Computational Modeling of Inner-Shell Spectroscopies

Outline

- Experimental Techniques
- Theoretical Approximations
- Example: Liquid water
- LCLS: Supercooled water droplets
- Following a chemical reaction in real time

Emphasize integration of experiment and theory

Features of X-ray spectroscopy

Good features:

- Element specific (core-levels well separated)
- Chemical specific (chemical shifts)
- Maps local electronic structure
- Structure and orientation

But:

- Chemistry of initial or final state?
- Core-hole effects

Core Spectroscopic Processes



XRS: X-ray Raman Spectroscopy

Core-Level Spectroscopy

X-ray Photoelectron Spectroscopy

- Local occupied core states

• X-ray absorption spectroscopy

Local unoccupied valence states

• X-ray emission spectroscopy

- Local occupied valence states
- Selective probing via resonant excitation

Core-level localized on atom

 Element specific information (background free)



X-ray Photoelectron Spectroscopy (XPS)



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Fig. 1. Illustration of a typical experimental configuration for X-ray photoelectron spectroscopy experiments, together with the various types of measurements possible, including (a) simple spectra or energy distribution curves, (b) core-level photoelectron diffraction, (c) valence-band mapping or binding energy vs \vec{k} plots, (d) spin-resolved spectra, (e) exciting with incident X-rays such that there is total reflection and/or a standing wave in the sample, (f) using much higher photon energies than have been typical in the past, (g) taking advantage of space and/or time resolution, and (h) surrounding the sample with high ambient sample pressures of several torr (with acknowledgement to Y. Takata for part of this figure).

XPS

- Initial and final state effects
- Compare systems A and B
- The XPS shift between them is the difference between initial state difference and final state difference (in total energies)
- For A and B different sites in the same system the initial state cancels out
- Care must be exercised when using potential models, i.e. interpreting XPS in terms of initial state charges
- Final state relaxation and screening often dominate
- XPS "chemical reaction" Z+1 approx.

$$\Delta E_{\rm B} = E_{\rm ion,A}(N-1) - E_{\rm G,A}(N) - (E_{\rm ion,B}(N-1) - E_{\rm G,B}(N)) = E_{\rm ion,A}(N-1) - E_{\rm ion,B}(N-1) - (E_{\rm G,A}(N) - E_{\rm G,B}(N))$$



Final State Screening





The C1s binding energy decreases in the alkanes with increasing chain length due to an increasingly efficient screening [15].



XPS Adsorbate Final State Screening



N₂ physisorbed on graphite Unscreened XPS state Screened state seen (weakly) in Auger (3-4 fs lifetime)

Carbon chemisorbed on Ni Strong coupling Fully screened = lowest XAS Argon physisorbed on metal Pt Unscreened, stabilized by full image charge XPS (+1) state < XAS neutral



Core level localized mainly inside valence Removing a core electron \approx adding nuclear charge XPS shift similar to difference in binding energy between Z+1 atoms in different positions

Water and Lone-Pair Interactions



Lone-pair interactions





Pt(111), Cu(111), Cu(110) surfaces

Geometric Structure Effects



Electronic Structure Effects



Wetting of Metals: O1s XPS



T. Schiros et al. JCP 132, 094701 (2010); J. Electron. Spec. Rel. Phen. 177, 85 (2010)

Water d-band Model



Charge density difference: $\Delta \rho = \rho$ (water+metal) - ρ (water)- ρ (metal)

T. Schiros et al. JCP 132, 094701 (2010)

Digging the s-hole

2.8 to 2.0 Å mimics difference between atomic and ionic radius



T. Schiros et al. JCP 132, 094701 (2010)

previously also proposed by P. S. Bagus and K. H. Hermann, PRB 33, 2987 (1986)

Wetting of Metals: Geometric Structure

Without unoccupied *d*-states available to redistribute charge, how can water wet a noble metal? Cu(110)





Smoluchowski "electron smoothing" effect at a corrugated metal surface



Same material, dramatically different wetting properties depending on surface plane exposed. Schiros *et al.*, J. Chem. Phys. **132** (2010) 094701

Water Bonding Interactions

Repulsive Attractive e-edipole-image dipole Orthogonalization energetic cost due to orbital overlap E_F_- E_{F} Cu 3d • Olp 🍋 Olp Pauli Repulsion Coulomb + charge transfer O lp Metal s-band

Polarization

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



Ambient conditions: Wettability tuned by the presence of OH: Cu(110) vs. Cu(111)

Yamamoto et al., J. Phys. Chem. C 111, 7848 (2007)

X-ray Absorption Spectroscopy





Experimental Details



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



Valence Shell Properties



Chemical Sensitivity

Chemical Shift of C=O π **Resonance**



Core level shifts and

Molecular orbital shifts

Final State Rule

The energetic position of the spectral features are given by the properties of the final state

XAS: core hole final state



Z+1 approximation



Nilsson and Pettersson, Surf. Sci. Reps. 55, 49 (2004).

Transition Metals







Ebert et. al. Phys. Rev. B 53, 16067 (1996).

Total intensity reflects number of empty holes

Properties of 3d Metals



Initial State Rule



The integrated spectral intensity reflects the number of holes in the intial state, ground state

CO and N₂ π* Chemical Shift





Shape Resonances





Linear Dichroism



The Search Light Effect



Surfaces, Polymers etc.

Björneholm et.al. Phys. Rev. B47, 2308 (1993)

Molecular Orientations

Glycine on Cu(110) loses acidic proton COOCH₂NH₂

(110) surface two fold symmetry, spectra can be resolved in 3 directions



EXAFS

Extended X-ray Absorption Fine Structure



X-ray Emission Spectroscopy (XES)



XAS to XES Spectroscopy



A. Nilsson et.al. J. Electron Spectr. 110-111, 12 (2000) Nilsson and Pettersson, Surf. Sci. Reps. 55, 49 (2004).

X-ray Emission and Photoemission

XES and PES, the same final state



N/Cu(100)

PES (Hell)

Clean Cu

10

N/Cu



Project molecular orbitals onto selected atoms

Nilsson and Pettersson, Surf. Sci. Reps. 55, 49 (2004).

Binding energy (eV) T. Wiell et al. Surf. Sci. 304, L451 (1995)

0

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Radical Atomic Interaction

Radical

 N_2 breaking internal bond



The d-band Model



Hammer and Nørskov, Adv. Catal., 2000, 45, 71.

Atomic Adsorbates



Nilsson et. al, Catal. Lett. 100, 111 (2005)

Atom Selectivity



Nilsson et.al. Phys. Rev. Lett. 78, 2847 (1997) Bennich et. al. Phys. Rev. B57, 9275 (1998) Nilsson and Pettersson, Surf. Sci. Reps. 55, 49 (2004).

π–Orbital Interaction



Nilsson and Pettersson, Surf. Sci. Reps. 55, 49 (2004).

π–bonding





The virtual radical state can interact with the d-band

Nilsson and Pettersson, Surf. Sci. Reps. 55, 49 (2004)

σ–Orbital Interaction



Nilsson and Pettersson, Surf. Sci. Reps. 55, 49 (2004)

previous also proposed by P. S. Bagus et al. PRB 28, 5423 (1983) P. S. Bagus and K. H. Hermann, PRB 33, 2987 (1986)

CO adsorption

X-ray Emission



The same bonding mechanism as with N_2

Föhlisch et. al. J. Chem. Phys. 112, 1946 (2000)

Charge Density Difference Plots



Nilsson and Pettersson, Surf. Sci. Reps. 55, 49 (2004).

CO Adsorption in Different Sites





Increasing π and σ interaction with increasing coordination

Föhlisch et.al. Phys.Rev. Lett. 85, 3309 (2000)

Compensation Bonding and Repulsion



Compensation small difference in CO bond length and adsorption energy

Both σ and π polarization increase with the
coordination: π towards the surface to form the bond
σ away to minimize repulsion

Weak bond

Föhlisch et.al. Phys.Rev. Lett. 85, 3309 (2000)

Polarized X-rays Orientations and Directions



Probing Charge orientations and Spin directions