Advanced Photon-In Photon-Out
Hard X-ray Spectroscopy

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Photon-in Photon-out X-ray Spectroscopy

monochromatic analyzer (Rowland geometry)

detector → monochromator → X-ray beam → sample → detector

PSD

dispersive analyzer (e.g. von Hamos geometry)

PSD → monochromator → X-ray beam → sample → detector
elastic scattering

- electron
- orbit
- nucleus
emission from core level

nucleus

electron
orbit
emission from valence level
inelastic scattering with electronic excitation
inelastic scattering with collective excitation
the hydrogen bond is directional
probing of valence electrons

local structure of water configurations

molecular orbitals of the water molecule

occupied

1b₂

3a₁

1b₁

unoccupied

4a₁

2b₂
The Structure of Liquid Water

X-ray Spectroscopy

Thermodynamical data
heat capacity
density
compressibility
viscosity

dynamics
IR, NMR, ...

Diffraction (neutron, x-ray)
RDF's oo, oh

Experimental Model systems
gas-phase

ice

custers

MD

X-ray Absorption
Structure of Liquid Water

0.5 eV resolution


Suggested Model of Water based on Combination of SAXS, XES and XRS

Disordered ‘soup’

Ice like patches
\(~10-15 \text{ Å}\)

- On the time-scale of the scattering and spectroscopic processes two local structural species coexist with tetrahedral-like patches of dimension of order 10-15 Å in dynamic equilibrium with H-bond distorted and thermally excited structures.

- Both the characteristic dimension based on SAXS and the local structure of the tetrahedral-like component based on XES/XRS are relatively insensitive to temperature whereas that of the H-bond distorted component continuously changes as it becomes thermally excited and expands, leading to loss of contrast in SAXS.

- The tetrahedral-like patches form as low energy-low entropy structures of lower density. The higher density, thermally excited H-bond distorted structure is a high entropy structure.

- The detailed structure of the two types of species and the time-scale on which these fluctuations exist are not yet determined.
Water in Reverse Micelles

• model system for confined water
• how does confinement change the hydrogen bonding network of water?

   • different types of water in reverse micelles
   • surface water molecules are immobilized by hydrophilic head group ("interfacial water")
   • water molecules in the core behave like bulk water ("core water")
   • most existing studies are based on vibrational spectroscopy

• current view: slower dynamics in smaller reverse micelles\textsuperscript{1-3}

• however, interfacial water may have weaker hydrogen bonding\textsuperscript{1}

Increased Fraction of Weakened H-Bonds

- Increase in pre-edge
- Slight decrease in post-edge

- Spectral changes are consistent with the increase of weakened H-bond species (similar as increasing the temperature)
- More broken hydrogen bonds (consistent with Dokter et.al.)
- More structured water as suggested by some from slower dynamics (vibrational study) can be excluded

**Oxygenic Photosynthesis**

**photosynthesis:**
- only fundamental source of food on earth
- has created our atmosphere and ozone layer
- has created fossil energy sources (crude oil, coal, gas)
- shows alternative ways to obtain energy in the future!

‘Bavaria Buche’, ~ 500-800 year old beech, Altmühltal, Germany, leave area ~ 8500 m²
Oxygegenic Photosynthesis

Where do plants split water?

\[ \text{Mn}_4\text{O}_x\text{Ca cluster} \]
Kok Cycle of Water Splitting

Calculated valence to core spectra for Fe(IV)-O and Fe(IV)-OH Compound II derivatives

Lee et al, submitted
O-Mn Crossover XES in PSII

What is the mechanism of photosynthetic oxygen evolution?


Currently only $S_0$ through $S_3$ states can be trapped
Photon-in photon-out hard x-ray spectroscopy requires very intense sources, we just scratching the surface.

New sources and instruments needed to use the full potential of these powerful techniques.

New sources will help to answer:

What is the structure of water?
How do plants split water?

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