A Soft X-ray Undulator Beamline for High Pressure Photoemission Spectroscopy At NSLS-II

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High Pressure XPS Basic Principles

Why Perform Photoemission Spectroscopy Under Elevated Pressure Conditions?

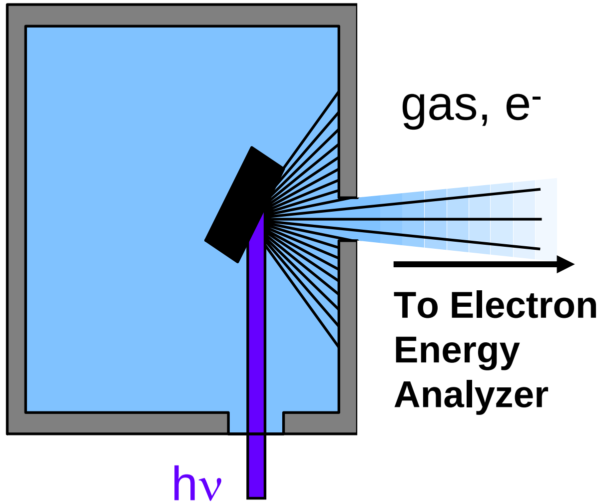
- Photoemission is Chemically Specific, Quantitative and Surface Sensitive

<u>Most Surface Chemical Processes Do Not Occur Under UHV Conditions</u>

- *Atmospheric Chemistry: Surfaces of Ice particles, Liquid Aerosol Particles*
- *Environmental Chemistry: Mineral/Liquid Interface can Control Contamination in Ground Water*
- *Catalysis: Most Industrial Processes Occur at Pressures at or Above Atmospheric Pressure*

<u>General Concept</u>

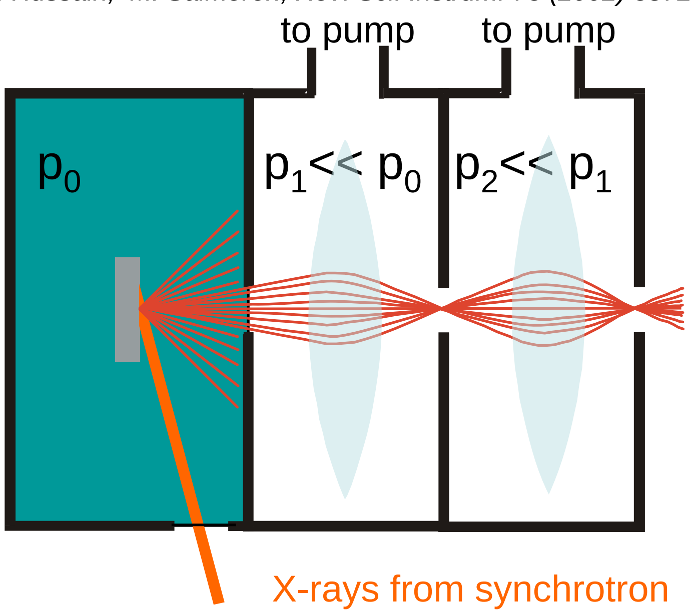
H. Siegbahn, K. Siegbahn
J. Electron Spectrosc. Relat. Phenom. 2 (1973) 319.



Photons enter through a window
Electrons and a gas jet escape
through an aperture to vacuum

<u>High Pressure XPS Berkeley Lab Design</u>

D.F. Ogletree, H. Bluhm, G. Lebedev, C.S. Fadley,
Z. Hussain, M. Salmeron, Rev. Sci. Instrum. 73 (2002) 3872.



Differentially-pumped electrostatic
Transfer lens allows operation at
p > 5 torr

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High Pressure XPS Current and Future Beamlines

Current and Future HP-XPS Experiments (Synchrotron Based)

In operation
ALS (2 currently operating)

1) Undulator Beamline Mainly dedicated to environmentally relevant systems
   - Water adsorption on various surfaces
   - liquids, solutions
   - Also some catalysis/surface science
2) Bending Magnet beamline similar to 1) in systems studied
   - “spillover” from 1)

BESSY
Dedicated Beamline, investigates catalytically relevant systems

Planning Stages
ALBA
ELETTRA
Soleil
Diamond
SSRL
Maxlab
New Taiwan Synchrotron
NSLS

- **High-Pressure XPS Field is Growing and Competitive**
- **Room for Further Growth**
- **NSLS-II May Allow New Experimental Methods and expand Field Further**

High P XPS Bend Magnet → 9.3.2

High P XPS Undulator (STXM Also) → 11.0.2

Beamline	% Allocated	Cutoff Score
1.4 (IR)	77	--
4.0.2 (EPU)	32	2.00
5.3.2 (Polymers XAFS)	55	2.30
6.0.1 (Femtosecond0	63	--
6.1.2 (Soft X-Ray Micrsocopsy)	30	2.37
6.3.1 (Materials Sciences)	89	2.40
6.3.2 (Calibration and Standards)	66	2.90
7.0.1 (XPS, STXM, SXF, SPEM)	23	2.06
7.3.1 (PEEM)	100	--
7.3.3 (SAXS)	--	--
8.0.1 (SXF)	40	2.38
8.3.2	69	--
9.0.1	100	--
9.0 2 (Chemical Dynamics)	40	2.48
9.3.1 (XAMS)	100	--
9.3.2 (APSD/AMC, High-Pressure XPS)	45	
10.0.1. (HERS/AMO)	25	2.11
10.3.2 (Micro XAFS)	48	2.31
11.0.1 (Magnetic Microscopy, Spectromicroscopy; PEEM3)	57	--
11.0.2 (Molecular Environmental Sciences)	30	1.98
11.3.1 (Small Molecule Crystallography)	66	2.26
12.0.1 (ARPES)	25	2.20
12.2.2 (High Pressure)	41	2.43
12.3.2	34	2.58
All Beamlines*	**54.6**	

Energy Range for High Pressure XPS

ENERGY RANGE:

Soft X-Ray 100 to 2000 eV

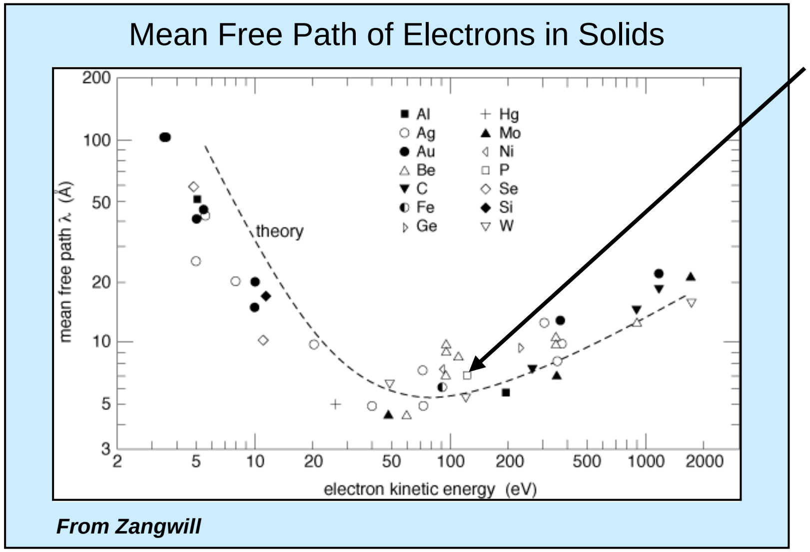
For Chemical and Catalytic Applications we want to be able to probe and be surface sensitive to:

Examples

K-edges C1s: ~284 eV, N1s: ~400 eV, O1s: ~530 eV

Transition Metal L-edges: Ti (~460 eV), Fe (~720 eV), Cu (~75 eV)

P (~135 eV), K (~295 eV), Cl (~200 eV)

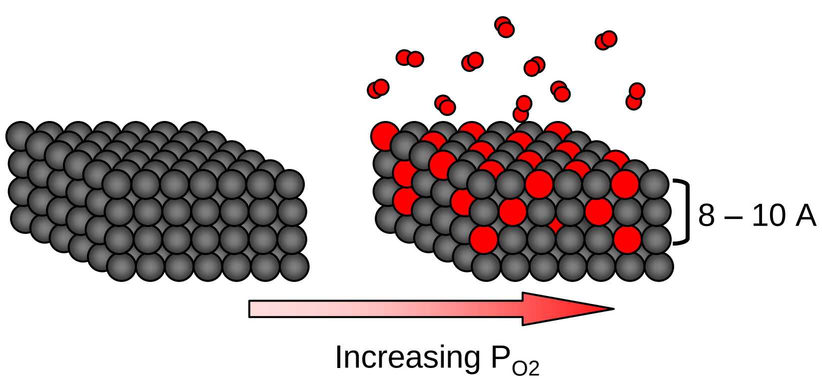


Inelastic Scattering Of Electrons in Solids Makes Electrons In the 50-200 eV KE Range Surface Sensitive

EXAMPLE: OXIDATION OF METAL, DEPTH PROFILING

What is the depth and extent of oxidation as a function of Oxygen pressure?

- Plot O/Metal Ratio as function of photon energy or probe depth



O1s Binding Energy: 530 eV

Need ~1000 eV Photons to Have 1 MFP to Study Oxidation Occurring 8-10 A Deep

~ 2000 eV for up to 20 A deep

Need Good Flux at Photon Energies Greater Than 1000 eV

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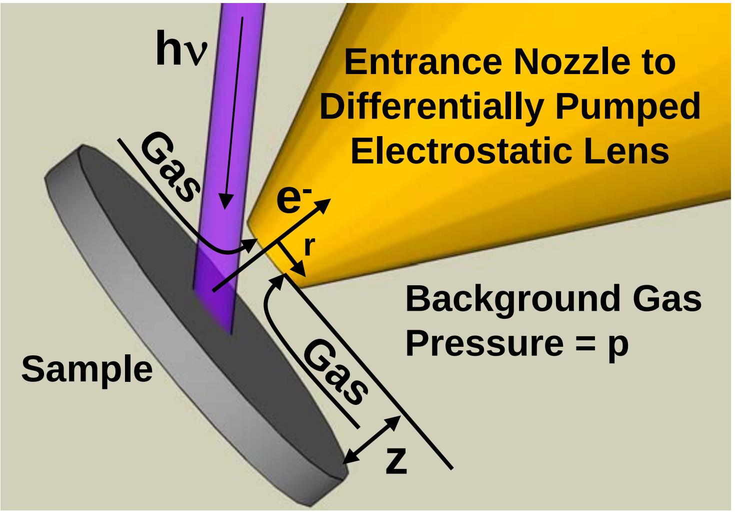
High Pressure XPS and Limitations: Advantages of an Undulator Source

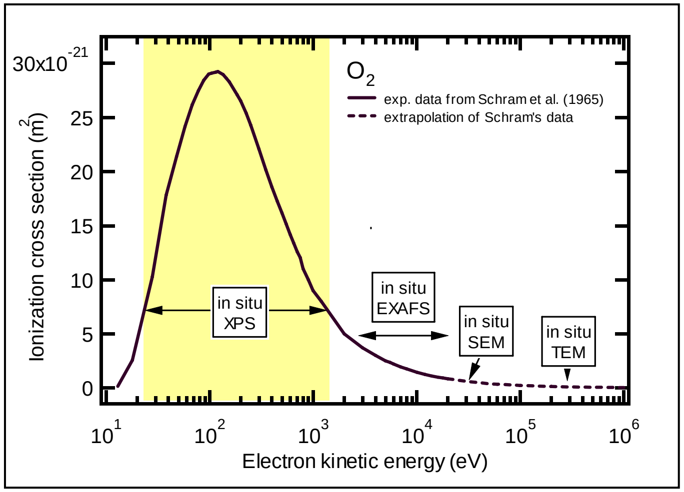
Signal Intensity is Limited by Gas Phase Scattering of Photo-emitted Electrons

Gas is Pumped Through Entrance Aperture



z is limited to distances ~ 2r
(At 2r p ~ 0.95p_o)

Electron Ionization Cross Section of Gas



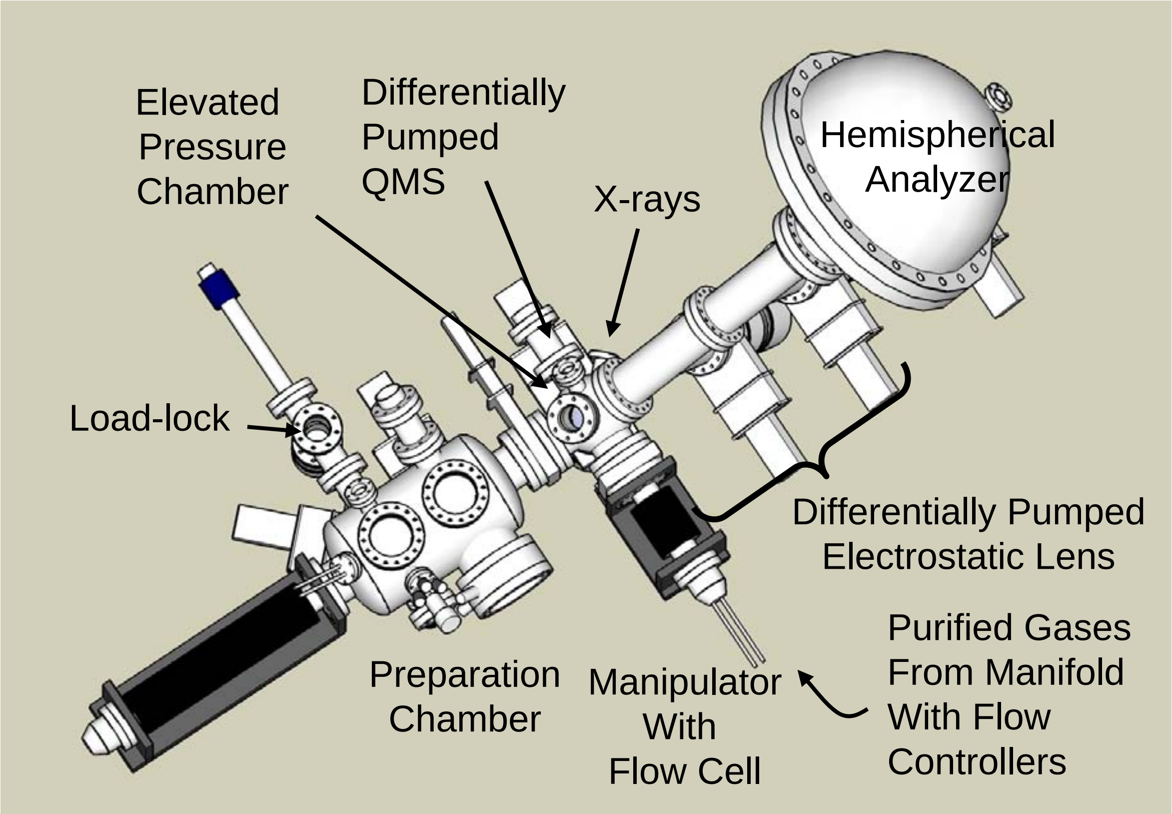
Inelastic Scattering is Mostly Due to Ionization of Gas Phase Molecules

$$I_p \propto I_{vac} \exp(-z\sigma(E)p)$$

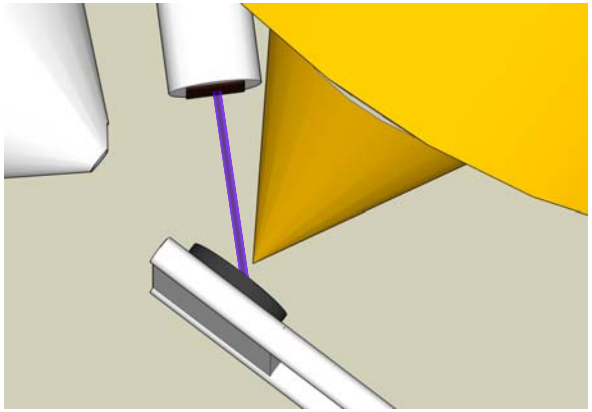
Undulator Source: High Brightness

- Smaller x-ray size allows reduction of r (entrance aperture radius) allows reduction in z (sample-aperture distance) without reducing Pressure at the Sample
- This reduces gas-phase scattering of photoelectrons
  - Higher signal intensity at given P
  - Allows higher Pressures (estimate up to 100 torr with NSLS-II VUV EPU 100 Undulator)

High Pressure Photoemission End-Station



Experimental Geometry



X-rays enter through SiN_x window (typically 100 nm thick, 0.5 x 0.5 mm^2 active area)

Distance between sample and window Approximately ½ inch

<u>Elevated Pressure Chamber</u>

small volume: flow-cell type measurements, contamination reduction
differentially pumped QMS for gas analysis

<u>Gas Manifold</u>

Catalysts for gas treatment/purification, Gas cabinets for Hazardous Gas Storage, Flow Controllers

<u>Preparation Chamber</u>

Surface Preparation Tools: Sputter and Annealing, LEED, Temperature Programmed Desorption, Metal Evaporators

<u>Sample Types</u>

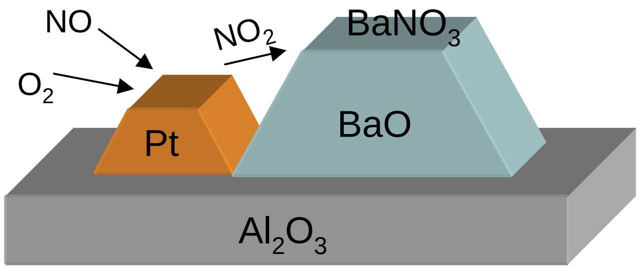
Single Crystal Model Catalysts, Powders, With Modification Possibly Liquids and Ice

Novel Experiment With Undulator Source: Dynamic Measurements on the ms Timescale

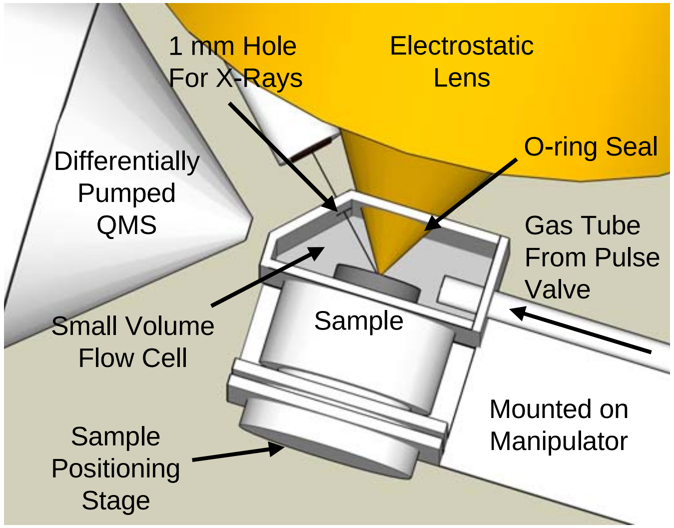
Example NO_x Storage Catalyst

<u>Fuel Lean Conditions</u>
1) Oxidation of NO Storage of NOx

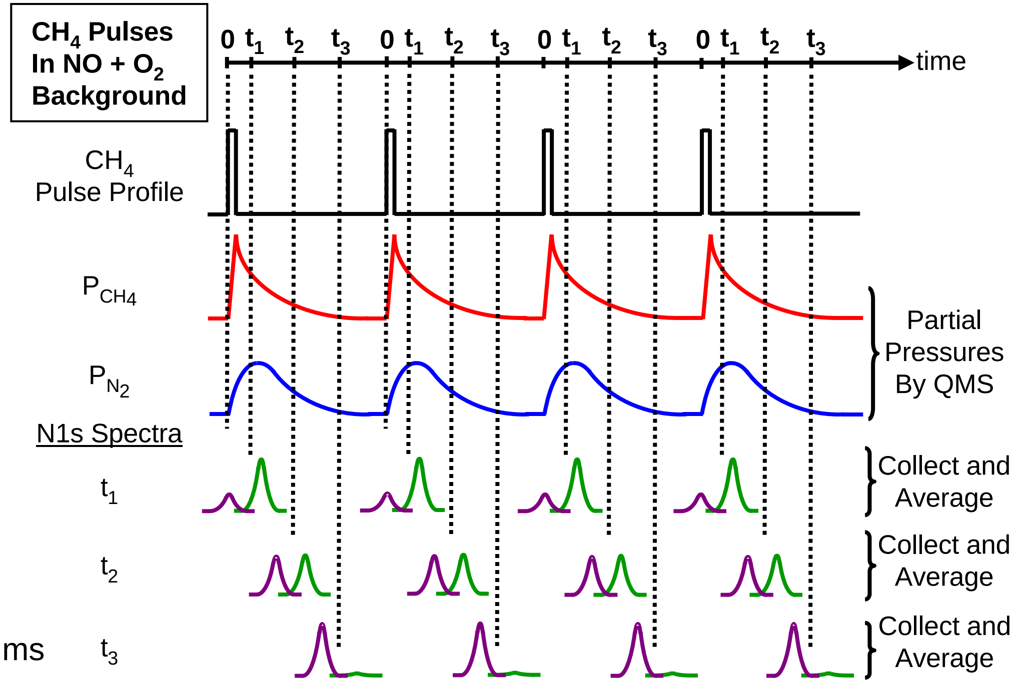
<u>Fuel Rich Transients</u>
3) Release and reduction of NOx



Flow Cell in High P XPS Set-up



Stroboscopic Measurements using Delay-Line Detector



Using Parameters (total dwell time) for Spectra at ALS BL 11.0.2
- 1000 secs to collect a spectrum that represents 5 ms at specified delay time after the pulse
- Experiments may be difficult to achieve at Bend Magnet

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Summary

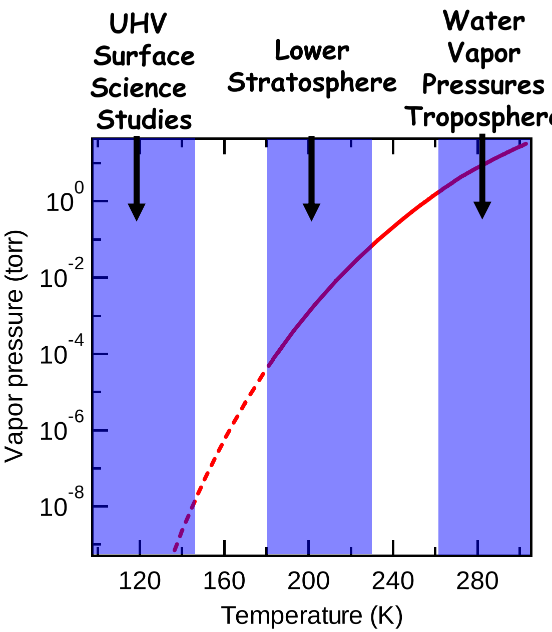
- High Pressure XPS is a currently active field of research
  - rapidly expanding
  - competitive
  - room for further growth

- To perform these experiments an Undulator Source is desirable
  - Smaller Spot Sizes at the Sample
  - Increased Intensity
  - May allow higher operating pressures

- NSLS-II Undulator Source May Facilitate New Novel Experiments that allow the study of catalyst chemical changes on the ms timescale

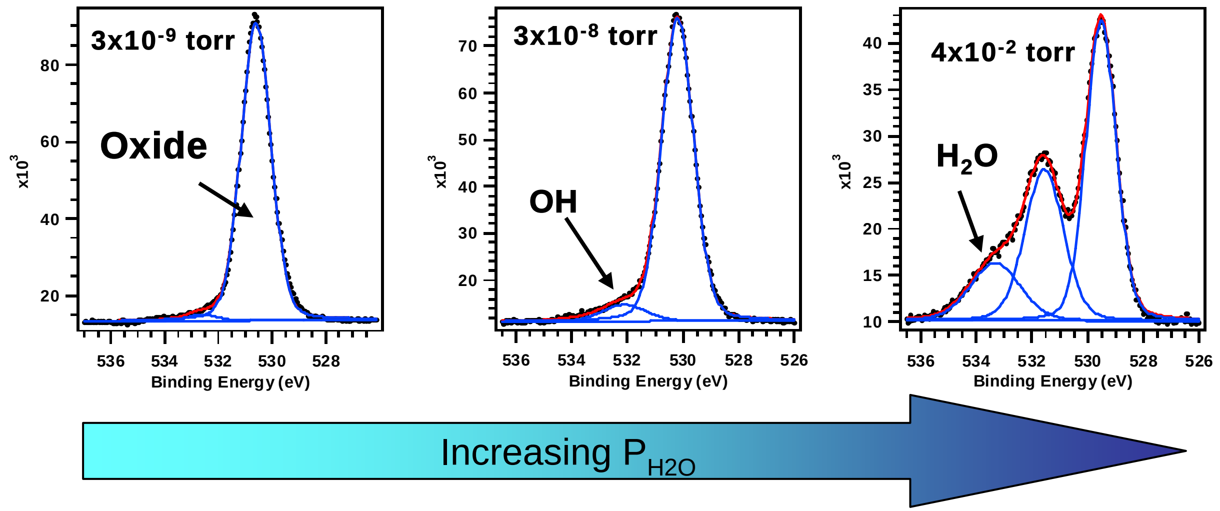
Other Examples of Current Research Using High Pressure XPS

Environmental Applications

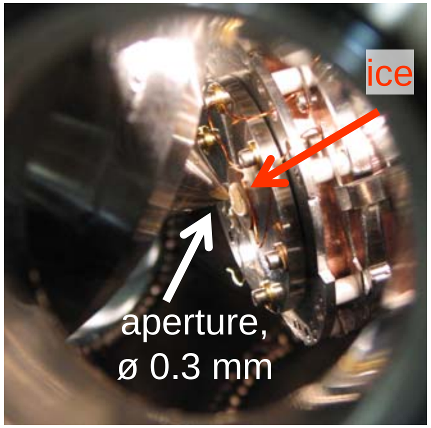


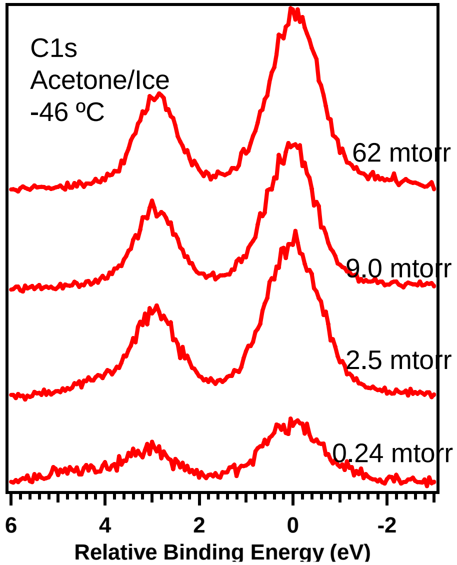
Water Adsorption On Mineral Surfaces

H2O/MgO(100)

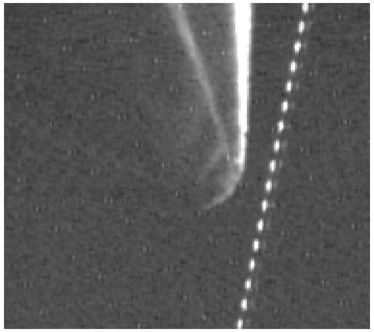


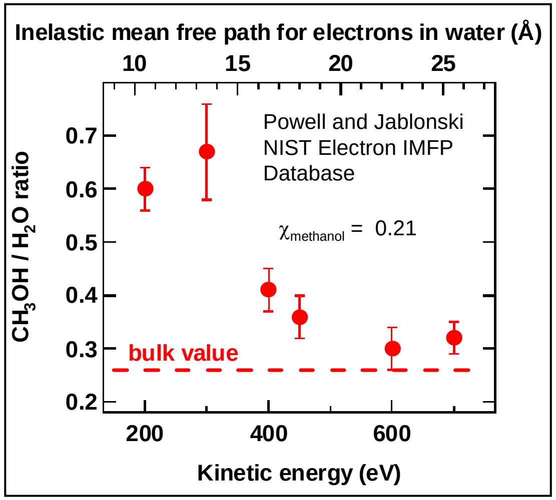
Adsorption on Ice





Liquid/Vapor Interface





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Advanced Light Source Beamline 11.0.2

H. Bluhm et al, J. Electron Spectrosc. Relat. Phenom. 150 (2006) 86.