X-ray Raman Scattering: using hard x-rays to study low energy processes

Outline

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Introduction

XRS is the x-ray energy-loss version of x-ray absorption spectroscopy; a technique used to obtain element-specific information on local electronic structure and chemistry by examining the “near-edge absorption” fine structure.

We will review a paper, just now being submitted for publication, that describes XRS measurements on several phases of water by examining the oxygen K-edge. Differences in the spectra are interpreted as affects of hydrogen bonding on valence electrons.
X-ray Raman Scattering: the physical process

Electron-Photon interaction

\[ A = \text{vector potential of photon} \]
\[ p = \text{electron momentum operator} \]

Fermi Golden-rule gives transition probability for scattering

\[ \psi = \left( \frac{2\pi}{h} \right) \left| f, j \left| \left[ H_1 + H_2 \right] \right| 0, i \right| \right|^2 \]
\[ \times \delta \left( E_f - E_0 - \hbar (\nu_i - \nu_j) \right) , \]

| a, b > specifies the combined electronic state of the material with energy \( E_a \) and photon state of energy \( \hbar \nu_b \).

The delta function specifies scattering is energy conserving.
At photon energy far from absorption edges* and wavelength near atomic dimensions only the $A^2$ term is important.

For an unpolarized incident beam scattered by angle $\theta$ :

$$w = \frac{4\pi^3 e^4 h}{m^2 v_i v_j} (1 + \cos^2 \theta) |\langle f | \exp[i(k_j - k_i)r] |0\rangle|^2$$

$$\times \delta(E_f - E_0 - h(v_i - v_j)),$$

The dipole approximation keeps $1 + ikr$ when expanding the complex exponential. It gives the basic expression :

$$w = \frac{64\pi^5 e^4 h}{m^2 c^2} (1 + \cos^2 \theta) \sin^2(\theta/2) |\langle i | r | f \rangle|^2$$

Raman scattering favors large $\theta$ and has the same matrix element as x-ray absorption spectroscopy.

* of K-edges for low Z elements to be discussed
BIG PICTURE: X-RAY Raman scattering from graphite

Energy loss spectrum recorded when scattered radiation is collected at fixed energy and incident beam energy is scanned.

A probe with sensitivity to soft x-ray edges but with penetration power associated with hard x-rays.
Instrumentation

Sample – spherical crystal analyzer (or array) – detector on adjustable ROWLAND CIRCLE to scan collection energy.

Scattering crosssection is small (like all x-ray scattering) but XRS has no “diffraction-like” enhancement, therefore bright sources and array of analyzer crystals is required.
Techniques utilizing similar (same) apparatus

Inelastic x-ray scattering at 1 eV resolution:
study \((q, E)\) dependence of electronic excitations
e.g. plasmons

Resonant inelastic x-ray scattering:
for work close to absorption edges, uses \(\mathbf{A}^*\mathbf{p}\) interaction

High resolution x-ray emission spectroscopy
exploits chemical shifts of K and L fluorescence lines
associated with oxidation and spin state, as well as type
and distance of neighboring ligands
How useful is XRS?

- How long does it take to collect an energy loss spectrum?
  
  See next figure
  
  **APS ID18**: \( I_0 \sim 3 \times 10^{13} \text{p/s}, \quad \Delta E_T \sim 1.1 \text{eV} @ 6.76 \text{KeV}, \quad 30 \text{ min/spectrum} \)
  
  Using **8** - 3.5” diameter \( \text{si}(440) \) analyzers

- How does information content compare with other techniques?
  
  Quite favorable according to next figure

  Two such techniques are:
  
  **EELS** (electron energy loss spectroscopy)
  
  Soft x-ray absorption spectroscopy

  Both methods have severe limitations because probe interacts very strongly with sample and environment
Excitations of Aromatic Molecules

**Figure 1.** C 1s oscillator strength spectra of benzene, naphthalene, anthracene, phenanthracene, triphenylene, pyrene, and 1,2-benzanthracene. All of the spectra were derived from energy loss spectra recorded under near-dipole scattering conditions (2500 eV impact energy, 2° scattering angle) with 0.55 eV fwhm resolution. The hatched lines indicate the C 1s IPs as determined by X-ray photoelectron spectroscopy or estimated from XPS of similar species.8

**Figure 2.** (thick lines) C 1s inelastic X-ray scattering spectra of benzene, naphthalene, anthracene, triphenylene, and 1,2-benzanthracene. (thin lines) ISEELS spectra of the same species, broadened by smoothing to match the width of the lowest energy  π* band. Offsets
Application of XRS to the study of water

Spectroscopic characterization of microscopic hydrogen bonding disparities in supercritical water

The local hydrogen bonding environment in supercritical water (380 °C, 300 bar, density 0.54 g/cm³) was studied by x-ray Raman scattering at the oxygen K-edge. The spectra are compared to those of the gas phase, liquid surface, bulk liquid and bulk ice, as well as to calculated spectra.

Supercritical (sc) water becomes a highly reactive solvent even for hydrophobic solutes and it is of paramount importance to elucidate its structure and bonding in order to explain its properties.

XRS at the O K-edge of water probes unoccupied molecular orbitals, which are strongly modified by H-bonding on the H side; this yields information on the local structure at the proton side.
**Experiment:**

Performed at the APS undulator beamline 18-ID

Si(4,0,0) double crystal monochromator

Scattering analyzer:

super critical (sc) water analyzed with 3 Ge(5,5,5) crystals $\Theta_B = 86.4^\circ$,

$E_0$ scan from 10.01 to 10.09 keV, scattering angles 82-98, $q=6.5$-7.5 Å$^{-1}$

(“not quite dipole limit but insignificantly affects spectrum comparing to XAS”)

ambient liquid water and ice analyzed with 2 Si(4,4,0) crystals $\Theta_B = 88.2^\circ$,

$E_0$ scan from 6.980 to 7.055keV, scattering angle 55.8°, $q=3.2$ Å$^{-1}$

Energy step sizes: 0.1 eV in the near-edge region, 1 eV elsewhere.

sc water was kept in an alumina (polycrystalline sapphire) tube in a He high pressure/high temperature cell separated from ambient atmosphere by Be windows. Hard x-rays are essential to get sufficient transmission of the incident and inelastically scattered photons.
Results of XRS measurement (with reference soft x-ray XAS)

Sc water spectrum result of 75 scans X 40 min/scan = 50 hrs.

At peak of XRS spectrum:
signal: 1-2 Hz, bkg: 2 Hz

In XAS:
first two features characteristic of free molecules, post-edge indicates significant H-bonding.
From the discussion of these data:

… qualitative comparison implies that in sc water the molecules are in dynamical equilibrium between fully H-bonded configurations and gas-like phase with no donating H-bonds.

This may be correlated with the density fluctuations which are characteristic of the supercritical state and which entail inhomogeneties in the local density as evidenced by small angle scattering studies with x-rays (SAXS) and neutrons (SANS)…

… the denser regions would correspond to the fully H-bonded molecules while the molecules in gas-phase like configurations would make up the less dense regions or be H-bonded at the interfaces to the dense regions through one or two acceptor H-bonds.

The absence of the 535 eV peak and the broader intensity distribution in the post-edge region indicate that the local H-bonding configurations, though saturated, are markedly different from those in liquid water and in ice.
Beyond the near-edge region: “1st neighbor EXAFS”
They compare sc water to the better known structure of crystalline ice.

The second maximum at energies around 560 eV can be used to directly estimate the distances between nearest neighbor O atoms. We observe a shift of 3.3±0.8 eV between sc water and ice…corresponds to an elongation of the mean nearest-neighbor O-O distances in sc water by 0.3±0.1 Å to 3.1±0.1…This agrees with neutron and x-ray diffraction results, which place the first maximum in O-O RDFs for sc water at various conditions between 3 and 3.2 Å…
They also show some results of model calculations (no detail on methods), but this goes beyond the purpose of this talk.

**They conclude:**

We find mainly two disparate H-bonding configurations in sc water at the conditions studied here with the dominating fraction of 65±20% of the molecules having four intact but distorted H-bonds. The configurations are distinctly different from the regular tetrahedral H-bonding configurations in ice due to H-bonds that are significantly longer or shorter and/or bent…as compared to ice… We determine an average nearest-neighbor O-O distance for the fraction of H-bonded molecules at the conditions studied here of 3.1±0.1 Å. This is consistent with results from x-ray and neutron diffraction at similar conditions…

… Our results suggest that sc water is inhomogeneous because of a balance of disparate local configurations with fully H-bonded (dense regions) and non-H-bonded molecules (less dense regions). This unusual structure likely determines its unique properties.
• **What are the significant limitations?**
  
  signals are weak and edge to be studied must be located at energy loss far enough from Compton peak to allow background subtraction
  
  signal can increased by enlarging analyzer collection area BUT then q-range increases and dipole approximation is violated
  
  larger signal (and bkg.) come from higher I₀ but don’t want to burn up or modify low z sample

• **Could XRS benefit significantly from an ERL source?**

  Yes if source can give higher throughput at higher incident beam energy resolution because low-Z edges have lots of fine structure that cannot now be easily measured.
  
  Also brilliance may push the method towards microscopy. Time structure?
References
Physics of x-ray Raman:
  detailed reference about the cross sections is from a chapter by Schuelke
'Inelastic scattering from electronic excitations', chapter 15, Handbook on Synchrotron

Water and XRS:

XRS on fused-ring aromatic molecules:

For another important application (using the same equipment) see:
  “High resolution 1s core hole x-ray spectroscopy….”,