Inner Shell Spectroscopy; Experiments

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What can we hope to learn?

Why X-rays?

What can we hope to learn?
The Soft X-ray Laser @ MaxIV
Swedish Initiative in Theoretical X-ray Science

**Theory**

**RIXS**
- Ågren
- QM/MM
- Complex polarization operator
- Non-linear effects

**NLXS**
- Norman
- Strong-field phenomena
- FEL

**Dynamics**
- Pettersson
- Core-hole induced dynamics
- Liquids, Ultrafast processes

**Correlations**
- Eriksson
- Solid State
- DMFT
- High-pressures
- New states of matter

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Why are X-Rays so Useful?

Imaging - Seeing the Invisible

1895

1993

Atomic and Molecular Structure
- where are the atoms -

Electronic Structure and Bonding
- where are the electrons -

Magnetic Structure and Properties
- where are the spins -
Synchrotron radiation from undulator in storage ring

Electron bunch is “stored” in ring and used over and over.....

Each bunch contains $N_e \sim 10^9$ electrons
...but electrons emit spontaneously
photons not coherent

Intensity limited by independent photon emission – scales as $N_e$
Concept of a free electron x-ray laser

- Replace storage ring by a linear accelerator allows compression of electron bunch – use once, then throw away

- Send electron bunch through a very long undulator

Intensity scales as $N_e^2$ or increased by $10^9$
storage rings and x-ray lasers today

Storage Rings

NSLS-II ~ps ~ns nJ/pulse

~ms

FELs ~fs mJ/pulse

LCLS comparable average power
Linac Coherent Light Source

- Electron Energy: 15 GeV
- Photon Energy: 0.5-10 keV
- Pulse length: 5-500 fs
- Flux: $10^{12}$
- Frequency: 120
- E. Bandwidth: 0.1-2%
- Machine Length: 2 km

LCLS uses only 1/3 of linac
X-ray Facilities of Interest in Europe

- SR PETRA in Hamburg
- SR MAXIV in Lund
- FEL FLASH and XFEL in Hamburg
- FERMI in Trieste
LCLS Movie
Photon Interaction

Incident photon interacts with electrons
Core and Valence

Photon is
- Adsorbed
- Elastic Scattered
- Inelastic Scattered

Electron is
- Emitted
- Excitated
- Dexcitated

Cross Sections
Below 100 keV
Photoelectric cross section dominates

Stöhr, NEXAPS spectroscopy
Spectroscopy
Core Levels-Atom Specific Information

**X-rays probes core levels**

Element Sensitive

Chemical Shifts

Stöhr et.al

Hufner, Photoelectron Spectroscopy
Polarized X-rays Orientations and Directions

Absorption Intensity $\sim | < f | D | i > |^2$

$D = E \cdot r$ is dipole operator

Linear

Right circular

D ~ z ~ r $Y_1^0$

Left circular

D ~ x - i y ~ r $Y_1^{-1}$

Selection rules:
$\Delta l = \pm 1, \Delta s = 0, \Delta j = 0, \pm 1$

Probing Charge orientations and Spin directions
Core Level Spectroscopy

Unoccupied states

Fermi level

Occupied states

Core level

Laser spectroscopy

Creation of core holes

Ionization
X-ray Photoelectron Spectroscopy (XPS)

Excitation
X-ray Absorption Spectroscopy (XAS)

Decay of core holes

Non Radiant
Auger Electron Spectroscopy (AES)

Radiant
X-ray Emission Spectroscopy (XES)

Excitations of valence electrons
Photoelectron Spectroscopy (PES)

PES spectrum ICl in the gas phase
PES spectrum solid Au
Experiment

Photon energy, polarization, incidence angles

Electron kinetic energy, emission angles, spin polarization
Spectrometers

\[ E_b = h\nu - E_{\text{kin}} \]

measurement of the electron kinetic energy

electrons are dispersed in electric or magnetic fields

hemispherical analyzer
Spectrometer System

Beamline 8.0.1 (ALS)
and the Uppsala
Surface-Science Endstation

U5 Undulator
Optical Elements
Hemispherical Electron Analyzer

Rotatable Analysis Chamber
Electron Analyser
NEXAFS Detector
(not visible)
X-ray Emission Spectrometer

Ion Pump
Background

Electron scattering by transport through solid

Energy losses gives a secondary background

Escape depth of elastic electrons of the order of 5-20 Å

Surface Sensitivity
Energy Scales

Binding energies

- Solids relative to Fermi level
  Directly from spectrum
- Gases relative to Vacuum level
  Determined using calibration gases with binding energies obtained from optical measurements
Binding Energies

Ground state picture

Koopmans theorem

Assuming the remaining electrons inert

Relaxation

Valence electrons change due to electron removal

Difference in total energy

total energy of the whole system including all interacting atoms
Spin Orbit Splitting

\[ 3p^6 + h\nu \rightarrow 3p^5 \approx (3p)^{-1} \]

Spin and angular momentum interaction

\[ J = l \pm s \]

For \( l = 1 \) and \( s = +\frac{1}{2} \) \( J = \frac{3}{2} \)

\( s = -\frac{1}{2} \) \( J = \frac{1}{2} \)

Two lines seen in spectrum \( 3p^{3/2} \) and \( 3p^{1/2} \)

Intensities ratio of the two lines given by the population of the orbitals

\[ \frac{(2J_{3/2} + 1)}{(2J_{1/2} + 1)} = \frac{4}{2} = 2 \]

\[ p \text{ shell} \rightarrow p_{3/2} \text{ and } p_{1/2} \text{ ratio} \rightarrow 2:1 \]

\[ d \text{ shell} \rightarrow d_{5/2} \text{ and } d_{3/2} \text{ ratio} \rightarrow 3:2 \]

\[ f \text{ shell} \rightarrow f_{7/2} \text{ and } f_{5/2} \text{ ratio} \rightarrow 4:3 \]
Lifetime broadening

The full width ($\Gamma$) of a spectral line is given by the lifetime ($\tau$) of the final state:

$$\Gamma = \hbar / \tau$$

Valence hole states for free atoms no broadening

Lifetime of core hole states is determined by sum of the rate for all decay channels:

Auger and fluorescence (X-ray emission)

$$\Gamma = \Gamma_{\text{aug}} + \Gamma_{\text{fluo}}$$

![Diagram showing level transitions and lifetime broadening](image.png)
Angular Distributions

Photoelectrons are ejected along the E-vector

Dipole selections rules

\[ s \rightarrow \varepsilon p \]
\[ p \rightarrow \varepsilon d \]
\[ d \rightarrow \varepsilon f \]
\[ f \rightarrow \varepsilon g \]

Outgoing waves
Band Structure

Angle resolved photoemission
Photoionization cross sections

Cross sections decreases with increasing photon energy

Resonance in Eu around 4d threshold
Core Level Electron Spectroscopy

Electrons interact strongly
Surface Sensitivity
5-20 Å

Dependent on electron kinetic energy

Chemical Shifts

Chemical shifts of core levels of the same element due to different chemical surroundings.
Z+1 Approximation

The valence electrons can not approximately distinguish an extra charge in the core region or in the nucleus

Core ionized final states

\[ \text{C*O} = \text{NO} \]
\[ \text{Ni*} = \text{Cu} \]
N$_2$ and CO on Ni(100)

$$E_b = E_{\text{Ground TOT}} - E_{\text{Final TOT}}$$

Two different N atoms

1.5 eV binding energy shift

The same ground state for both atoms

- Difference in Adsorption energies
  - $\Delta E = 1.5$ eV

- Similar ground state energy
  - $\Delta E = 1$ eV
Vibrations Core Levels

Frank Condon Principle
Core levels are non bonding orbitals
No vibrational excitations expected?
Relaxation in the ionized state
Different potential energy curves

Chemical shifted components

Adsorbed CO on Ni

Methane
CH$_4$

C1s

![Graph showing C1s photoelectron spectrum of Propyne, CH$_3$CCH](image)

C1s photoelectron spectrum of Propyne, CH$_3$CCH
hv = 330 eV

Intensity (arb. units)

O1s
hv = 700 eV
C1s
hv = 320 eV

![Graph showing vibrational levels](image)
Surface Core Level Shift (SLCS)

\[ E_b = E_{\text{Final TOT}} - E_{\text{Ground TOT}} \]

\[ E_B(\text{bulk}) = \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \]

\[ E_B(\text{surf}) = \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \]

\[ \Delta E_S = \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \]

\( \Delta E_S \) Surface segregation energy for \( Z+1 \) impurity in \( Z \) metal

We have a lower binding energy for Au at the surface than in bulk for Pt (111)

The more open surfaces have a larger \( \Delta E_S \)
Differentially-pumped electrostatic lens allows operation at $p(\text{H}_2\text{O}) < 5$ Torr (equilibrium vapor pressure of water at +1 $^\circ$C)

Bridging the pressure gap: from UHV to near-ambient conditions

Wettability tuned by the presence of OH: Cu(111)

Ambient Pressure XPS: Electrochemical Cell

Ambient Pressure XPS: Electrochemical Cell
Oxygen Reduction Reaction (ORR) on Pt

Demonstration of electrochemical cell in XPS system

Probing oxygenated species during the oxygen reduction reaction

OPEN CIRCUIT RESULTS

**ORR INTERMEDIATES DURING OPERATING FUEL CELL**

Non-hydrated OH at 0.9 V

\[ P(O_2) = 2 \text{ Torr} \]

\[ P(H_2) = 31 \text{ Torr} \]

Core Level Spectroscopy

Unoccupied states

Fermi level

Occupied states

Core level

Laser spectroscopy

Creation of core holes

Ionization
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Excitation
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Non Radiant
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Radiant
X-ray Emission Spectroscopy (XES)

Excitations of valence electrons
X-ray Absorption Spectroscopy

Dipole selection rule $\Delta l = \pm 1$

1s $\rightarrow$ 2p

Molecular orbital or scattering picture

NEXAFS or XANES


Stöhr, NEXAFS spectroscopy
Liquid Water XAS measurements

(a) Direct transmission mode (T-mode-XAS)

(b) Indirect mode via decay: Fluorescence Yield (FY-XAS)

$\text{Si}_3\text{N}_4 \quad \text{H}_2\text{O} \quad \sim \text{400nm} \quad \text{Si}_3\text{N}_4$

incoming beam

transmission

$\text{Diode}$

$I_0 \rightarrow I_1$

$I_1 = I_0 \exp \{ -\mu d \}$

$\text{Diode}$

$I_0 \rightarrow \text{fluorescent decay} \rightarrow I_1$

steady water in straw with a cut

Liquid Water XAS measurements II

(c) Indirect mode via decay: Auger Electron Yield (AEY-XAS)

(d) Indirect mode via energy loss: X-ray Raman Scattering (XRS)
**Comparison XPS and XAS**

XPS measures the photoemitted electron at fixed photon energy.

XAS measures the photo excitation and ionization cross section at different photon energies.
EXAFS

Extended X-ray Absorption Fine Structure

Interference of outgoing photoelectron and scattered waves

\[ \chi(k) = (-1)^l \sum_i A_i(k) \sin[2kr_i + \beta_i(k)] \]

Nearest neighbor distance

Coordination shells
Polarized X-rays Orientations and Directions

Probing Charge orientations and Spin directions

Absorption Intensity $\propto |\langle f | D | i >|^2$

$D = E \cdot r$ is dipole operator

Selection rules:
$\Delta l = \pm 1$, $\Delta s = 0$, $\Delta j = 0, \pm 1$
Linear Dichroism

The Search Light Effect

K-edge
- probe empty $p$ orbitals
- $E \rightarrow k$
  - no absorption
  - large absorption

L-edge
- probe empty $d$ orbitals
- $E \rightarrow k$
  - no absorption
  - large absorption

Molecular Orientations
Surfaces, Polymers etc.

Stöhr NEXAFS Spectroscopy
Molecular orientations

Glycine on Cu(110) loses acidic proton 
\[ \text{COOCH}_2\text{NH}_2 \]
(110) surface two fold symmetry, spectra can be resolved in 3 directions.
$O_2$ dissociation is mediated by chemisorbed precursors

Gas Phase $O_2$

Chemisorbed $O$
$T < 750 \text{ K}$

Chemisorbed $O_2$
$T < 130 \text{ K}$

Physisorbed $O_2$
$T < 45 \text{ K}$

$E_{\text{diss}}$

Potential energy

Rxn. coord.

Atomically adsorbed

Chemisorbed precursor

Physisorbed precursor
Shape resonances

Bond length with a ruler

Intermolecular bond length

C. Puglia PhD thesis
Initial state rule

The integrated spectral intensity reflects the number of holes in the initial state, ground state.
X-ray Microscopy

Scanning Transmission X-ray Microscopy (STXM)

Transmission X-ray Microscopy (TXM)

X-Ray Photoemission Electron Microscopy (XPEEM)

Present resolution in the 20 - 40 nm range
Core Hole Decay

\[ \Gamma = \Gamma_{\text{aug}} + \Gamma_{\text{fluo}} \]

XES one electron picture

AES two electron interaction; complex Correlation effects

Core hole life time

Sum of all decay channels

Resonant Processes

Non Radiant
- Resonant Photoelectron Spectroscopy (RPES)
- Resonant Auger Spectroscopy (RAES)
- Autoionization Spectroscopy (AIS)

Radiant
- Resonant Inelastic X-ray Scattering (RIXS)
- Resonant X-ray Emission Spectroscopy (RXES)

Participator decay one hole final state
Spectator decay two hole-one electron final state
Participator decay Recombination process ground state
Spectator decay one hole-one electron final state
Resonant Photoemission

Valence band features resonant enhanced at core level threshold

\[
I = \left| M_{\text{PES}} + M_{\text{Aug}} \right|^2
\]

Constructive and destructive interference of direct photoemission and Auger decay

Fano profile

Core Hole Clock Method

Probing charge transfer processes on a femtosecond timescale

\[ t = 0 \]

Charge transfer

\[ t = \tau \]

Auger decay

\[ \tau_{\text{Ar}2p} = 5.5 \times 10^{-15} \text{ s} \]

+1 Spectator final state  +2 Auger final state

46%  54%

\[ P_{\text{CT}} = \left(1 + \frac{\tau_{\text{CT}}}{\tau_{\text{Ar}2p}}\right)^{-1} \]

\[ \tau_{\text{CT}} = 4.7 \times 10^{-15} \text{ s} \]


Resonant X-ray Inelastic Scattering

Veritas at MAXIV
Resonant X-ray Inelastic Scattering

**Free molecules**

Dipole selection rule:

\[ g \rightarrow u \] transitions

**Solids**

Conservation in \( k \) vector

**Graphite**


X-ray Emission Spectroscopy

Atom specific

Orbital symmetry selective

CO gas

Calculation

Intensity (a.u.)

Binding Energy (eV)

X-ray Emission and Photoemission

XES and PES, the same final state

Ground State → Core Hole Creation → hv → Core Hole State

hv → X-ray Emission

hv → hv → Photoemission

Valence Hole State → e⁻ → E_F


Atom Selectivity

Selective excitation of inner and outer nitrogen atoms

Catalysis in Real Time
The Catalyst Challenge

Understanding reaction mechanism and dynamics
LCLS pump-probe experiments
400 nm fs-laser induced reactions of CO and O on Ru(0001)

Two-temperature model
50 fs, 140 J/m²

Electron temperature
Phonon temperature

Time (ps)

Temperature (K)

Two-temperature model
50 fs, 140 J/m²

Electron temperature
Phonon temperature

<1ps electronic excitation
>1ps phononic excitation

400 nm fs-laser pump
O and CO are both excited to produce CO$_2$.

Observation of the Transition State.
Pump-probe of CO oxidation

X-ray laser  Optical laser

O  CO 2\pi^*
Transient Time Scales

- O activation 300 fs
- CO activation 500 fs
- Formation of *OC--O 800 fs
- Formation of OC---O* 800 fs

Ultrafast Observation of the Transition State Region in Catalytic CO Oxidation on Ru(0001)

New Era in Probing Catalysis

- First surface chemical reactions with LCLS
- Proof of principle
- Precursor to CO desorption in a weakened surface chemical bond
- Transition State with CO—O interaction in CO oxidation
- H+CO → HCO, Fischer-Tropsch, ammonia synthesis, etc.
- Higher pressure (~100 torr), solid-liquid interfaces, photocatalysis
- Shorter FEL pulses, THz radiation control
- “Chemical Physicists dream”

SLAC (SUNCAT, LCLS, SSRL)  
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Contributions

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