X-Ray Raman Spectroscopy — Applications

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X-ray Absorption Spectroscopy (XAS)

\[ \sigma(\omega) = 4\pi^2\alpha\omega^{-1}\sum_{f}\left|\langle f | \vec{\varepsilon} \cdot \vec{r} | i \rangle\right|^2 \cdot \delta(E_f - E_i - \hbar\omega) \]

- Dipole selection rules (\(\varepsilon.r\))
  - s\(\rightarrow\)p
  - p\(\rightarrow\)d

Incident energy tuned to a resonant absorption edge: \(\hbar\omega\)

Co K-edge \(\rightarrow\) \(\sim 7709\) eV
Convenient hard x-ray energy – Penetration several micrometers in LiCoO\(_2\)

Allows in situ/operando battery XAS studies

Co K-XAS: LiCoO\(_2\)

Co 1s initial state
X-ray Absorption Spectroscopy (XAS)

- Soft x-rays have short penetration lengths in materials
  - 525-550 eV photons (O 1s initial states)
  - penetration length only a few hundred nm in LiCoO₂

Resonant radiation is used — a bit restrictive

Incompatible or challenging to use with additional experimental apparatus, such as —
  - Electrochemical cells
  - Diamond anvil cells
High Pressure Studies

Synchrotron hard X-rays couple well with high pressure science

The penetrating ability of hard x-rays is crucial

Kr K-edge $\rightarrow \sim 14326$ eV

Hard x-rays ideal for extreme environments, but can we somehow access low energy excitation?

Nonresonant Inelastic X-ray Scattering (NIXS)

- Obtain information on low energy excitations
  - Measure intensity of scattered x-rays as a function of energy loss ($\hbar\omega$) and momentum transfer ($q$)

NIXS allows all excitations (meV-keV) to be monitored

Incident energy: 6-30 keV
Energy Loss Scale

Core-electron excitation: aka, X-ray Raman
XRS: Element Specific

Huotari et al., Nat. Mater. 10(7), 489 (2011).
NIXS at APS — some specific types

<table>
<thead>
<tr>
<th>Resolution</th>
<th>Probed Excitation(s)</th>
</tr>
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<tbody>
<tr>
<td>1-3 meV</td>
<td>Phonon dispersion, phonon density of states</td>
</tr>
<tr>
<td>100-300 meV</td>
<td>Valence electron excitations – quasiparticles in strongly correlated systems</td>
</tr>
<tr>
<td>0.4-1.5 eV</td>
<td>Core or semi-core electron excitations, plasmons</td>
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</tbody>
</table>

- NIXS performed at many other sectors as well — 3, 9, 13, 16, and 33
- Specifically, high pressure XRS studies performed at sectors 13 and 16

**HERIX (APS, 30ID)**  
\[ \Delta E \sim 1 - 2 \text{ meV} \]

**MERIX (APS, 30ID)**  
\[ \Delta E \sim 100 - 200 \text{ meV} \]

**LERIX (APS, 20-ID)**  
\[ \Delta E \sim 0.4 \text{ eV} – 1.4 \text{ eV} \]
X-ray Raman Scattering: NIXS of Core Shell Electrons

\[ S(q, \omega) = \sum_f |\langle f | e^{iq\cdot r} | i \rangle|^2 \delta(E_f - E_i - \hbar \omega) \]

Small momentum transfer: \( e^{iq\cdot r} : iq\cdot r \)
Dipole transitions only, i.e. \( \Delta l = \pm 1 \)

Large momentum transfer, \( q: \)

\[ e^{iq\cdot r} : = 1 + \frac{iq\cdot r}{1!} + \frac{(iq\cdot r)^2}{2!} + \ldots \]
Non-dipole terms may be allowed!

Problem: Scattering cross section for process of interest very low

Energy loss (\( \hbar \omega \)) plays the same role as incident energy in soft XAS

Truly bulk-sensitive alternative to soft XAS

Both probe and signal hard x-ray photons!!

- Small \( q: s \rightarrow p \) transitions (dipole)
- Large \( q: new s \rightarrow s \) transitions
  or \( new s \rightarrow d \) transitions

XRS Early History

Davis and Mitchell, Phys. Rev. 32 (3), 331 (1928)

Compton scattering from graphite and assigned a spectral feature to the location of C 1s initial states

Followed by experiments from 1s and 2p initial states of Be and C

The C K line corresponds to an energy loss of 279 volts. This is in good agreement with K energy level of carbon.

Results interpreted by Compton as potentially the x-ray analogue of “Raman lines” in the visible light regime.

Compton, Reviews of Modern Physics 1, 74 (1929).
XRS Development (60’s-70’s)

XRS conclusively demonstrated by Suzuki et al.
Theory by Mizuno and Ohmura — showed equivalence of XRS to XAS

XRS Development (cont.)

Significant developments of XRS - detailed experiments began in the late 1980’s

Extended oscillations: Same information as EXAFS

Sc$_2$O$_3$ : Sc M-edges and Sc L-edge $\rightarrow$ 3d transition metal oxide

Wolfgang Caliebe : June 1995 data from NSLS, USA

XRS Development (contd.)


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![Graphs of Cross-sections](image)

**Photoelectric, coherent, and incoherent cross-sections Vs photon energy**

XRS — Depends on incoherent cross-section, note the extremely small cross-section at ~ 10 KeV

XRS often present on top of large Compton background

- Need high incident flux, large detection solid angle, and excellent stray background rejection
Further improvements move XRS from a scientific curiosity to a well developed experimental tool

- 3rd generation synchrotron sources/optimized beamlines
- Anodically-bonded Si or Ge crystals for spherically-bent crystal analyzer, SBCA
- Dedicated multielement spectrometers
- SBCA used as an imaging optic in combination with 2D detectors
- Several independent theories for XAS and q-dependent XRS

(1) Huotari et al., Nat. Mater. 10(7), 489 (2011)
How to measure XRS efficiently?

SSRL (40+14+7)

SPring-8 (15)

ESRF ID16 (9)
Verbeni et al., J. Sync Radiat. 16, 469 (2009)

APS LERIX (19)
LERIX –Sector 20, APS

(Fister, Seidler et al., Rev. Sci. Inst. 2006)

- q-dependent XRS with 0.4 eV-1.5 eV resolution
- 19 Spherically-bent Si 111 wafers or diced analyzers, with each SBCA coupled to its own detector
- Total solid angle for 19 SBCA is ~1.2% of $4\pi$ sr
Measuring q-dependent XRS efficiently

Scan energy loss by changing E1 with mono and fixing E2 with analyzers. Each analyzer coupled with a detector to measure 19 q’s simultaneously.
Measuring q-dependent XRS with LERIX: example

- Broad Compton scattering background shifts to higher energy as q increases
- Wide scan taken at coarse steps showing the richness of the excitation spectra

Pressure changes bonding in graphite
XRS reveals the evolution of bonding and transformation of graphite to a new superhard phase
Approximately half of the sp² converted to sp³
XRS Applications: Water- Sub and supercritical conditions

O K XRS of water at different temperatures and pressures along the liquid-gas coexistence curve.

Interpret OK-XRS spectral changes with structural models obtained with DFT-MD simulations
The average number of hydrogen bonds per molecule decreases to \( \approx 0.6 \) at 600 \(^\circ\)C and \( p = 134 \) MPa

Sahle C J et al. PNAS, 110, 6301, 2013
Some high-pressure studies in diamond anvil cells:

- B$_2$O$_3$ glasses: Lee et al., Nat. Mat. 4, 851 (2005)

Some studies of liquid water and ice:

q-dependent XRS : some examples

q-dependent XRS: examples (contd.)


A more complete picture of the DOS
q-dependent XRS : 3d TM Oxides

Low-q dominated by dipole term:
Strong local field and band structure effects

TD-DFT calculations
Gurtubay et al. PRB 70 201201 (R)
(2004)

At high-q atomic part takes over and non-dipole transitions have strong contributions

Balasubramanian, Nagle, Seidler et al., Unpublished
Multipole transitions from semicore initial states: f-electron systems; lanthanides

- **Cerium N\textsubscript{4,5}-edges: 4d → 4f transitions** ($\Delta l = 1, 3, \text{and} 5$)

Multipole transitions: extended to actinides

- Actinide O_{4,5} edges: 5d → 5f transitions (Δl = 1, 3, and 5)

Total reflection XRS: surface sensitivity

- **Sample:** 10 nm-thick La$_{0.6}$Sr$_{0.4}$CoO$_3$ (LSCO) on SrTiO$_3$ (STO)
- **$\alpha_c = 0.28^\circ$ at 10 keV**

**Probe:**
- LSCO for $\alpha < \alpha_c$
- STO for $\alpha > \alpha_c$

Carbon speciation in bulk soils

Mishra, Kemner et al.; unpublished

Studies related to management of greenhouse gases
Improving soil carbon sequestration: important as a mitigation strategy
Determine in situ (without chemical extraction procedures) carbon speciation in bulk soils

Large penetration depth enables studying
- Soil aggregates.
- Organics in soils and/or minerals.
- Hydrated samples under ambient or high/low-temperatures.

Accurate speciation
- No effect of sample inhomogeneity.
- No need for vacuum conditions.
- True bulk sensitivity

Brandes et al., 2010; JSR
Using Soft X-ray

CaCO₃
XRS of standards

Mishra, Kemner et al.; unpublished

<table>
<thead>
<tr>
<th>Standard</th>
<th>Peak energy this study</th>
<th>Peak energy published</th>
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<tbody>
<tr>
<td>p-Benzoquinone</td>
<td>283.8</td>
<td>284.52</td>
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<tr>
<td></td>
<td></td>
<td>285.08</td>
</tr>
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<td>286.22</td>
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<td>288.21</td>
</tr>
<tr>
<td></td>
<td></td>
<td>289.82</td>
</tr>
<tr>
<td>Benzoic Acid</td>
<td>285.0</td>
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<td>Citric Acid</td>
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<td>288.8</td>
<td>288.75</td>
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XRS comparison with $^{13}$C NMR analysis Alaska Soil

Mishra, Kemner et al.; unpublished

<table>
<thead>
<tr>
<th>Carbon moieties</th>
<th>Alaska Soil</th>
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<tbody>
<tr>
<td>XRS</td>
<td>NMR*</td>
</tr>
<tr>
<td>Alkyl-C</td>
<td>18%</td>
</tr>
<tr>
<td>Aryl-C</td>
<td>17%</td>
</tr>
<tr>
<td>O-Alkyl-C</td>
<td>11%</td>
</tr>
<tr>
<td>Phenolic-C</td>
<td>11%</td>
</tr>
<tr>
<td>$\Sigma$ (Carboxylic-C + Carbonyl-C)</td>
<td>51%</td>
</tr>
</tbody>
</table>

* NMR data courtesy Chao Liang
How Does the Battery Store and Generate Electricity

During discharge each electrode undergoes a half cell reaction

At the anode the reaction is:

$$\text{LiC}_6 \rightarrow 6\text{C} + \text{Li}^+ + e^-$$

At the cathode it is:

$$\text{Li}_{0.5}\text{Co(III)}_{0.5}\text{Co(IV)}_{0.5}\text{O}_2 + 0.5\text{Li}^+ + 0.5e \rightarrow \text{LiCo(III)O}_2$$

The driving force for the external current is the difference in electrode potentials of the half cell reactions. This yields an operating voltage of $\sim 3.9 \text{ V}$
Need to study O K-edge and TM L/M-edges to probe oxygen participation in charge compensation and TM d-dos

For Li to F: 1s
For Mg to Zn: L and/or M edges (2p/3p initial states): access to d-DOS
Can be performed using sub-keV-XAS (soft-XAS) or EELS

**Problem:** The interesting redox chemistry involves light elements (Li, O, C) and TM 3d orbitals, but sample environment (an operating battery) is not quite compatible with soft x-rays

Proof of Principle: XRS Experiments

Some LiC₆ data: Li K-edge

- Both chemically (lithium intercalated HOPG) and electrochemically prepared samples studied
- Penetration depth of 10 KeV x-rays in LIG well over 2mm → true bulk information obtained
- Good quality data obtained for both C 1s and Li 1s IXS
- Small amounts of residual electrolyte do not pose any problem
- Li 1s position shifts to higher energy relative to Li metal

LiC$_6$ data .... : C K-edge

Low q: sample oriented with q $\sim$ parallel to c-axis

Probes bonding along c-axis ($\pi$-feature enhanced)

High q: sample oriented with q $\sim$ in basal plane.

Probes bonding in basal plane ($\sigma$-feature enhanced)

NIXS q-dependence (in dipole limit) similar to polarization-dependence in soft XAS for non-cubic systems

Sensitive to anisotropic bonding in oriented non-cubic systems
XRS→Coordination sensitivity of Li$_2$O$_2$

Bethe-Salpeter (BSE) treatment: accurately accounts for electron–core hole interactions

BSE theory: Eric Shirley (NIST)

2 structures with distinct O–O bond distance

Féher’s: 1.28 Å
Föppl’s: 1.55 Å

Li$_4$Ti$_{5}$O$_{12}$ Ti $L_{23}$-edge

Ti 4+

$\text{XRS intensity (arb. units)}$

450 455 460 465 470

Energy loss (eV)

$\text{Ti}^4+$

$t_{2g}$

$e_g$

$L_3$

$L_2$

Ti$_2$O$_3$ Ti $L_{23}$-edge

Ti 3+

$\text{XRS intensity (arb. units)}$

450 455 460 465 470

Energy loss (eV)

$\text{Ti}^3+$

$t_{2g}$

$e_g$

$L_3$

$L_2$

$\text{XRS intensity (arb. units)}$

1.6 - 4.0 Å$^{-1}$

4.8 - 6.8 Å$^{-1}$

7.4 - 8.9 Å$^{-1}$

9.4 - 10.5 Å$^{-1}$
Chemical lithiation of $\text{Li}_{4+x}\text{Ti}_5\text{O}_{12}$

Elastic energy: $\sim 9889.5$ eV
Use Si (555) reflection in LERIX
Energy resolution: $\sim 1.3$ eV

In the dipole limit, Ti 2p XRS dominated by transitions from spin-orbit split Ti 2p levels to unoccupied Ti 3d levels; direct probe of projected unoccupied d-dos

Exact shape and position of peaks can be well understood by atomic multiplet calculations

Ti 2p XRS clearly shows the partial reduction of Ti$^{4+}$ to Ti$^{3+}$ on lithiation of $\text{Li}_4\text{Ti}_5\text{O}_{12}$

In situ capabilities of XRS: LiCoO$_2$

- See clear evidence for hole formation at $t_{2g}$ orbitals during charge (i.e. Co$^{4+}$ formation) in O K- and Co M$_1$-edges
- In addition with Co M$_{2,3}$, L$_{2,3}$, and Co K-edge XAS a detailed set of electronic excitation spectra obtained

Electrochemical

Chemical

Bulk sensitive core shell XRS of light elements (Li, O,C : 1s) as well transition metal (TM: 2p, 3p and 3s) can be performed

Ken Nagle, Swati Pol, Balasubramanian, Seidler, (unpublished)
Instrument Developments

6 movable chambers: 12 analyzers each
K-B mirrors: focus ~8x16 μm (VxH)

LERIX: proposed upgrade tied to APS upgrade

20x20 μm beam
0.3-0.5 eV resolution
Improved detectors
Improved SBCA reflectivity
100+ ... analyzers

ESRF ID20 (UPBL6)
XRS can be used to study most elements in the periodic table

With newer generation instruments, XRS is poised to become a technique of choice to study the fundamental electronic excitations in a variety of materials — under real world and/or extreme conditions

Theory to generate the excited state spectra has progressively improved and promises to provide key insights on details of electronic structure
Acknowledgements

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