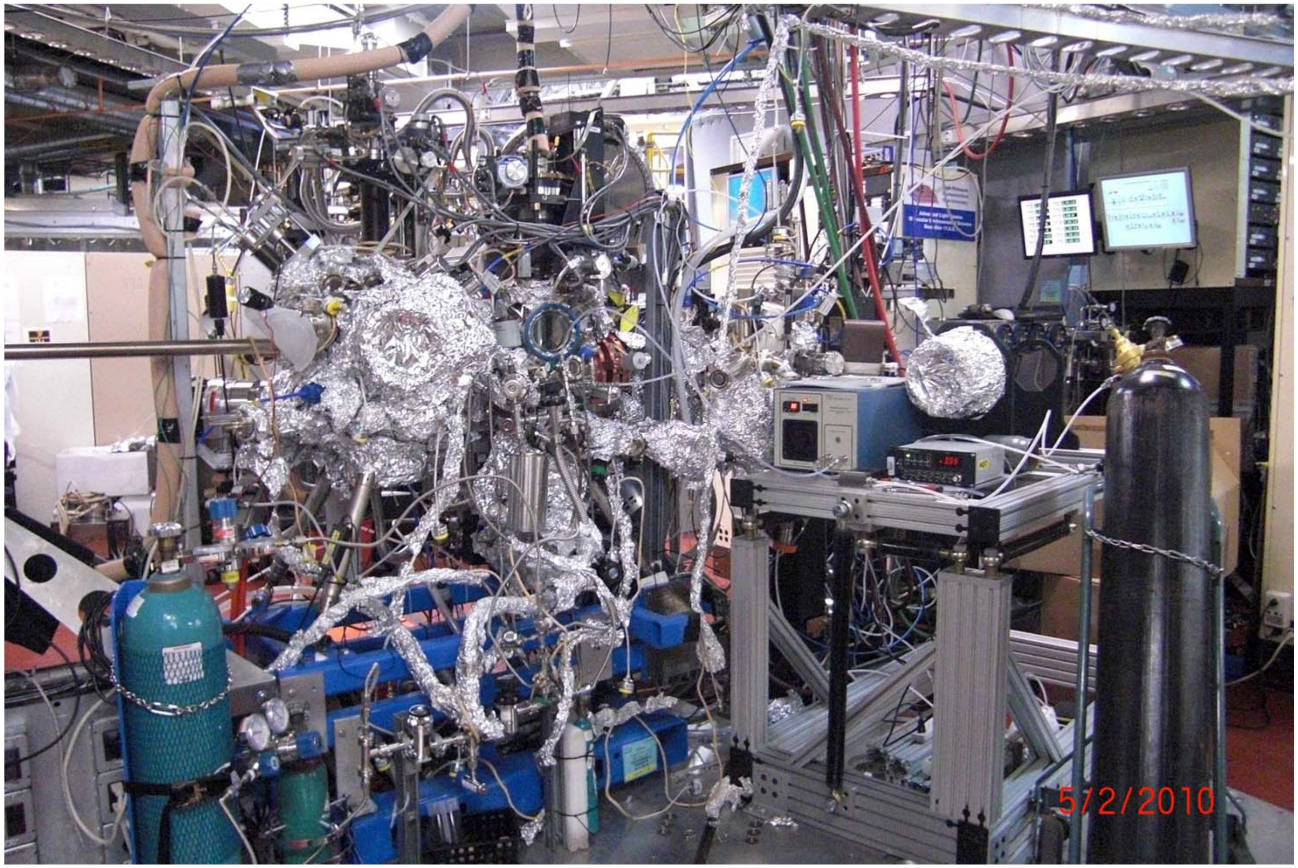
Elipsometry



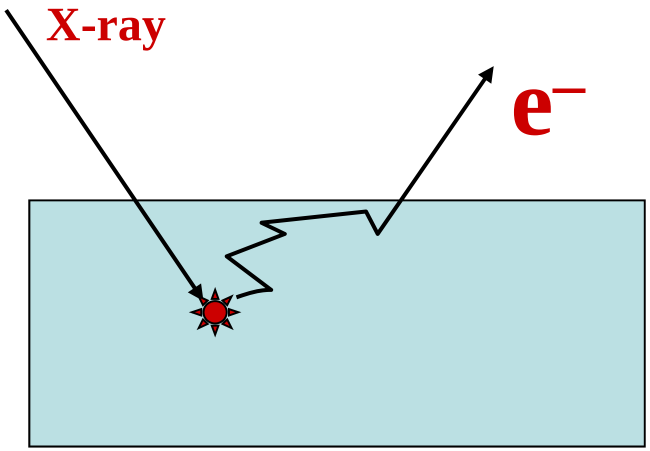
Formation of up to 30nm thick layers under conditions where thermodynamics would not predict a separate phase (HCl / ice).

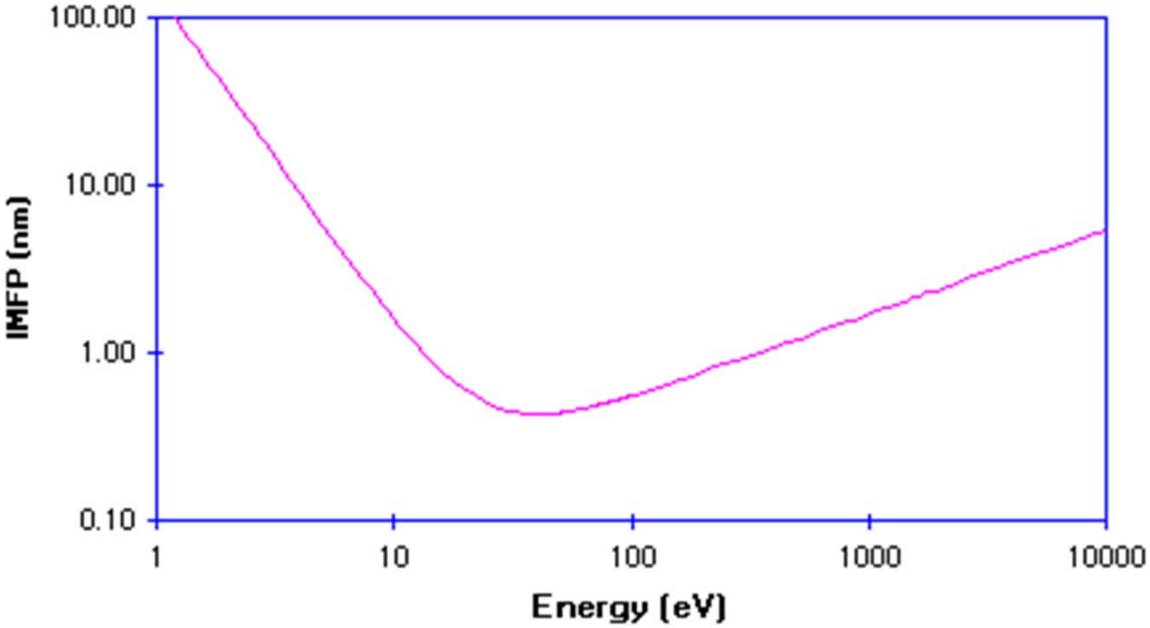
McNeill et al. (2006, 2007)

Trouble in the laboratory



X-ray photoelectron spectroscopy

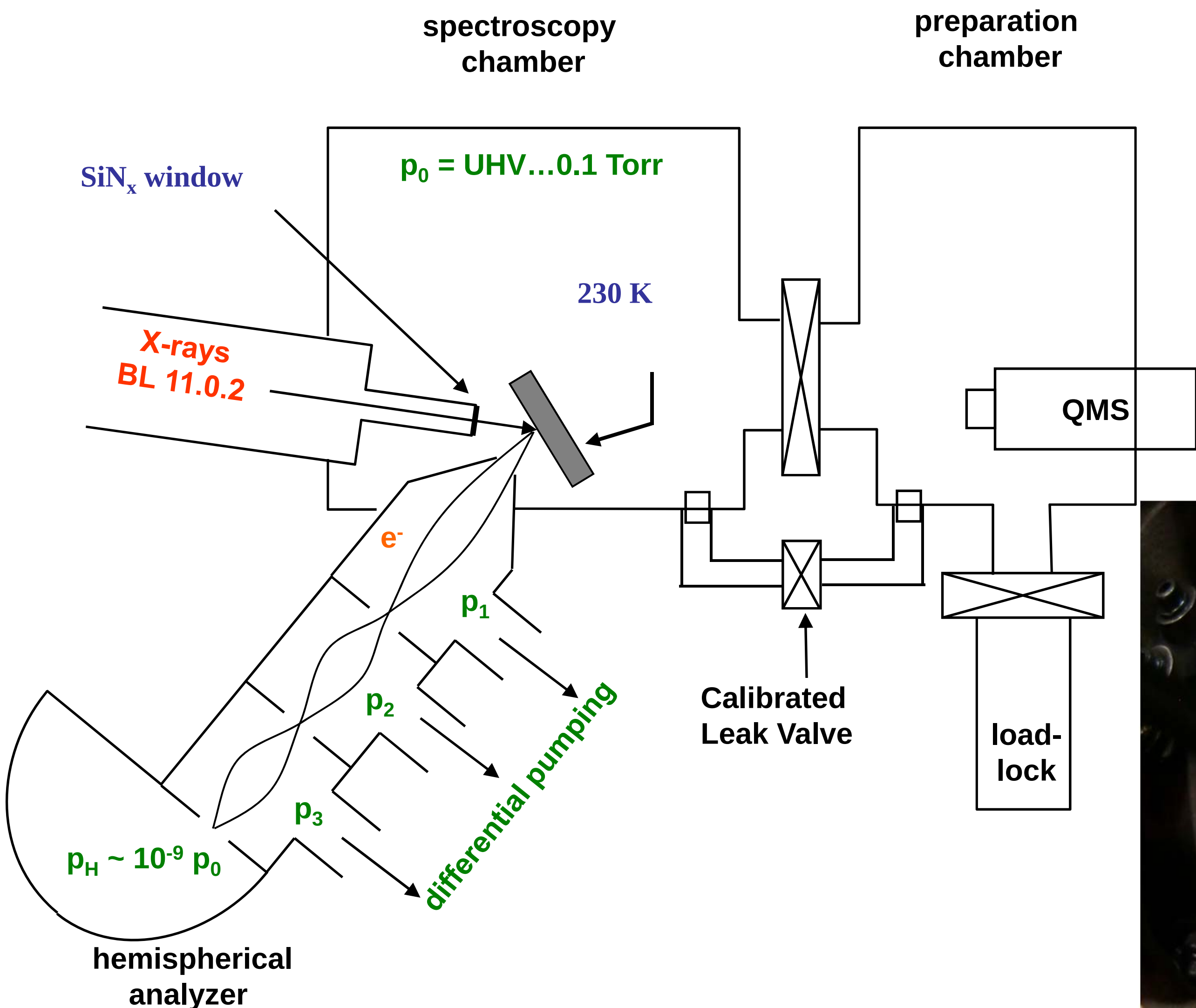


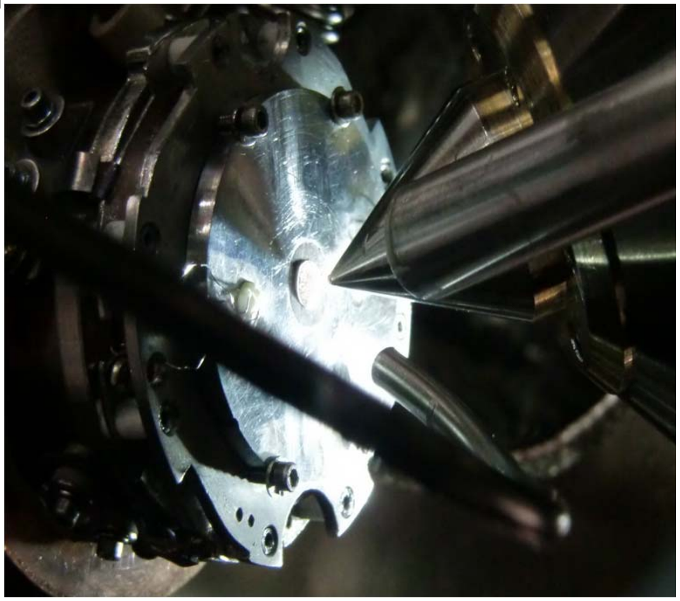


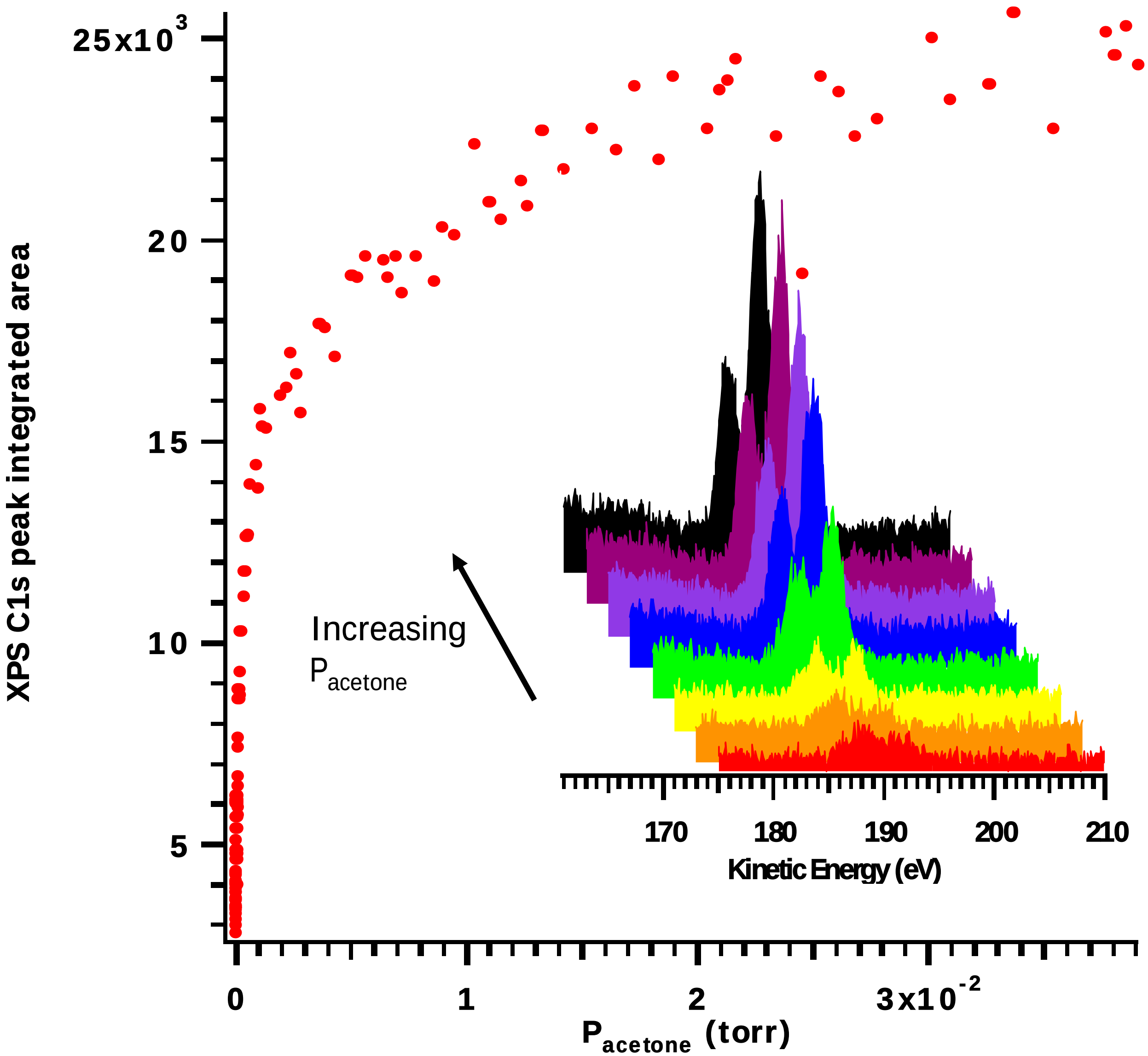
Loss of electrons due to inelastic scattering of the photoelectrons

- Inelastic mean free path is a strong function of kinetic energy.
- Molecular scale surface sensitivity
- Probing depth varies with kinetic energy.
- Depth profiles can be obtained by varying the incident photon energy with a tunable X-ray source, i.e., at a synchrotron

Ambient pressure X-ray photoelectron spectroscopy





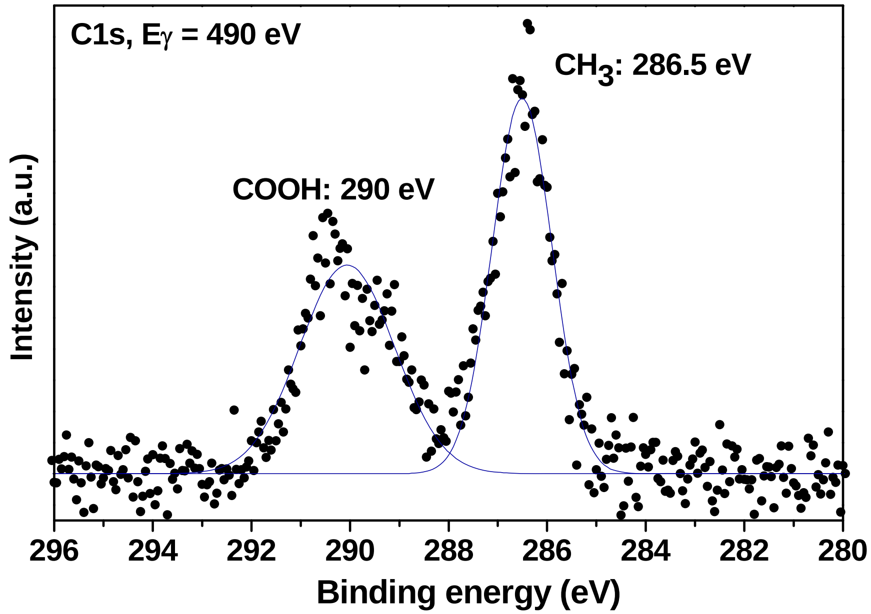


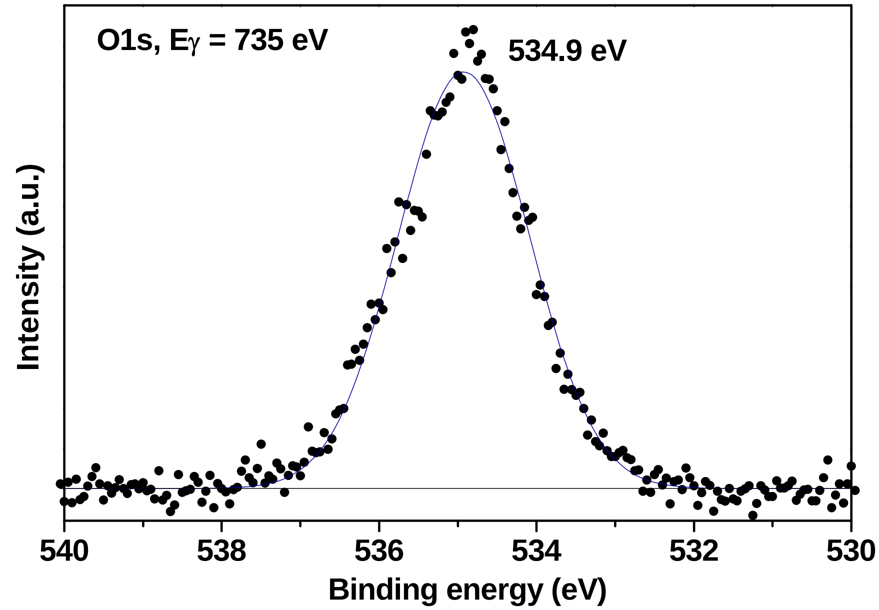
Starr et al. (2011)

XPS of acetic acid on ice: O1s, C1s

- **C1s**
  1 Torr, -39° C
  2 peaks, $PA(CH_3)/PA(COOH) = 1$
  literature BE of CH_3: 285 eV
  Δ BE: 3.5 eV

- **O1s**
  1 Torr, -39° C
  1 peak, no differentiation between oxygen from ice and AA

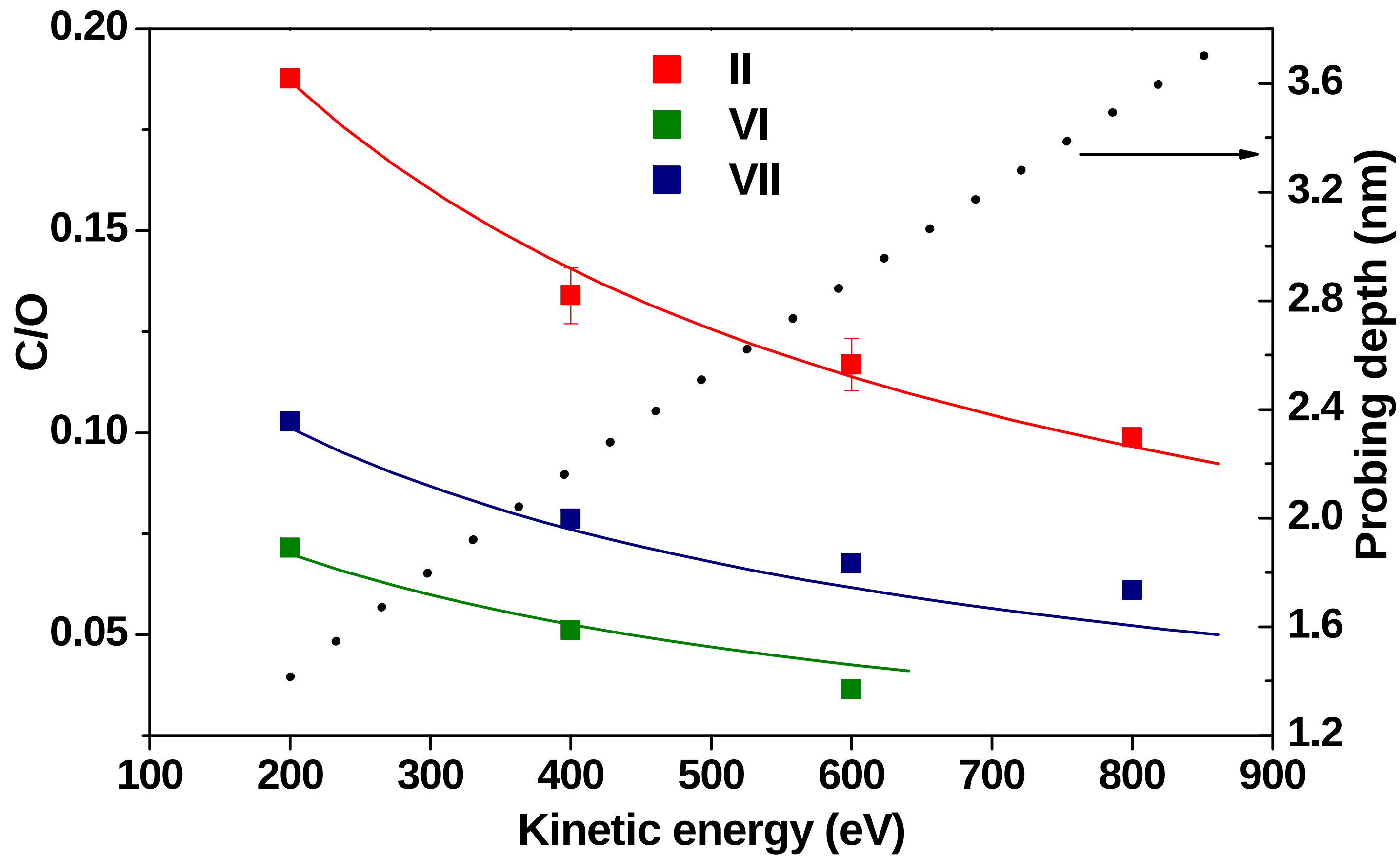




C/O ratios scale with intended pressure of acetic acid
Krepelova et al., in preparation

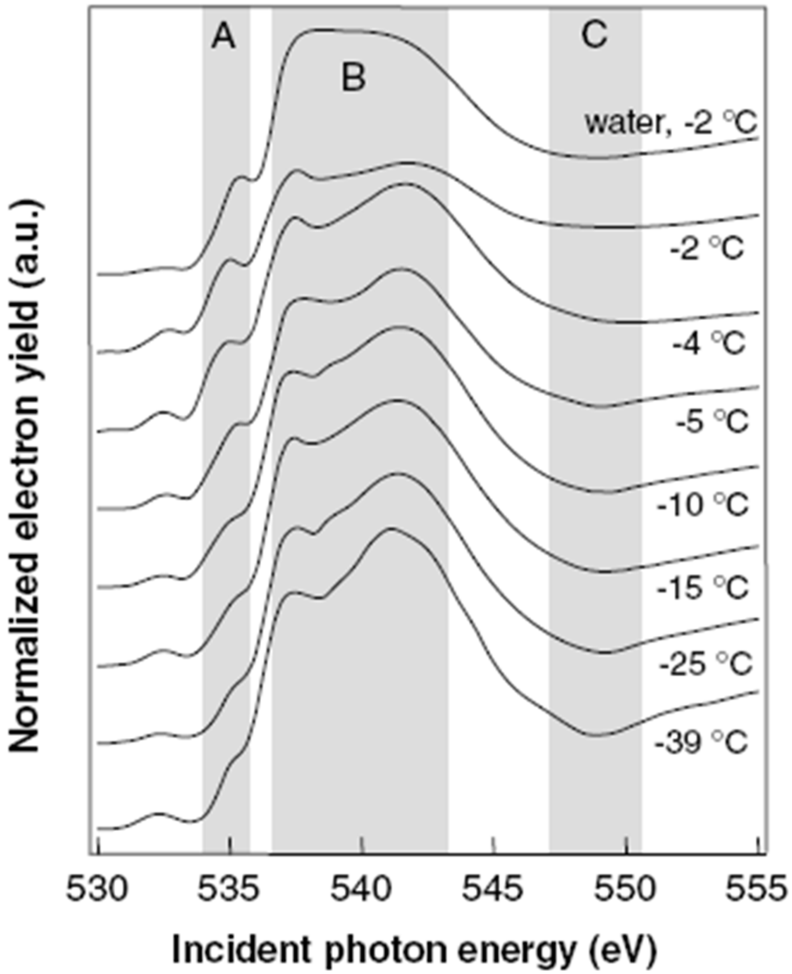
PAUL SCHERRER INSTITUT

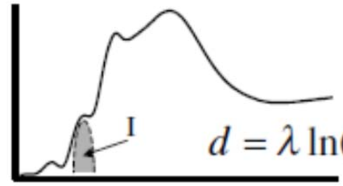
Acetic acid on ice: Depth profile measurements



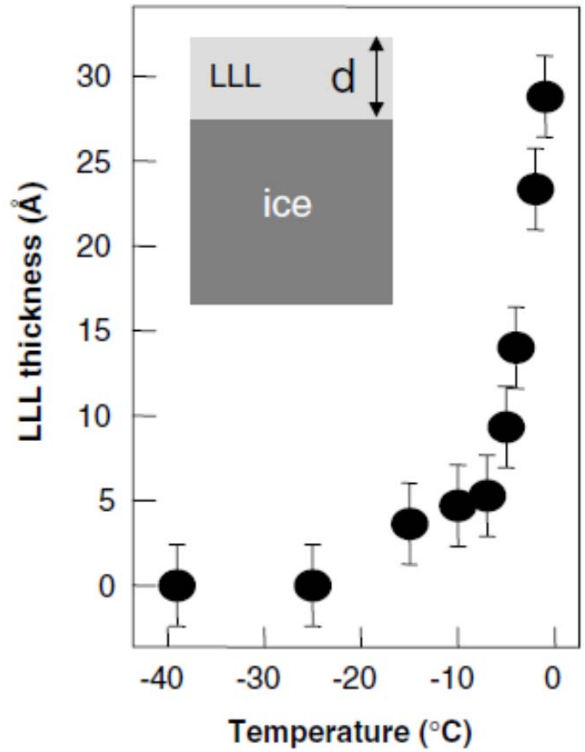
Acetic acid residing on the ice surface only (Krepelova et al., in preparation)

The ice QLL as seen from electron yield NEXAFS





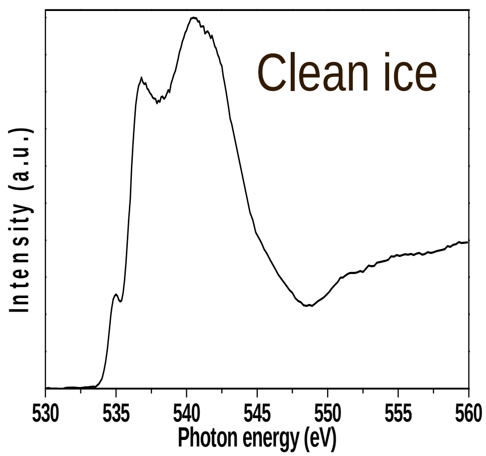
$$d = \lambda \ln\left(1 - \frac{I - I_{ice}}{I_{water} - I_{ice}}\right)$$

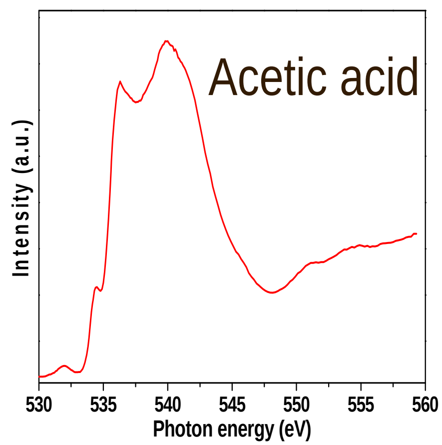


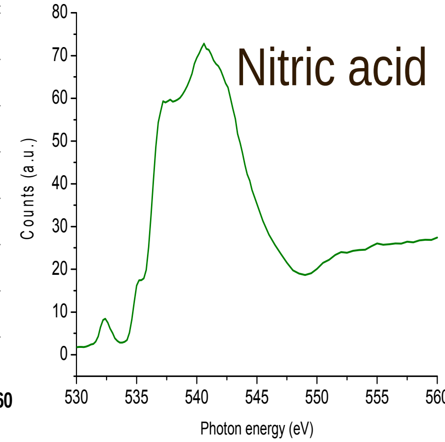
Bluhm et al.: J. Phys.: Condens. Matter **14**, L227 (2002).

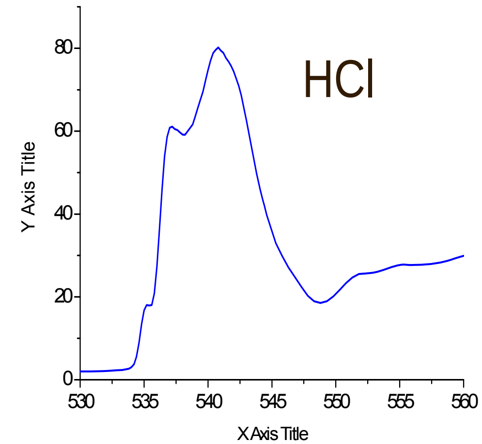
Solution at the ice surface in presence of soluble adsorbates?

230 K

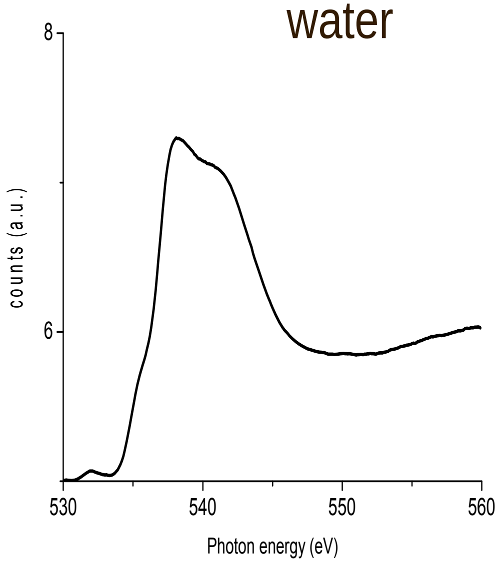




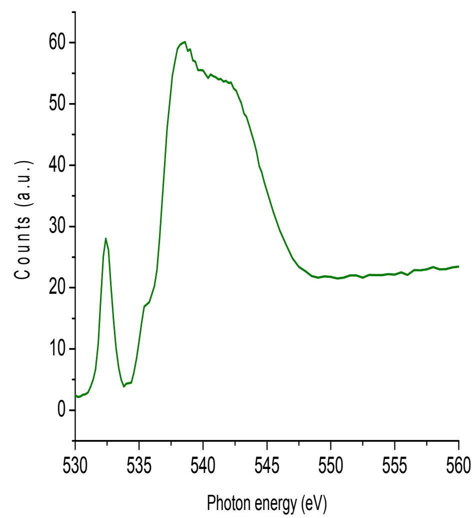




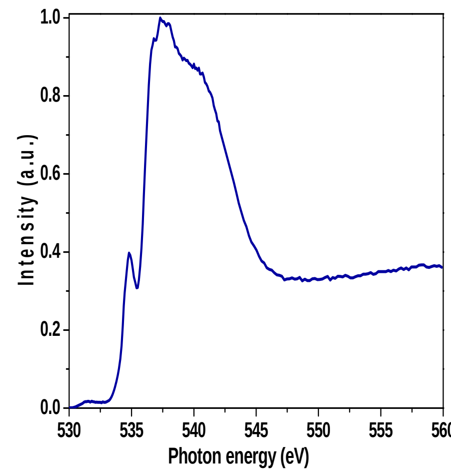
water



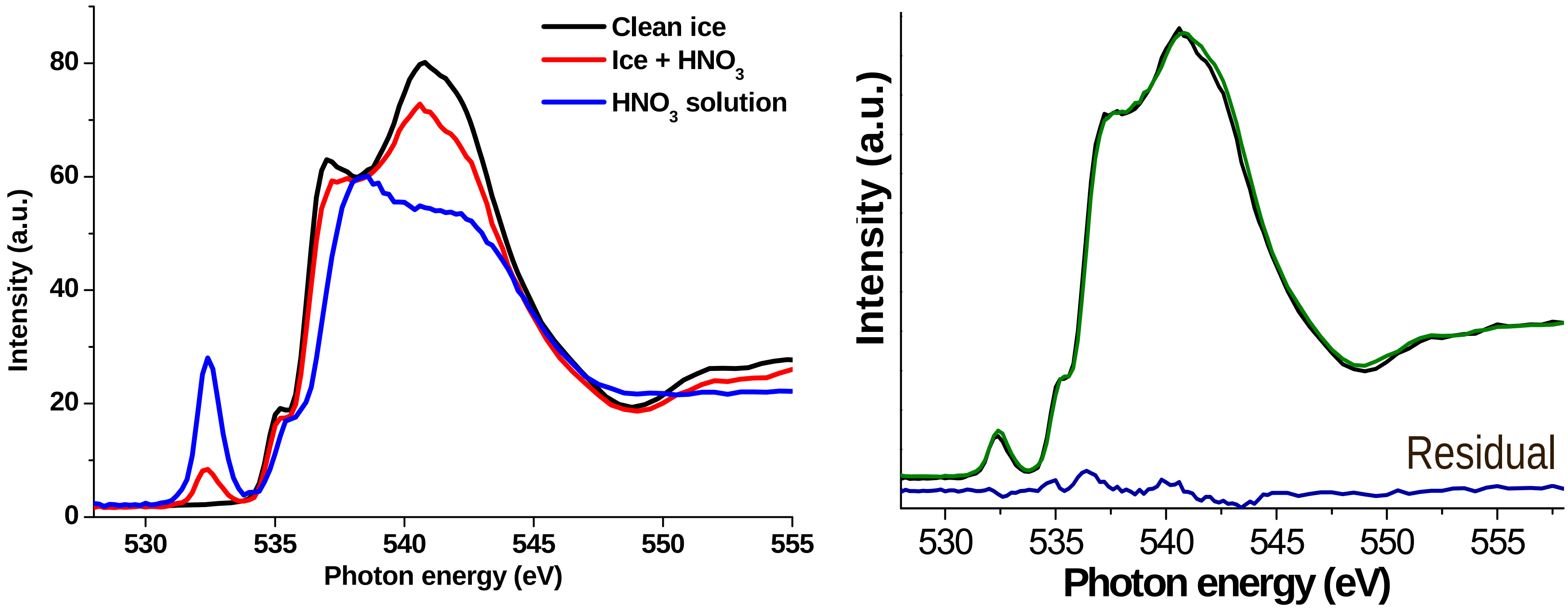
HNO_3 solution



NaCl solution 256 K



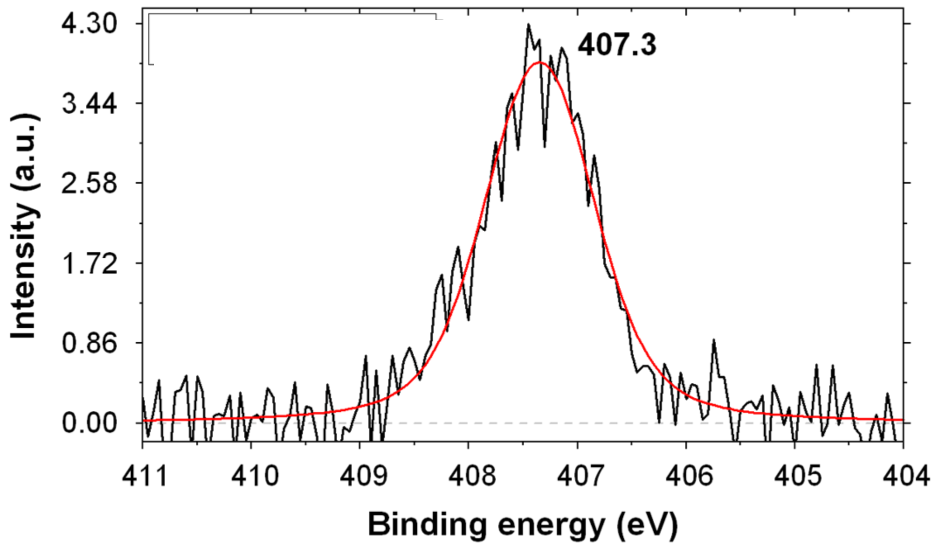
Nitrate on ice : superposition of ice and nitrate solution



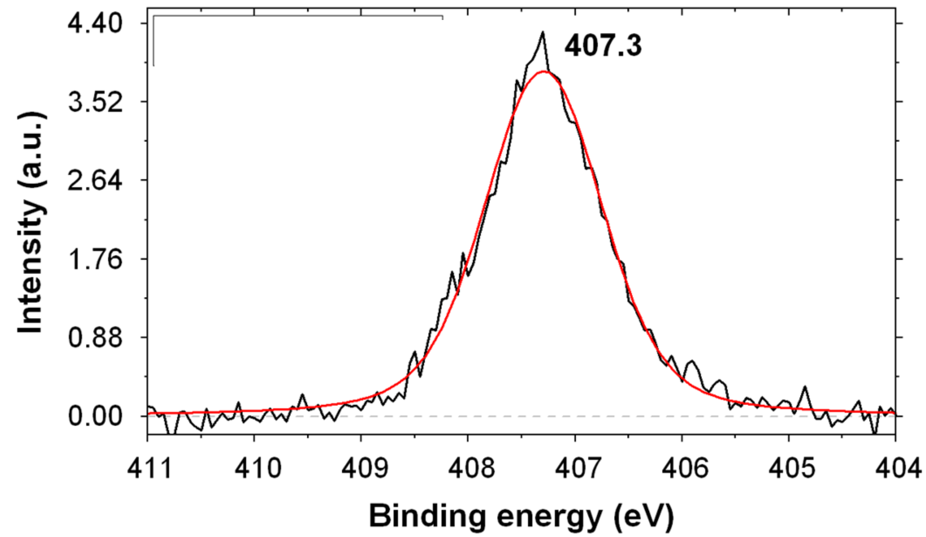
- Oxygen K-edge NEXAFS spectra of ice with nitrate
  ≈ 20% nitrate solution spectrum + 80% clean ice spectrum
- Within the probing depth of about 2.4 nm, 20 % of H_2O molecules are engaged in hydrating nitrate (about 5 H_2O per nitrate ion), and 80% are ‚affiliated' with ice
- NEXAFS is a local probe, no information about long range order.

Krepelova et al., Phys. Chem. Chem. Phys., 2010

Nitrate at the ice surface: XPS



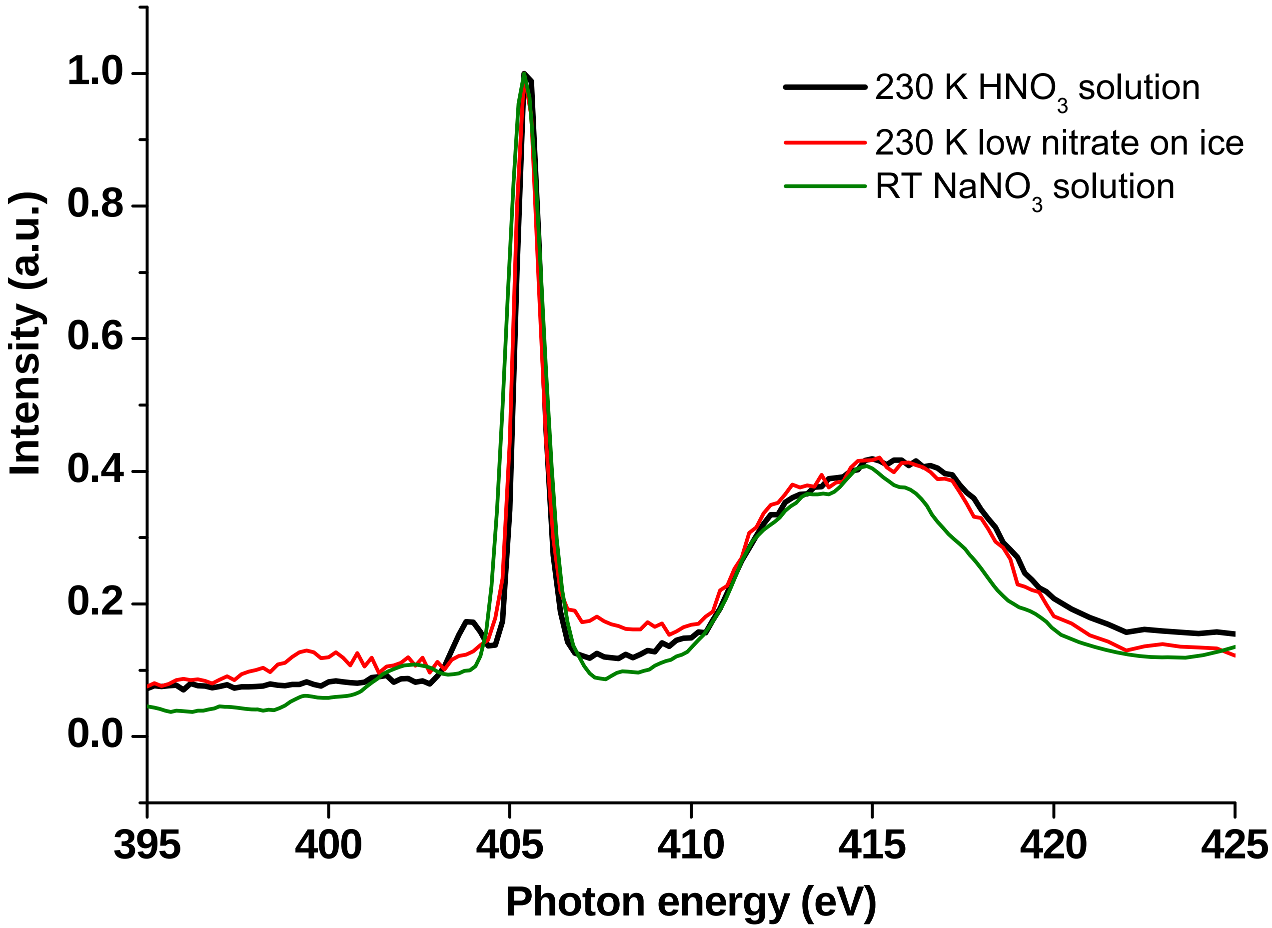
Low nitrate coverage



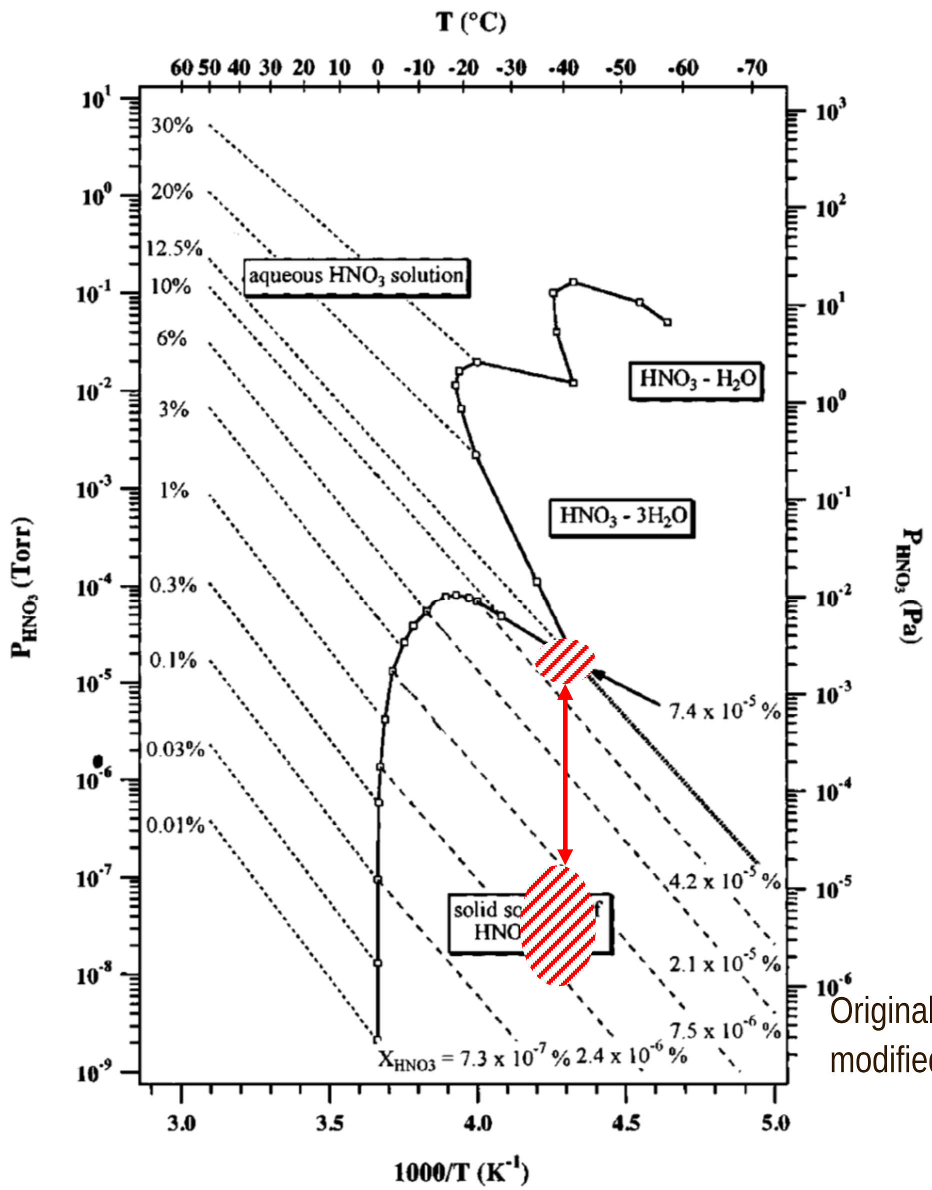
HNO_3 solution

- One single N-species at the ice surface, with BE consistent with nitrate.
- BE and peak shape independent of coverage and of whether nitrate/ice or nitrate solution
- N/O ratios 0.005 – 0.028, corresponding to about max 0.5 ML (10^{14} cm^{-2})
- For conditions of HNO_3 solution, N/O ratios >0.05, consistent with an about 12% HNO_3 solution

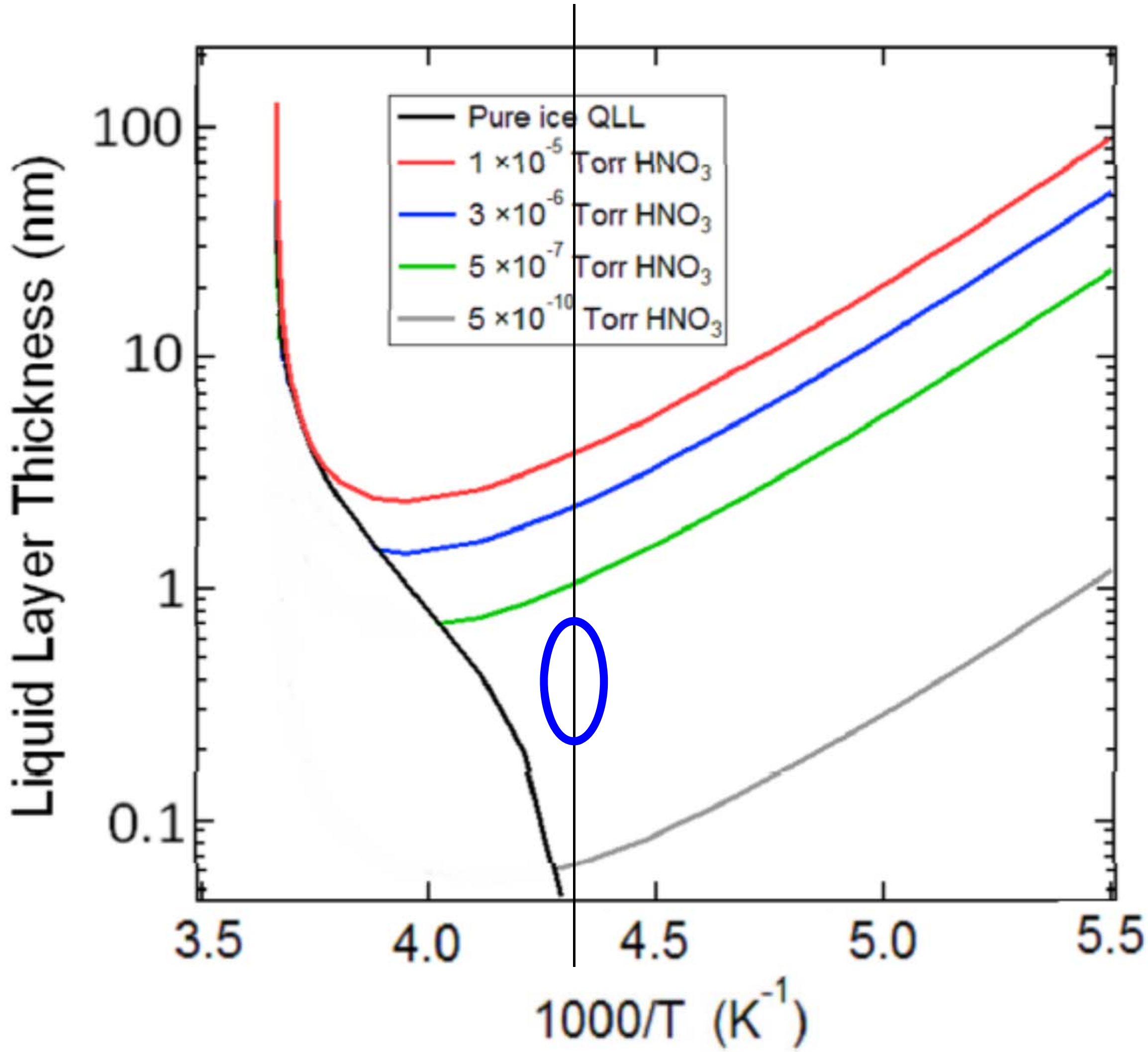
N K-edge NEXAFS of nitrate on ice



Nitrate on ice experiences similar local environment as nitrate in concentrated HNO_3 solution

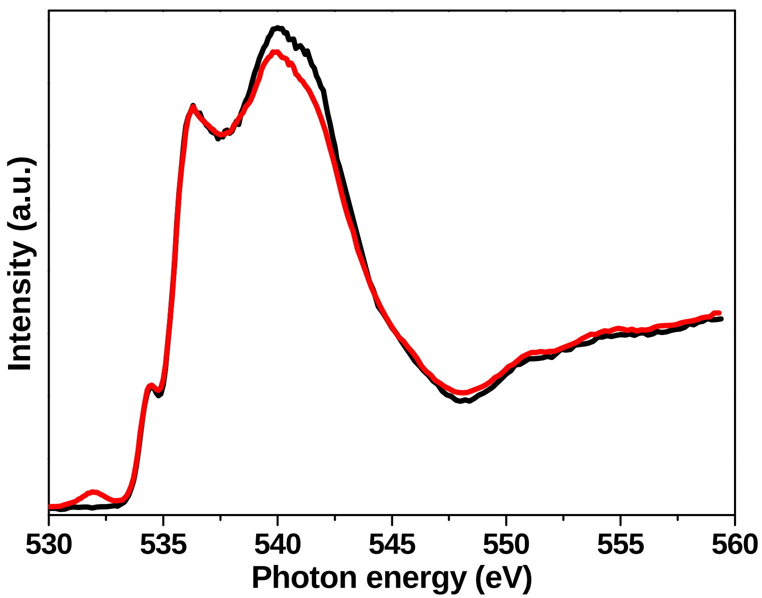


Original phase diagram by Thibert and Dominé (1998) modified by Huthwelker et al. (2006)



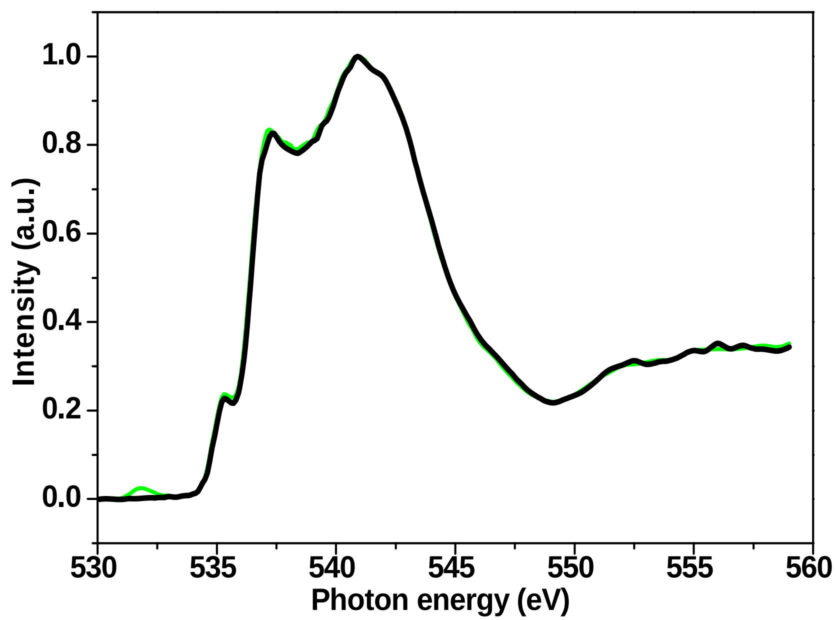
Pure ice QLL
1 ×10^-5 Torr HNO3
3 ×10^-6 Torr HNO3
5 ×10^-7 Torr HNO3
5 ×10^-10 Torr HNO3
Liquid Layer Thickness (nm)
100
10
1
0.1
3.5
4.0
4.5
5.0
5.5
1000/T (K^-1)

Acetic acid



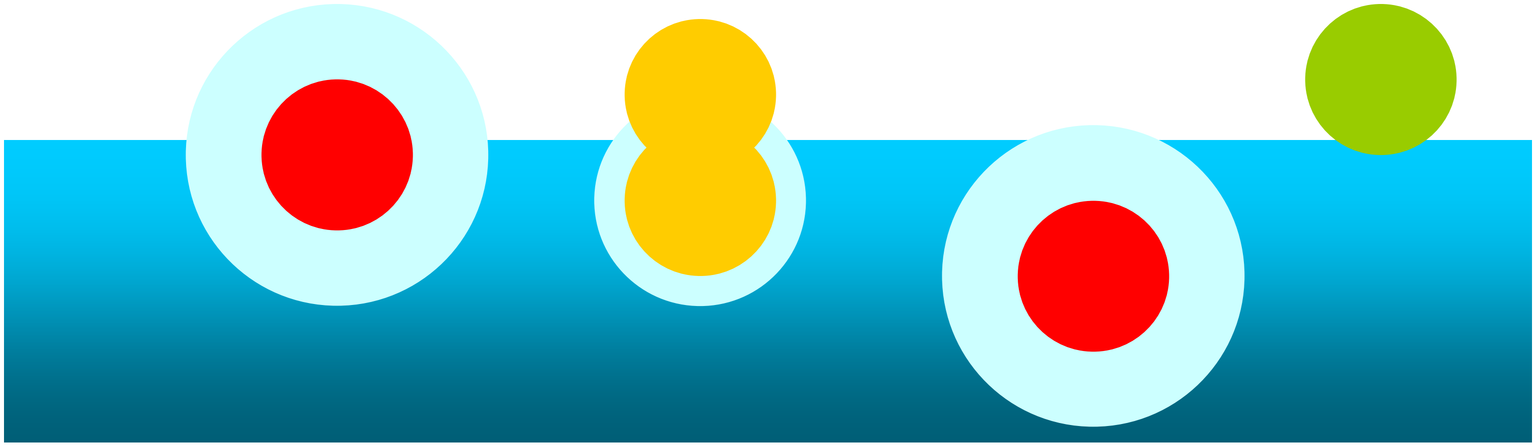
Slight changes to post/main/preedge peak ratios, scaling with surface coverage (preliminary)

Acetone



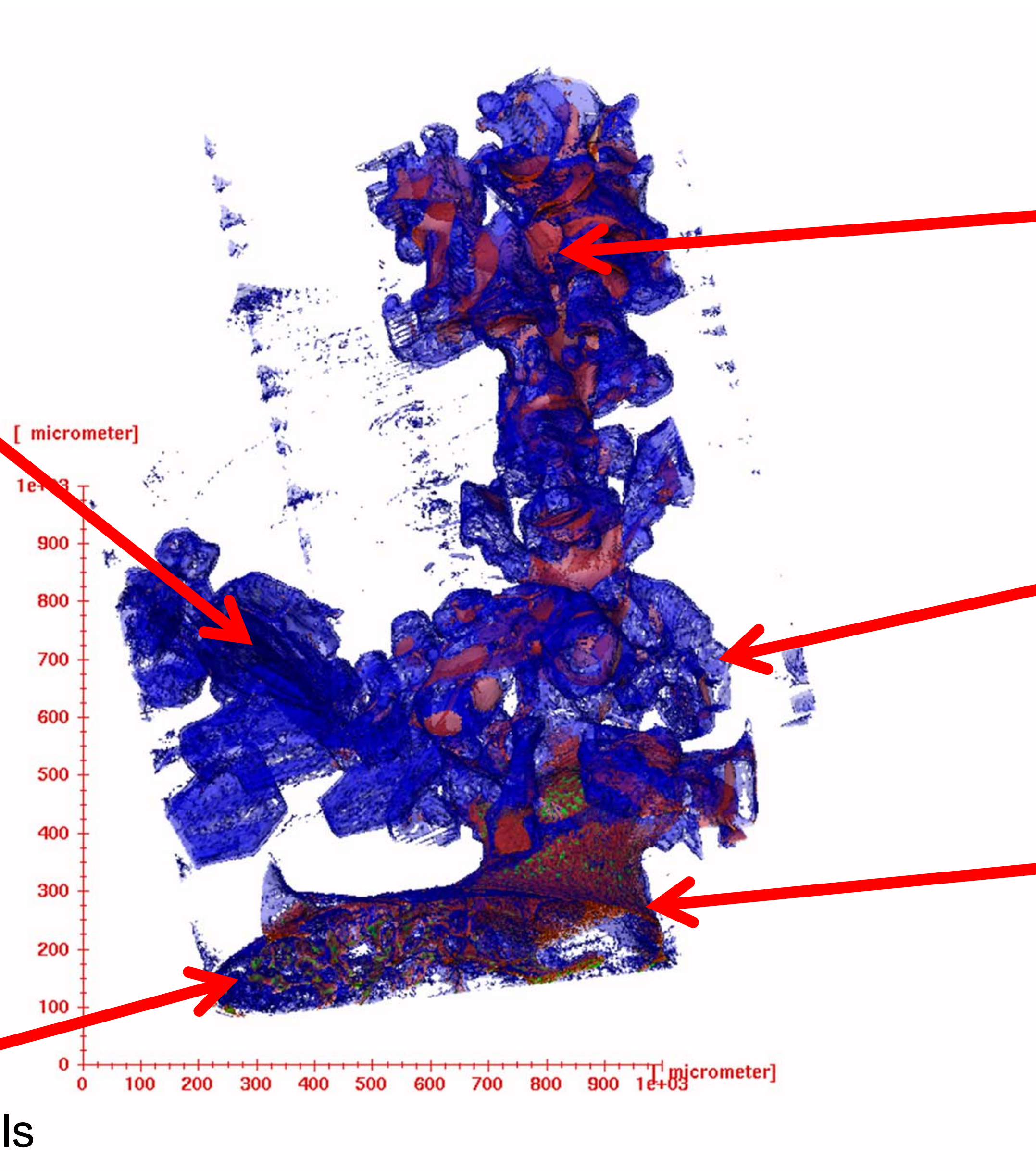
No change to O NEXAFS up to saturated acetone coverages

Is ice surface more liquid in presence of adsorbed solutes?



QL water associated with nitrate ions only to the extent necessary for hydrating the ions

PAUL SCHERRER INSTITUT



Part of FF
Contains
no salt

NaBr solution
(liquid)

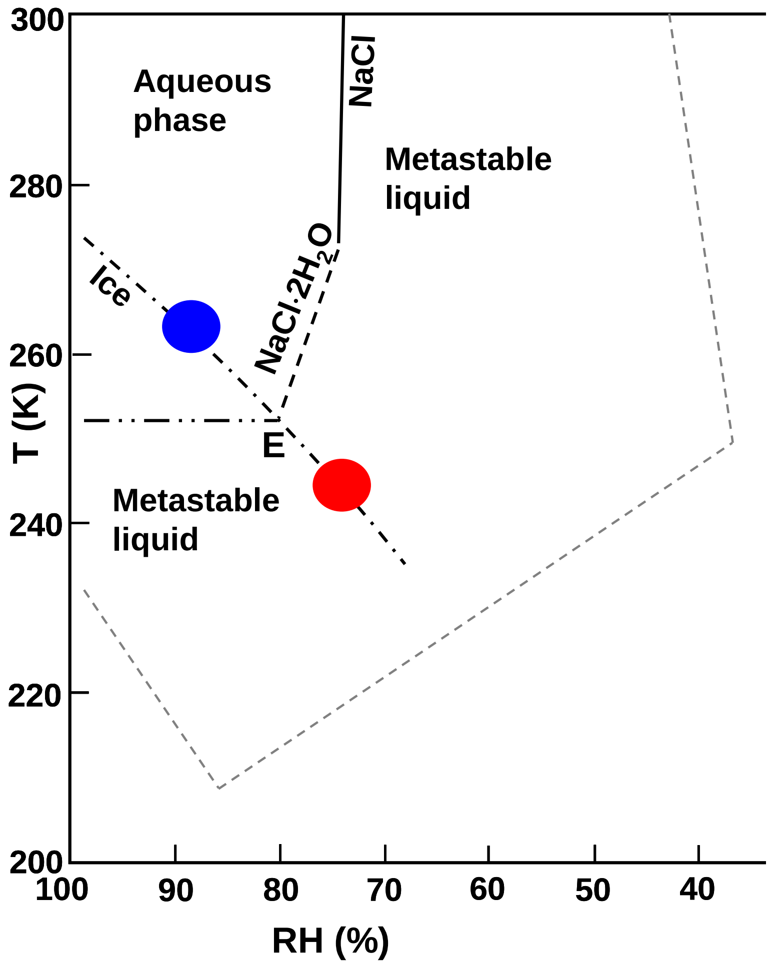
Vapor
Grown
Frostflower

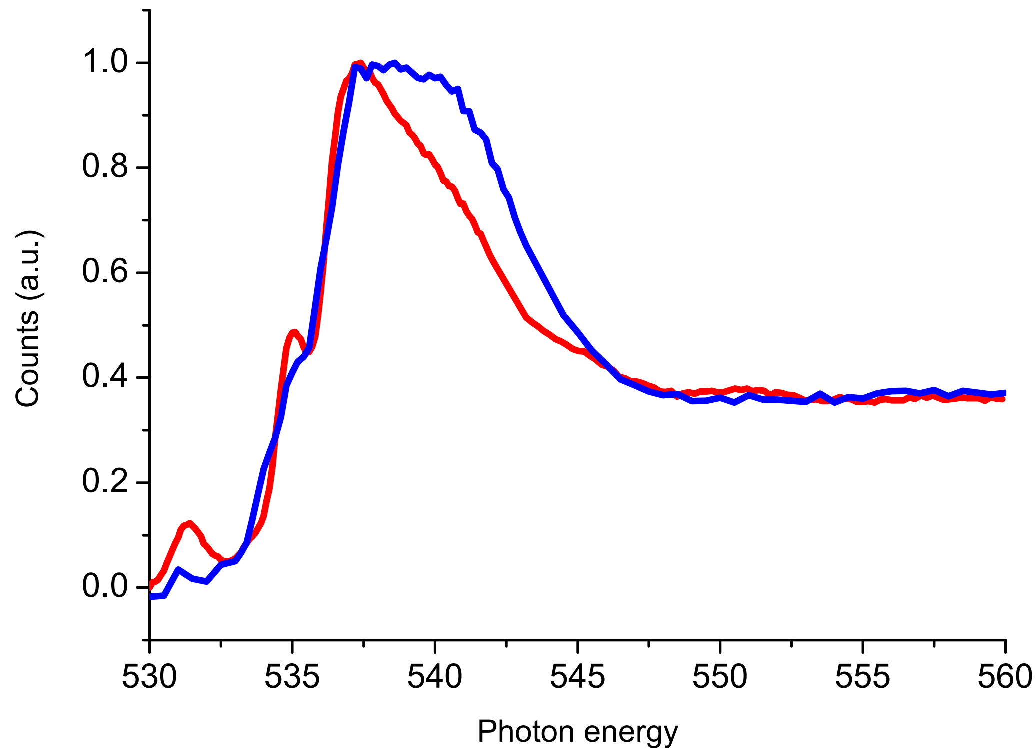
Simulated Sea
Ice, frozen
NaCl/NaBr solution
(1:1)

In Sea ice
See NaCl crystals
And
NaBr solution (red)

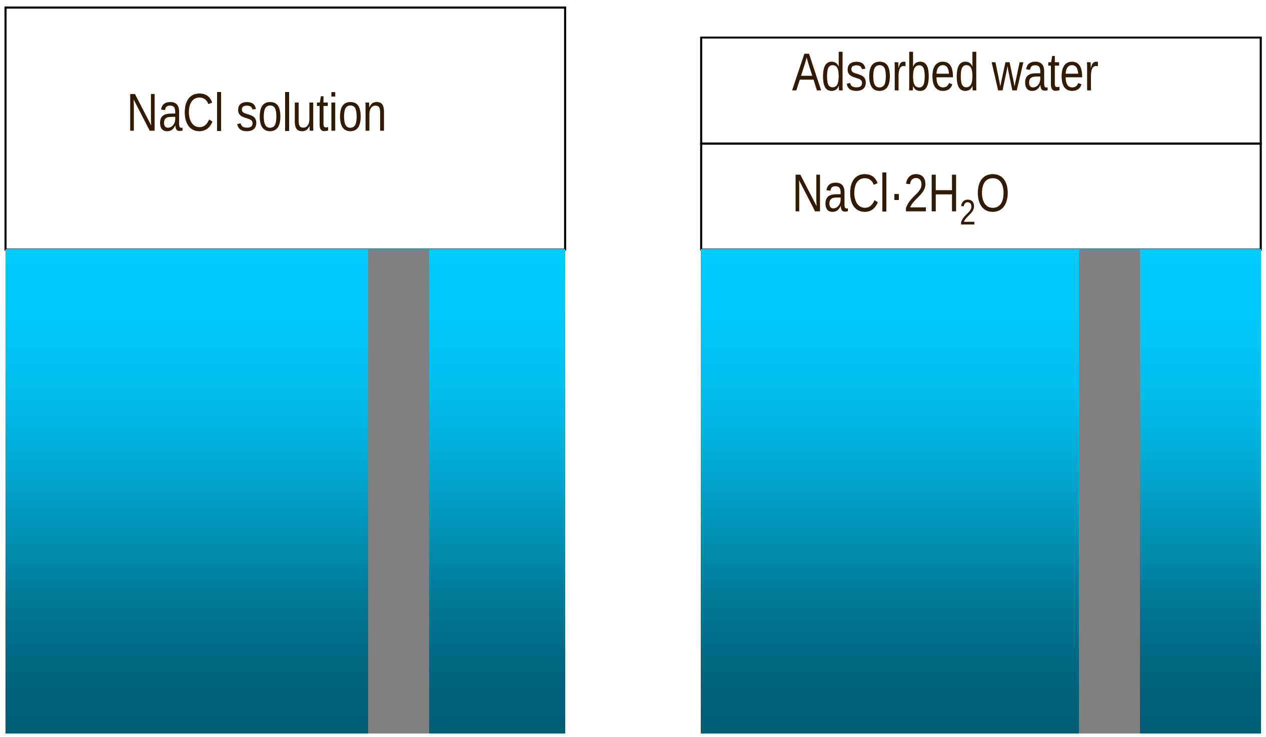
Hutterli, Huthwelker et al.

Freezing sea salt solutions and brine layer





Krepelova et al., ChemPhysChem, 2010



above

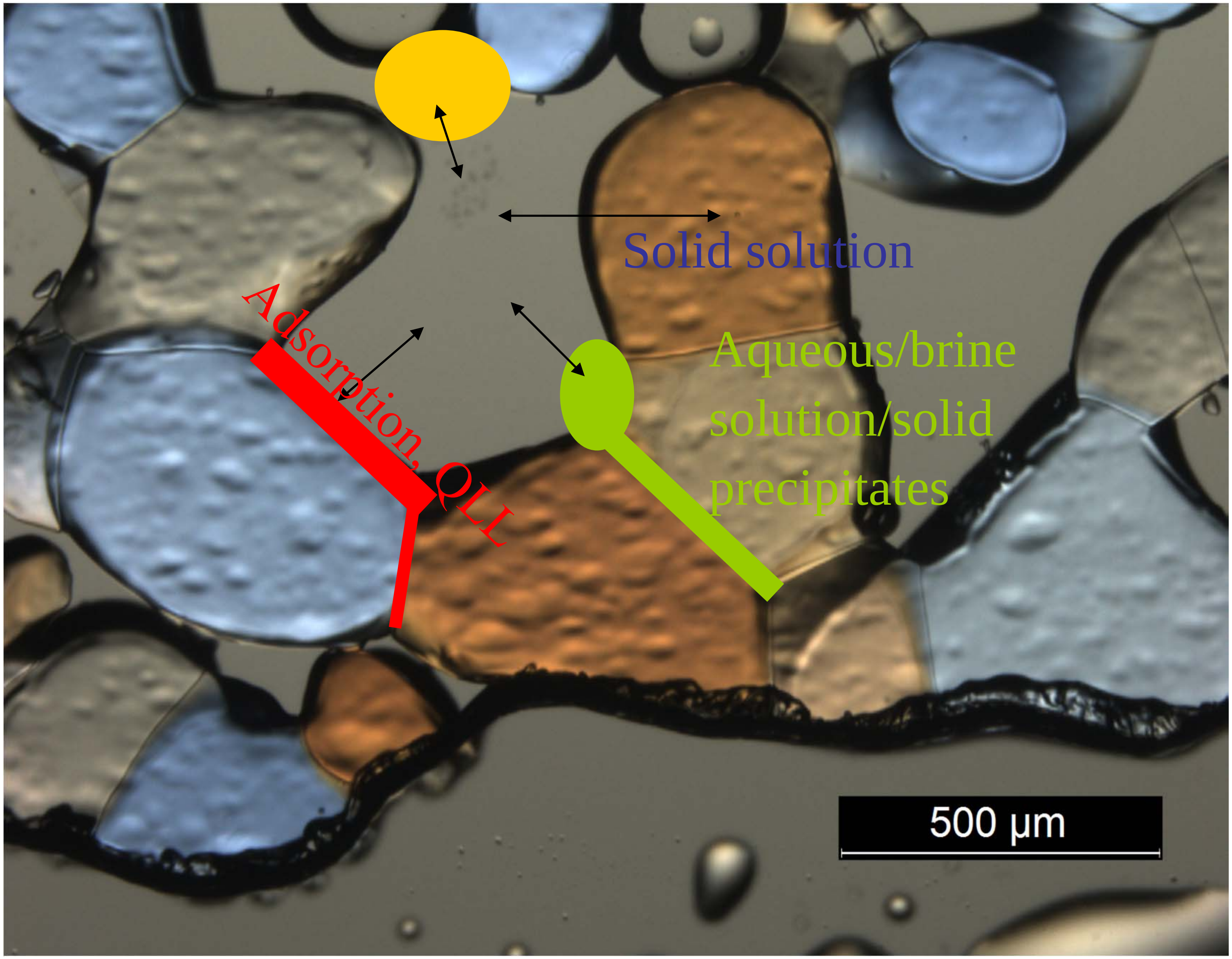
below

eutectic

PAUL SCHERRER INSTITUT

Conclusions

- ✓ The QLL is a surface phenomenon: Need for surface sensitive techniques (sensitivity for structure and chemistry)
- ✓ Ambient pressure XPS provides information about elemental composition of top most few nm in equilibrium with gas phase water and trace gas species
- ✓ Auger electron yield NEXAFS provides near surface probe to identify adsorbed species and to map changes in the hydrogen bonding environment induced by soluble molecules, thus a direct probe of the molecular environment important for chemistry.
- ✓ Strongly soluble molecules such as HNO_3 or their dissociation products are adsorbed in hydrated form at the ice surface. Under conditions where no solution may exist, the amount of adsorbates is confined to a monolayer of hydrated molecules.
- ✓ Apart from those H_2O molecules engaged in hydrating solutes, the liquid-like character of the ice surface does not change. For nitrate, about 5 'liquid' H2O molecules per nitrate ions are present at the surface. For acetic acid it is much less. Acetone makes two hydrogen bonds to the ice surface
- ✓ The surface of frozen NaCl solutions behaves as expected from the NaCl – water phase diagram: above the eutectic, a brine is excluded to the surface, below the eutectic, NaCl $\cdot 2H_2O$ is formed, with some adsorbed water on top.
- ✓ Within the bulk, disequilibrium may persist over longer times for both frozen bromide and chloride solutions (kinetic effects?).
- ✓ Acidity in freeze concentrated liquid?


Solid solution
Adsorption, QLL
Aqueous/brine solution/solid precipitates
500 µm

Acknowledgements

Surface Chemistry group at PSI: A. Krepelova, M. Kerbrat, T. Bartels-Rausch, M. Birrer
T. Huthwelker (PSI/SLS)
J.C. Hemminger, D. Tobias, M. Krisch, M. Brown and AirUCI (UCI, Irvine, USA)
H. Bluhm, D. Starr, J.T. Newberg (Advanced Light Source, Berkeley, USA)
Swiss National Science Foundation
Swiss Federal Office of Education and Science
EU-FP6 SCOUT-O3