New Scientific Opportunities with soft x-ray SR

Zahid Hussain
Scientific Support Group, Leader
Advanced Light Source
Lawrence Berkeley National Laboratory
The mission of the ALS is to
Support Users in doing
Outstanding Science

(From 2002 BES review of the ALS)
WHAT DOES SR BRIGHTNESS BUY YOU?

Very High Energy Resolution

Submicron Spatial Resolution

Coherence

Photoelectron Spectrum of H₂

$hv - 27 \text{ eV}$

$v'' = 4$

$v'' = 3$

$v'' = 2$

$v'' = 1$

Binding Energy (eV)

Intensity

20 µm

Magnetic structure of LaFeO₃ layer on surface oxide.
Ultimately, the electronic, magnetic, chemical, mechanical, optical, thermal, and structural properties of matter depend on the behavior of electrons.
What are some of the important areas of science where soft x-ray SR could make big impact?

Where do we stand now?

How could we get there?

**Big Science** (large facilities, ~5-10 yrs effort, $10's M)

**VS.**

**Small Science** (modest experimental effort, big payoff)

“Science is in the sample”,

Daniel Chemla, ALS
New Scientific Opportunities, Summary

- **Ambient Pressure Photoemission** (in situ measurements, catalysis/corrosion, environmental science, biological systems)

- **Ultra-high Momentum and Energy Resolution**
  ARPES (Scienta electron energy analyzers, strongly correlated electron systems (high temperature superconductors, CMR)

- **Coherent Scattering** (magnetic imaging, dynamics)

- **Momentum-Resolved Inelastic Scattering** (optically forbidden transition, bulk sensitivity)

- **Spectromicroscopy** (SMART/PEEMIII, X-Ray Imaging, STXM)

- **Ion Spectroscopy** (study of positive and negative ions by measurements of ion fragmentation and/or electron spectroscopy)

- **Time-resolved spectroscopy** (f-sec research)
X Rays Are An Important Probe of Matter

- **Spectroscopy**
  - Interact with electrons in atoms
  - Element and chemical state sensitivity

- **Microscopy**
  - Short wavelength/Small focal spot
  - Image small objects

- **Absorption coefficient appropriate**
  - Penetrate matter
- **Can be polarized** (linear, circular)
- **Variable (tunable) energy**

- **Short-pulse time structure**
- **Partially coherent**
Quantum Number Selectivity:

✓ Absorption

\[ \omega \varepsilon_2 \Rightarrow \Delta E = E_f - E_i \]

✓ Angle-integrated photoemission

\[ N(E, \hbar \omega) \Rightarrow E_f, E_i \]

✓ Angle-resolved photoemission

\[ N(E, \hbar \omega, \theta, \phi) \Rightarrow E_f, E_i, \mathbf{k} \]

✓ Spin-polarized photoemission

\[ (N_\uparrow - N_\downarrow) / (N_\uparrow + N_\downarrow) \Rightarrow E_f, E_i, \mathbf{k}, \sigma \]
Photoelectron Spectroscopy

(a) Energy Analyzer
E_{kin}
S = spin
Detector

(b) Bound - Free
Core Valence
E_F E_{vac}

No. of Electron States = D.O.S.

h\nu = E_{kin} + E_{binding} + \Phi

Kinetic Energy (E_{kin})

N(E_{kin})

Inelastic

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Photoelectron Spectroscopy

Provides information about

- Kind of atom
- Number of atoms
- Chemical shift
Chemical Shift
Chemical Shift

5 Å SiOₓ on Si(100)

Si 2p₃/₂
hν=130 eV

Initial-State Energy (eV Relative to Bulk Si 2p₃/₂)

Photoemission Intensity (arbitrary units)

SiO₂  Si³⁺  Si²⁺  Si¹⁺  Si +4  +3  +2  +1

Si(001)
• Ambient Pressure Photoemission:
  Pressure ~ (up to 17 torr, vapour Pressure of H2O @RT)
  30 years of surface science knowledge for understanding of electronic structure of surfaces/interfaces in UHV (model systems)
  ➤ Now it is possible to apply under real conditions ....

• Absorption/emission spectroscopy (photon in/photon out): study of unoccupied and occupied valence bands
  Pressure ~ (up to 1-20 atmospheric pressure theoretical analysis a must, (example)
  Totally new science!!
Ambient pressure soft x-ray spectroscopy: Concept

- Synchrotron beam enters through window
- Controlled gas atmosphere
- Photoelectrons from sample surface AND near-surface gas
- Differentially pumped electron transport
Ambient pressure soft x-ray spectroscopy: Basic Concept

Electrostatic Lenses cross-over at pumping apertures
Several groups have used differentially-pumped XPS

— K. Siegbahn, H. Siegbahn et al.
  • Gas phase photoemission
  • Surfaces of low vapor-pressure liquids
— Modified XPS sample holder
  • Moveable differentially-pumped sample cell
— M. Grunze et al.
  • Surface reactions and catalysis

What’s new?
— Differentially-pumped electron optics for higher signals
— Synchrotron light-source allows smaller apertures
— Pressure range extended 1-2 orders of magnitude
Prototype Ambient Pressure Photo-Emission System

HP-PES Differentially Pumped Optics

Modify conventional surface science vacuum system
Ambient Pressure Photoemission: Schematic

Sample with Z motion, cold finger and resistive heater

Experimental cell supplied by gas lines

X-rays incident at 15° through a 100 nm Al window

Analyzer lens, pumped independently
Ambient pressure soft x-ray spectroscopy: Possible Applications

- In situ studies of surface reactions
  - closing the catalysis “pressure gap”
- Surface science of liquids
  - Segregation at solution liquid-vapor interfaces
  - Fundamental Electrochemistry
- Environmental Chemistry
  - Surfaces exposed to water vapor near ambient conditions
  - Solvation and ion-transport
  - Corrosion
- Biological Science
  - Study in the presence of water (in situ)
In Situ Catalysis

Partial oxidation of methanol to formaldehyde over copper

\[
\text{CH}_3\text{OH} + \text{O}_2 \rightarrow \text{CH}_2\text{O}
\]

Active site exists under reaction conditions

Hendrick Bluhm et al.
NEXAFS of Ice Premelting

Incident photon energy (eV)

Auger Yield

water, -2 °C
ice, -2 °C
-4 °C
-5 °C
-10 °C
-15 °C
-25 °C
-39 °C

Fluorescence Yield, Ice, -25 °C

XPS C1s
-25 °C

contamination peak

292 284

-4 °C

-25 °C

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Highly Correlated Electron Systems

Mott Insulator

- One-electron Band Theory
- Mott Insulators

Doped Mott Insulators

- High-$T_c$ Superconductivity
  - Cuprates
- Colossal Magnetoresistance
  - Manganites
- Stripes & Orbital Order
  - (many Oxides)
- Anomalous Transport & Spectroscopic properties

An unsolved problem in Many-body physics
Highly Correlated Electron System

uncorrelated system

ground state

with external perturbation…

correlated system

The responses are different due to correlation effect!
Colossal Magnetoresistance (CMR) Effect

Novel Electronic Phases

CO: Charge Order (Stripes)
FI: Ferromagnetic Insulator
AFI: Antiferro. Insulator
CAF: Canted AFM Insulator
CMR: Colossal MagnetoResis.

- Large drop of resistivity upon relatively small magnetic fields
- Para → Ferromagnetism
- Most dramatic on the insulating phase (short range orbital order)
Study of Highly Correlated Electron Systems

High Momentum and Energy Resolution Photoemission: A technique of choice for the study of electronic structure of correlated systems

- Confirming breakdown of one electron band theory
- Splitting of band in NiO due to e-e interaction
- Determination of the Fermi Surface (example)
- D-wave anisotropy of the super-conducting gap
- Static and dynamics stripes in LSCO (example)
- Observation of strong e-phonon coupling (example),

Continue photoemission development to achieve:

Ultra high momentum resolution ~ 1% of BZ
Energy resolution ~ 1 meV
The need for ultra-high energy and momentum resolution angle-resolved photoemission (ARPES)

Goal -

- Making connections to transport, thermodynamics, and other low-energy scale properties of solids, especially those where these properties are exotic or poorly understood.

- In particular, where these properties are k-dependent, anisotropic, and/or low dimensional.
ultra-high energy resolution ARPES-Capabilities

Key physical properties measurable in ARPES:

- Energy vs. wave vector\((k)\)
- Fermi Surface
- Mean Free Paths
- Effective carrier masses
- Scattering rates
- Electron Self energies
- Scattering or nesting vectors
- Number of carriers
- Pseudogaps and superconducting gaps

The only technique that can get all these in a single self consistent way.

Usually the only way to measure these in a k-resolved way. Only worthwhile if done with energy resolution comparable or better than other key energy scales, temperatures.
Typical Valence Band Photoemission Spectrum from a High Temperature Superconductor

Intrinsically weak signal experiments
Observation of electron phonon coupling in high Tc superconductors

• Mechanism of high-temperature superconductors (HTSCs) unexplained
  — Electron-phonon interaction underlines conventional superconductors
  — Previous experiment and theory suggest a different mechanism is operative in HTSCs

• Angle-resolved photoemission (ARPES)
  — High angular resolution at the ALS probes electron dynamical parameters
  — Feature at characteristic energies give insight into operative physical processes

• New APRES evidence from three families of HTSCs
  • Kink in electron-momentum (dispersion) curves ubiquitous in all three different classes of samples
  • Common kink energy and other evidence suggests electron-phonon coupling
  • Revives question of role of phonons in driving superconductivity in HTSCs
Strong electron phonon coupling in High Tc Superconductors

(Left) Electro-phonon coupling modifies the electron-momentum dispersion curve near the Fermi energy. (Right) Dispersion curves for three families of high-temperature superconductors show a common kink at an energy (arrow) that matches an oxygen lattice vibration. The parameter $\delta$ is the doping concentration that determines the transition temperatures in the materials. $k'$ is the reduced momentum (momentum at the Fermi energy $k_F$ minus the actual momentum $k$).

High Energy Resolution Spectroscopy (HERS)
Endstation at BL 10.0.1, Advanced Light Source
Limitations of photoemission - need of new spectroscopy

However Photoemission:
Measures single particle spectral function of occupied states
It is highly surface sensitive
Spectra could become complicated for 3-D systems

Example: YBCO, difficulty due to surface state

Look for additional tools!!

Resonant Inelastic soft x-ray scattering
Momentum-resolved provides information about the unoccupied band and anisotropic (direct/indirect) nature of energy gaps in solids.

Great for study of fast Correlated motion of electrons in CMR magnites and HTc cuprate
Techniques of choice:

- **Angle resolved photoemission (ARPES):**
  Single-particle spectrum $A(k, \omega)$

- **Inelastic Neutron Scattering (INS):**
  Spin fluctuation spectrum $S(q, \omega)$

- **Inelastic x-ray scattering (IXS):**
  New info on the Charge Channel: $N(q, \omega)$

This extra experimental info can help understand correlated systems
Manganese exhibit interplay of charge, spin, lattice and orbital degrees of freedom

An unexplored degree of freedom in transition metal oxides:

**Orbital Density Waves**

Ordering of orbitals produce long-range orbital density waves - a new type of collective excitation in crystals

**E. Saitoh et al. Nature** 410, 180 (2001)

Interacting degrees of freedom (complex electron systems)

Energy and Length scales determine the physics of these systems
Resonant Inelastic soft X-ray Scattering (Raman Spectroscopy with finite $q$)

- **Energy loss:** $\omega = \omega_2 - \omega_1$
- **Momentum transfer:** $q = k_2 - k_1$
- **Resonance:** $\omega_1 \sim \omega_{\text{edge}}$

Why???

- Can be applied in the presence of **magnetic/electric field**
- **Bulk sensitive** probe for studying unoccupied electronic states
- Optically forbidden d-d excitation
- Finite $q$ transfer allows to study indirect Mott gap
- Couples to **charge density** directly (Neutrons couples to spin).
- Energy Resolution **not** limited by the core hole lifetime: achieve $k_B T$ resolution

Why???
Soft x-ray resonances (3p -> 3d) provide the most sensitive channels of excitations to study orbital wave excitations.

- Optical Phonons: ~ 40 - 70 meV
- Magnons: ~ 10 meV - 40 meV
- Orbital fluctuations (originated from optically forbidden d-d excitations): ~ 100 meV - 1.5 eV

Requires study of energy losses with energy resolution better than 10 meV.
Previous experiments (@ ALS):

- Energy resolution = 200 meV
- Throughput = low

Need better energy resolutions (<10 meV) and higher throughput


Expt carried out @ ALS
meV Resolution VLS Spectrograph

Optical Design

Ray Traces

- Resolution approaching 1 meV.
- Overall length = 2 meters.
- Designed for Mn 3p (47 eV)
- Source size = 4 microns.

\[ h\nu = 47 \text{ eV} \pm 5 \text{ meV} \]
Resonant Inelastic soft X-ray Scattering

Calculation based on photon energy of 650eV and 3.85 Å lattice constant

Brillouin zone size which can be covered by this spectrometer

Five spectrometers with 30° rotations can cover most of the Brillouin zone
Resonant Inelastic soft X-ray Scattering

System with five spectrometers to cover most of the scattering angles with rotary seal underneath to perform ±15° rotation

Individual spectrometer contains:
- Spherical focusing mirror
- Variable line spacing grating
- High efficiency back-illuminated CCD camera
Intense, transversely coherent soft x-ray beams will allow extension of dynamic laser light scattering to probe temporal fluctuations on the scale of nanometers.
Coherent Soft X-Ray Science

- Coherent scattering from dynamic systems
- Fourier optics at soft x-ray wavelengths

From Attwood
Magnetic Structure and Fluctuations in a Co:Pt Multilayer

- Candidate for future magnetic recording media
- Perpendicular magnetic anisotropy
- Magnetic domains ~ 100 nm
- ‘Tunable’ magnetization loop

50 repeats (7Å Pt + 4Å Co)
Imaging Magnetic Domains with a Soft X-ray Microscope

- Contrast provided by huge magnetic circular dichroism near the Co L$_{23}$ absorption edge $[2p_{3/2} - 3d]$ at $\nu \sim 780$ eV
- Wavelength $\lambda \sim 15.8$ Å allows good spatial resolution
Return Point Memory Effect

Macroscopic (Madelung, 1905):

- The ‘major magnetization loop’ is well-defined - it reproduces after saturation;
- Excursion onto a ‘minor magnetization loop’ leaves from and reconnects to the major loop at a single point.

Microscopic:

- Is the magnetic domain structure reproducible around such major and minor loops?
• Speckle pattern ≡ diffraction pattern of the magnetic domain structure;
• Domain sized inversely related to angular width of the ‘doughnut’;
• Contrast provided by x-ray magneto-optic effects near the Co L-edge.
• New apparatus will enable us to measure the individual Fourier components fluctuating at MHz time scales;
• We will measure domain flipping (Barkhausen noise) and domain wall motion with a combined spatial and temporal resolution not available with other techniques.
**Dynamic Light Scattering**

**Ar-Ion Laser**
\[ \lambda = 3511\text{Å} \]

**Undulator**
\[ \lambda = 16\text{Å} \]

**Spatial Filter**
\[ F_{\text{coh}} \sim 10^{17}/\text{s} \]

**Fluctuating sample**

**Correlator**

**Monochromator:**
\[ \frac{\lambda}{\Delta\lambda} \sim 10^3 \]

**Spatial Filter**
\[ F_{\text{coh}} \sim 10^{10-11}/\text{s} \]

**Fluctuating sample**

\[ C(\tau) = \frac{1}{T} \int I(t + \tau)I(t)dt \]

**\( \tau_{\text{decay}} \sim 1\mu s - 1\text{hr} \)**
The combination of the large soft x-ray magnetic contrast with high coherent flux of the new CSX beamline will enable many experiments that probe spatiotemporal magnetic fluctuations.

Coherent Soft X-ray Magnetic Scattering End Station
- Applied field to 0.52 T of arbitrary orientation
- ‘Continuous’ scattering angle from 0° to ~165°
- Functional prototype for higher field device

Speckle-diffraction Pattern through a Co:Pt film.

Octapolar Flangosaurus with yoke
Why dynamic soft X-rays coherent scattering?

- **More coherent flux** - Scales like $\lambda^2 \times$ brightness (2000 times more coherent flux for $\lambda = 0.4\text{nm}$ than for 0.1nm)

- **High sensitivity for 3d metals**: Resonant 2p-3d transitions (excited electrons into spin polarized empty 3d states)

- **Wide range of Spatial resolution**: 1 nm (wavelength of rad.) - 40 $\mu$m (transverse coherence length)

- **Time resolution**: $> \mu$s - 5ns) limited by time correlator

- **No multiple scattering** complications (photons are weak scatters).

- **Bulk sensitivity**

- Can be applied in the presence of magnetic/electric field.
Time-Resolved X-Ray Spectroscopy

- **Ultra-fast time regime:** \( \leq 200 \text{fs} 
  - Electron excitation/de-excitation (fs)
  - Bond breaking
  - Carrier-carrier scattering
  - Hole-optical phonon scattering
  - Charge density wave/charge transfer

- **Time regime:** \( \leq 2 \text{ps} 
  - Carrier acoustic phonon scattering
  - Relaxation of biological system after light absorption (Rhodopsin); Phase transition (diamond \( \leftrightarrow \) graphite)

- **Time regime:** \( \geq 1-100 \text{ps} 
  - Stripe fluctuation in High Temp Superconductor
  - Magnetic recording
  - Protein folding (ps-s)
Time-Resolved X-Ray Spectroscopy Techniques

- Laser Time Slicing of SR, $\tau \sim 100 - 200$ fs
- Bending Magnet $\sim 10^5$ photons/s
  - Undulator $\sim 10^8$ photons/s
  - Phase transition

- Streak Camera; $\tau \sim 1-2$ ps, limited by detector
  - Could use dispersive methods in time and energy
  - Ultrafast lattice dynamics (coherent phonons)
  - Polaron in condensed matter (magnites)

- Dynamics Coherent Soft X-Ray Scattering, $\tau > 1$ ns - $\mu$s
  - Stripe fluctuation in High Temp Superconductor ($\text{ns-}$ $\mu$s)
  - Magnetic recording ($\text{ns}$)
  - Protein folding ($\text{ps-s}$)
GENERATION OF FEMTOSECOND X-RAYS FROM THE ALS

Schoenlein et al., *Science*, 287, 2237, 2000
Science of Heterogeneous systems, Interfaces, heteromagnetism

• Real Space Microscopy (transmission, scanning or imaging)
  • Biological systems (water window, in-situ conditions, resolution ~20-30 nm, Tomography (Larabell et al)
  • Environmental Science

• Spectromicroscopy of interfaces down to nm resolution
  (PEEM III, SMART, aberration corrected optics)?
  • Exchange bias in magnetic layers (Co/LaFeO3), (example)

• Reciprocal space Imaging with Coherent Soft x-ray Scattering; Spatial resolution ~ 1nm - 40µm
  • Magnetic domains (Co/Pt multilayer), (example)
  • Stripe fluctuation in High Temp Superconductor

Development of these techniques necessary for Nanotechnology: “shape the world atom by atom” Ronald Hoffmann
HIGH SPATIAL RESOLUTION MICROSCOPY OF HYDRATED MATERIALS

Reactions at Fe-oxides

- pH 9.5
- pH 7.5

S. Myneni et al., Science 278, p.1107

Manganese-Eating Bacteria

- 646 eV
- 517 eV

B. Tonner K. Nealson et al.

Malarna

C. Magowan et al.
PNAS 94, 6222

Cell Nucleus Labeled for Splicing Factor

C. Larabell, S. Lelièvre, D. Hamamoto, M. Bissell

Alkali-Aggregate Reaction

K. Kurtis, P. Monteiro et al.
Cement & Concrete Research
Exchange bias in magnetic nanostructures

Linear dichroism at Fe L edge images AFM domains (left). Circular dichroism at Co L edge images FM domains (right). Comparison of images shows that the Co domains align with the AFM domains (light and dark regions inside outlined areas).

**Acknowledgements**

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<tr>
<td>Daniel Chemla, Neville Smith, Howard Padmore, Eli Rotenberg, Mike Martin, John</td>
</tr>
<tr>
<td>Bozek, Wayne McKinney, Phil Heimann, Ernie Glover, Elke Arenholtz, Andres Scholl</td>
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<tr>
<td>(ALS, LBNL)</td>
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<tr>
<td>Zahid Hasan (Princeton)</td>
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<td>ZX Shen, Xingjiang Zhou, Pasha Bogdanov, SSRL/Stanford</td>
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<tr>
<td>A. Lanzara (UC Berkeley/LBNL), Dan Dessau (Univ of Colorado)</td>
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<td>Dave Attwood, Jim Underwood, Jeff Kortright, Miquel Salmeron, Hendrik Bluhm,</td>
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<tr>
<td>Chuck Fadley, Frank Ogleoree, Bob Schoenlein, Roger Falcone, MSD, LBNL</td>
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<tr>
<td>Steve Kevan (Univ of Oregon) and Larry Sorensen (Univ of Washington)</td>
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<td>Satish Mynenei (Princeton)</td>
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Conclusions

We may need to look harder but
a lot of new physics still to come!!