Inelastic X-ray Scattering and Advanced Spectroscopy Facility for SPEAR3

Uwe Bergmann

- motivation
- X-ray Raman scattering (XRS)
- X-ray Emission and Selective X-ray Absorption
- resonant inelastic X-ray scattering (RIXS)
- numbers and parameters
The Local Structure of Water

- Hydrogen bonding
- Experimental techniques:
  - Neutron and x-ray diffraction
  - Infrared/fs spectroscopy
  - Collective excitations (dynamics)
  - XAS → local structure

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"

Structure → Properties

Critical point
Photosynthetic Oxygen Evolution

**photosynthesis**

\[ \text{CO}_2 + \text{H}_2\text{O} \xrightarrow{??} (\text{CH}_2\text{O})_n + \text{O}_2 \]

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

**photonsystem II**

how?

**oxygen evolution**

\[ 2 \text{H}_2\text{O} \xrightarrow{\text{photosystem II}} \text{O}_2 + 4 \text{H}^+ + 4 \text{e}^- \]

the oxygen is derived from water

**cytochrome oxidase**

**aerobic metabolism**

\[ \text{ATP} + \text{CO}_2 + \text{H}_2\text{O} \xleftarrow{\text{cytochrome oxidase}} (\text{CH}_2\text{O})_n + \text{O}_2 \]

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

what we would like to have:

probe with sensitivity of soft x-rays but penetration of hard x-rays

tunable analyzer
0.1 - 1 eV

monochromator
Si(220), Si(400), Si(333)

SR beam

detector

sample

0.1 - 1 eV
**X-ray Raman Process (Non Resonant)**

\[ ? E = E_0 - E' \]

scattering probability (dipole limit):

\[ w \propto \cos^2 \theta \sin^2(\theta/2) \]  
(angular dependence, for horizontal scattering)

\[ w \propto Z^{-4} \]  
(element dependence)

\[ w \propto E^3 \]  
(energy dependence at constant q)

\[ w \propto ? E^{-1} \]  
(energy transfer dependence)
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
X-ray Emission, Selective XAS

chemical sensitivity of K fluorescence

level diagram

valence levels

3p

Kβ₂,₅, Kβ''

Kβ₁,₃, Kβ'

2p

Ka₁,₂

1s

chemical sensitivity of K fluorescence

Mn(II)O
Mn(IV)O₂
Mn(VII)O₄

Relative Energy [eV]

0 35

Intensity [a.u.]

Kα₂

Kα₁

Kβ'

Kβ₁,₃

Kβ''

Kβ₂,₅

Normalized Intensity [a.u.]

Normalized Intensity [a.u.]

Energy Shift [eV]

-25 -20 -15 -10 -5 0 5

Relative Integrated Intensity

Relative Integrated Intensity

10⁻⁴

10⁻³

10⁻²

10⁻¹

10⁰

10¹

10²

10³

10⁴

10⁵

0

Mn-O Distance [Å]

15 17 19 21 2.3

10⁻⁵

10⁻⁴

10⁻³

10⁻²

10⁻¹

10⁰

10¹

10²

10³

10⁴

10⁵

K₂MnF₆

Mn salen Nitrido

KMn(VII)O₄

chemical sensitivity of K fluorescence

chemical sensitivity of K fluorescence

chemical sensitivity of K fluorescence
Motivation

why XES?

- direct probe of unpaired spins in 3d transition metals
  ⇒ oxidation state, spin state
- sensitivity to ligand type and distance
- selective EXAFS for mixed valent compounds
- ‘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)
Principle of RIXS (1s,2p)

**State Diagram**
- **Ground State**: $1s^2 3d^n$
- **Intermediate States**: $1s3d^{n+1}$
- **Final States**: $2p^5 3d^{n+1}$
- **Excitation**: $1s \rightarrow 3d$
- **Decay**: $2p \rightarrow 1s$

**Energy Transfer**
- $h\nu = \Omega$
- $h\nu = \omega$
- $\Omega - \omega$

**RIXS Plane**
- Incident Energy $\Omega$
- Energy Transfer $\Omega - \omega$

**K-edge**
- $1s$ excitation
- $2p$ decay

**1s$^23d^n$**

**$\Gamma_L$**

**$\Gamma_K$**
Motivation

why RIXS?
- isolate LUMO resonances
- L-edge/M-edge like information
- less lifetime broadening
- less radiation damage (proteins)

future: pump probe experiments (LCLS)

samples (5-12 keV)
- first row transition metals, Se (K-edge)
- rare earths (L-edge)
(1s,2p) RIXS in Ni Compounds, Contour Plots

Glatzel et al, JACS, 124, 9668-69, 2002
Comparison of RIXS with K-edge and L-edge

CFS-scan versus K-edge

(a) Ni(I)
(b) Ni(II) ls
(c) Ni(II) hs
(d) Ni(III) ls

CIE-scan versus L-edge

a) Ni(I)
b) Ni(II) ls
c) Ni(II) hs
d) Ni(III) ls
Charge Excitations in $\text{La}_2\text{CuO}_4$ Studied RIXS

Kim et al, PRL, 89, 177003, 2002

authors argue:
- both A and B are highly dispersive excitation modes
- damped by the presence of the electron-hole continuum
Examples for RIXS, XES Applications

- bio catalysts, examples:
  - nitrogenases (V, Mo, Fe): \( \text{N}_2 \rightarrow \text{NH}_3 \) (nitrogen fixation)
  - hydrogenases (Ni, Fe): \( \text{H}^+ \leftrightarrow \text{H}_2 \) (hydrogen formation and consumption)
  - photosystem II (Mn): \( \text{H}_2\text{O} \rightarrow \text{O}_2 \) (water splitting and oxygen evolution)

- industrial catalysts, in situ measurements
  e.g. Fe zeolites

- magnetic materials, superconductors

- geo-biology
Some Numbers

B1 6 @ 500 mA, 54µ, 70mm, 1.5 mrad horz

<table>
<thead>
<tr>
<th></th>
<th>Reflex 80K</th>
<th>Bragg angle</th>
<th>(\Delta \theta) [µrad]</th>
<th>resolution [eV]</th>
<th>ph/sec (\times 10^{13})</th>
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</thead>
<tbody>
<tr>
<td>Si (111)</td>
<td>16.4</td>
<td>33.6</td>
<td>0.94</td>
<td>15.4</td>
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<tr>
<td>Si (220)</td>
<td>27.5</td>
<td>30.4</td>
<td>0.42</td>
<td>6.8</td>
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<td>Si (400)</td>
<td>40.7</td>
<td>21.1</td>
<td>0.18</td>
<td>2.9</td>
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<td>Si (422)</td>
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<td>20.2</td>
<td>0.11</td>
<td>1.7</td>
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<td>Si (333)</td>
<td>57.9</td>
<td>14.6</td>
<td>0.064</td>
<td>1.0</td>
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<tr>
<td>C (111)</td>
<td>25.5</td>
<td>31.7</td>
<td>0.47</td>
<td>~7</td>
<td></td>
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<tr>
<td>C (220)</td>
<td>44.6</td>
<td>25.2</td>
<td>0.18</td>
<td>~3</td>
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</table>

assumptions (7 keV, 1 eV band pass, 500 mA, perfect optics):

BL6 wiggler
1.5 horz mrad acceptance
SP3 standrad straight sigma

U20 undulator
10:1 horz demag, 2.5:1 vert demag
100 periods, 20mm/period
small gap undulator in east pit with beta_y =2.0m
source sigma per SLAC Pub 8870
third harmonic

from T. Rabedeau
What we would like to hear from you:

- techniques
- element(s) and edge/emission line(s)
- energy range
- energy resolution(s)
- beam size
- solid angle, q resolution
- sample environment, concentration, restrictions (examples: cryostat, fast scan, in situ cell)
Support Slides
Annex A: Other IXS / XPS beamlines

Inelastic X-ray Scattering
- ESRF has started some years ago a very successful IXS program with two fully dedicated beamlines ID16 and ID28. These beamlines mainly focus on ultra high resolution for phonon studies. More recently, a IXS spectrometer was installed on ID16. This instrument shared the beamtime with the high-resolution spectrometer and has to be swapped in and out the beam for measurements. A replica of this spectrometer was mounted on ID26 EXAFS beamline.

- Following the success of X21 at Brookhaven National Laboratory, an extensive effort has been made to promote IXS at APS. IXS-CAT beamline is soon to be commissioned. It covers both medium and ultra high-resolution techniques. In addition, an IXS spectrometer is also available on HP-CAT.

- Spring8 has started the commissioning of a new IXS beamline BL12XU operated by SSRRC (Taiwan). Its main interests go to medium to high resolution experiment emphasizing on non-resonant inelastic scattering with a possible extension to ultra-high resolution. The material science beamline BL11XU also possesses a 2-m spectrometer dedicated to resonant inelastic x-ray scattering with medium resolution. Other beamlines using inelastic x-ray scattering at Spring-8 although aiming at different purposes as respect to the present project worth being mentioned here: BL08W for Compton scattering, BL35XU for ultra-high resolution non resonant inelastic scattering and BL12B2 on a bending magnet for emission spectroscopy.

<table>
<thead>
<tr>
<th>Beamlines</th>
<th>Location</th>
<th>Source</th>
<th>Energy Range</th>
<th>$\Delta E / E$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ID16</td>
<td>SOLEIL</td>
<td>Undulator</td>
<td>3-12 keV</td>
<td>$10^{-5} - 10^{-4}$</td>
</tr>
<tr>
<td>ID28</td>
<td>ESRF (Grenoble)</td>
<td>Undulator</td>
<td>6-25 keV</td>
<td>$5 \times 10^{-6} / 10^{-4}$</td>
</tr>
<tr>
<td>ID26</td>
<td></td>
<td></td>
<td>6-25 keV</td>
<td>$5 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3-30 keV</td>
<td>$10^{-4}$</td>
</tr>
<tr>
<td>IXS-CAT</td>
<td>APS (USA)</td>
<td>Undulator</td>
<td>5-30 keV</td>
<td>$5 \times 10^{-5} / 5 \times 10^{-4} - 10^{-4}$</td>
</tr>
<tr>
<td>HP-CAT</td>
<td></td>
<td></td>
<td>5-30 keV</td>
<td>$10^{-4}$</td>
</tr>
<tr>
<td>BL12XU</td>
<td>Spring-8 (Japan)</td>
<td>Undulator</td>
<td>5-30 keV</td>
<td>$10^{-4} - 10^{-4}$</td>
</tr>
<tr>
<td>BL11XU</td>
<td></td>
<td></td>
<td>5-20 keV</td>
<td>$10^{-4}$</td>
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<tr>
<td>BL12B2</td>
<td></td>
<td>Bending Magnet</td>
<td>5-70 keV</td>
<td>$10^{-4}$</td>
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<tr>
<td>BL08W</td>
<td></td>
<td>Wiggler</td>
<td>70-300 keV</td>
<td>$10^{-3}$</td>
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<tr>
<td>BL35XU</td>
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<td>Undulator</td>
<td>6-75 keV</td>
<td>$5 \times 10^{-8}$</td>
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<tr>
<td>X21</td>
<td>NSLS (USA)</td>
<td>Wiggler</td>
<td>5-10 keV</td>
<td>$10^{-4}$</td>
</tr>
</tbody>
</table>

Table 18: Comparison between existing inelastic x-ray scattering beamlines. Characteristics of the current project are also shown (gray shading). $\Delta E / E$ indicates the approximate energy resolution achievable.
The spectrometer should include:

- High precision motors with an accuracy on the micron level
- Angular stability within the arc seconds over long range of travel and under vacuum conditions
- An adjustable radius. 0.5 to 3 m radius spherically bent silicon analyzer crystal will be used, allowing for a range of energy resolutions of around 100 meV to 1 eV depending on the incident energy band pass and on the specific needs of the experiment (solid-angle or momentum/energy resolution).
- A versatile geometry: The spectrometer will be designed with the capability of positioning a shielded detector in the backscattering geometry for use with various sample chambers, which will allow optimizing the energy resolution.
- Large q region, obtained here by the rotation of the horizontal arm over 180°.
- A precise sample goniometer head for sample orientation
- The capacity to install magnets, furnaces, or cryostat with a fine-positioning carrier for measurement of samples in extreme environments

Figure 11: Schematics of the IXS spectrometer on BL12XU at Spring-8
photon-atom interaction Hamiltonian:

\[ H = \frac{e^2}{2mc^2} \vec{A}^2 + \frac{e}{mc} \vec{p} \cdot \vec{A} \]

weak interaction \( \Rightarrow \)

+ multiple processes negligible
+ good penetration
- but many photons needed!

transition rate from \( |A> \) to state \( |B> \) (Fermi’s Golden Rule):

\[
W_{BA} = \frac{2\pi}{\hbar} \left| \langle B | H | A \rangle + \sum_I \frac{\langle B | H | I \rangle \langle I | H | A \rangle}{E_A - E_I + i\Gamma/2} \right|^2 \delta(E_B - E_A) + O(H^3)
\]

\( \vec{A}^2 \) - term \hspace{1cm} 1st order: elastic/inelastic scattering (XRS, Compton)

\( \vec{p} \cdot \vec{A} \) - term \hspace{1cm} 2nd order: fluorescence (e.g. RIXS)
The theoretical description of the RIXS process is similar to UV-visible resonant Raman spectroscopy (RRS). The operator $T_1$ (dipole or quadrupole) describes the transition from the ground state $|g\rangle$ to the intermediate state $|i\rangle$ with a $1s$ vacancy. The decay of the $1s$ hole occurs via the dipole operator $T_2$ into the final state $|f\rangle$ with a $2p$ hole. The sums over $i$ and $f$ extend over all intermediate and final states with energies $E_i$ and $E_f$, respectively, that are split due to the crystal field as well as spin-orbit and electron-electron Coulomb interactions. The spectral structures arising from the splittings contain the chemical information. The lifetime broadenings are denoted $\Gamma$.

$$F(\nu_K, \nu') = \sum_f \left| \sum_i \frac{\langle f|T_2^*|i\rangle \langle i|T_1|g\rangle}{E_g + h\nu_K - E_i - i\Gamma_i} \right|^2 \times \frac{\Gamma_f / \pi}{(E_f - h(\nu_K - \nu') - E_g)^2 + \Gamma_f^2}$$