Recent Advances in Hard X-ray Inelastic Scattering with Medium Resolution
(A Story about Water)

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• motivation
• x-ray Raman spectroscopy (XRS)
• x-ray emission spectroscopy (XES)
• selective x-ray absorption (S-XAS)
• resonant inelastic x-ray scattering (RIXS)
## Collaborators

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Photon-in Photon-out X-ray Spectroscopy

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The Local Structure of Water

Hydrogen bonding

Structure

Properties

Water

"essential for life"
"organisms consist mostly of water"
"most abundant substance on earth"
"only naturally occurring inorganic liquid"
"third most common molecule in the universe"

Experimental techniques:
- neutron and x-ray diffraction
- infrared/fs spectroscopy
- collective excitations (dynamics)
- XAS → local structure

Critical point

Soft x-rays

Pressure (Pa)

Temperature (K)
Photosynthetic Oxygen Evolution

**photosynthesis**

\[ CO_2 + H_2O \xrightarrow{\hbar\omega} (CH_2O)_n + O_2 \]

this process generates carbohydrates and the world supply of oxygen

**catalytic center**
- OEC is a 4 Mn cluster
- four states \( S_0 - S_3 \)
- EPR, K-edge, EXAFS, K\( \beta \), crystallography
- L-edge not possible

**photosystem II**

**how?**

**oxygen evolution**

\[ 2 H_2O \rightarrow O_2 + 4 H^+ + 4 e^- \]

the oxygen is derived from water

**cytochrome oxidase**

**life cycle**

**aerobic metabolism**

\[ ATP + CO_2 + H_2O \leftrightarrow (CH_2O)_n + O_2 \]

we consume oxygen to “burn” the energy of carbohydrates to produce ATP, the biological energy currency
Why water?
Photon-in Photon-out X-ray Spectroscopy

**Technique**
- x-ray Raman scattering (non resonant)
- selective x-ray absorption
- x-ray emission (non resonant)
- resonant inelastic x-ray scattering

**Experimental Procedure**
- scan of monochromator, analyzer fixed
- scan of analyzer, monochromator fixed
- scan of both

Diagram showing:
- Tunable analyzer
- Monochromator
- Detector
- Sample

Energy shift $\Delta E \sim 1 \text{ eV}$
Principle of X-ray Raman Spectroscopy

\[ \Delta E = E_0 - E' \]

\[ \text{scattering probability: } w \sim \cos^2 \theta \sin^2(\theta/2) \left| \langle i | r | f \rangle \right|^2 \]

for \( qr \ll 1 \), and \( |k_i| \cong |k_f| \)
# Motivation

### why XRS?

**sample specific:**
- true bulk probe
- no vacuum requirements
- *in situ* experiments
- high temperature/pressure

**technique specific:**
- no saturation effects
- non dipole transitions at large q
- pump probe experiments (LCLS)

### samples

**in general:**
- any sample with sufficient scattering strength

**in particular:**
- systems not suited for studies with conventional techniques
- concentrated low Z systems
- liquids
- reactive specimens
Local Structure of Water

data

![Graphs showing energy intensity for water (RT), surface, and ice with labeled axes and data points.]

calculations

![Diagram illustrating molecular structures with labels for double donor (DD), single donor (SD), and non donor (ND).]

- double donor (DD)
- single donor (SD)
- non donor (ND)
What the data suggest

- identification of large percentage of molecules with one 'broken' donor bond (SD)

⇒ indication of ring like configurations

- weak temperature dependence

<table>
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<tr>
<th>hydrogen bonds per molecule</th>
<th>25°C</th>
<th>90°C</th>
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<tbody>
<tr>
<td>Temperature</td>
<td>~3.5</td>
<td>~ 3.3</td>
</tr>
<tr>
<td>MD</td>
<td>~2.1</td>
<td>~ 2</td>
</tr>
<tr>
<td>experiment</td>
<td>~2.1</td>
<td>~ 2</td>
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Wernet et al, Science accepted

classical MD uses pair potentials

⇒ possibly incomplete description of hydrogen bonds

needed: *ab initio* MD simulations with > 500 molecules
Photon-in Photon-out X-ray Spectroscopy

- **Technique and Experimental Procedure**
  - **x-ray Raman scattering (non resonant)**
    - Experimental procedure: scan of monochromator, analyzer fixed
  - **selective x-ray absorption**
  - **x-ray emission (non resonant)**
    - Experimental procedure: scan of analyzer, monochromator fixed
  - **resonant inelastic x-ray scattering**
    - Experimental procedure: scan of both

**Diagram**

- Sample
- Monochromator
- Tunable analyzer
- Detector

Energy shifts: $\Delta E \sim 1 \text{ eV}$
why XES?

- direct probe of unpaired spins in 3d transition metals
  ⇒ oxidation state, spin state
- sensitivity to ligand type and distance
- ‘orientation’ of disordered sample

future: pump probe, single shot experiments (LCLS)

samples (5-12 keV)

- any sample (very dilute sample possible)
- 3d transition metals (K-emission)
- rare earths (L-emission)
X-ray Emission Spectroscopy

chemical sensitivity of K fluorescence

valence levels

3p

Kβ₁,3, Kβ'

2p

Kα₁,2

1s

level diagram

energy shift [eV]

normalized intensity [a.u.]

Kα₂, Kα₁

Kβ’, Kβ₁₃

Kβ₂₅, Kβ”

K2MnF₆

Mn(II)O

Mn(IV)O₂

Mn salen Nitrido

KMn(VII)O₄

Kα₁,2

Kβ’, Kβ₁₃

Kβ₂₅, Kβ”


Comparison: XANES versus Kβ₁,₃ XES

XANES spectra

mono-µ-oxo manganese

<table>
<thead>
<tr>
<th>(III-III)</th>
<th>(III-IV)</th>
<th>(IV-IV)</th>
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di-µ-oxo manganese

XANES difference spectra

mono-µ-oxo (III-IV)-(III-III)

di-µ-oxo (IV-IV)-(III-IV)

Kβ XES difference spectra

Visser et al, JACS 123 7031, 2001
$\mathrm{K\beta_{1,3}}$ XES on Photosystem II

Messinger et al, JACS 123, 7804, 2001
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**Motivation**

**why selective selective EXAFS?**

- chemical in addition to elemental specificity
- extended k-range $\Rightarrow$ higher resolution

**samples**

- any sample
- e.g. 3d metals, rare earths
Selective X-ray Absorption Spectroscopy

Extending the Resolution of EXAFS from 0.15 to 0.10 Å

$S_1$: 2 to 3 Mn-Mn at 2.72 - 2.84 Å

$S_2$: 2 to 3 Mn-Mn at 2.71 - 2.77 Å
Photon-in Photon-out X-ray Spectroscopy

**Technique Experimental Procedure**

- **x-ray Raman scattering (non resonant)**
  - Selective x-ray absorption
  - x-ray emission (non resonant)
  - Resonant inelastic x-ray scattering

**Experimental Procedure**

- Scan of monochromator, analyzer fixed
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Principle of RIXS (1s, 2p)

\[ h\nu = \Omega - \omega \]

**state diagram**

- **ground state**: \( 1s^23d^n \)
- **excitation energy**: \( \Omega \)
- **energy transfer**: \( \Omega - \omega \)
- **intermediate states**: \( 1s3d^{n+1} \)
- **final states**: \( 2p^53d^{n+1} \)

**RIXS plane**

- RIXS plane
- Incident Energy [eV]
- Energy Transfer [eV]

**Mn(II)**

- Fluorescence (a.u.)
- energy transfer \( \Omega - \omega \) [eV]
- excitation energy \( \Omega \) [eV]
Why RIXS?

- isolate LUMO resonances (3d) → orbital population,
- L-edge like information → sensitivity to spin,
- less lifetime broadening,
- less radiation damage.

example 1: low spin/high-spin Ni(II)

RIXS plane

example 2: high-spin Ni(III)

CET versus K-edge XANES
CIE versus L-edge XANES

Glatzel et al, JACS comm, 124, 9668, 2002
RIXS Spectra of Mn models and PSII

E: MnII(acac)$_2$(H2O)$_2$  F: MnIII(acac)$_3$  G: MnIV(sal)$_2$(bipy)

Glatzel et al, JACS, submitted
Conclusions

- XRS: low Z systems, non dipole DOS, EXAFS possible
- XES: spin state, chemical state, neighbor distance and type
- S-XAS: extended k-range, chemical/spin specificity
- RIXS: isolate LUMO resonances
  L-edge/M-edge like information with hard x-rays

Future

- better resolution, more efficient spectrometers
- lots of photons

planned 'Advanced Spectroscopy and Inelastic Scattering Facility' at SPEAR3, first workshop see:
End of Show
Comparison of Mn(II), Mn(III) and Mn(IV) 1s,2p RIXS