High-pressure XPS: a new tool for environmental science and catalysis

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The Instrument

Why high-pressure XPS?

Many processes and samples cannot be investigated in UHV ("Pressure Gap")

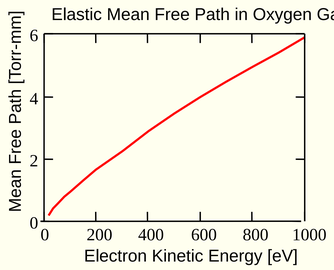
- catalysis, corrosion, some oxidation
- environmental chemistry
- biological samples under wet conditions (high vapor pressure of water!)

Fundamental limit in high-pressure XPS:

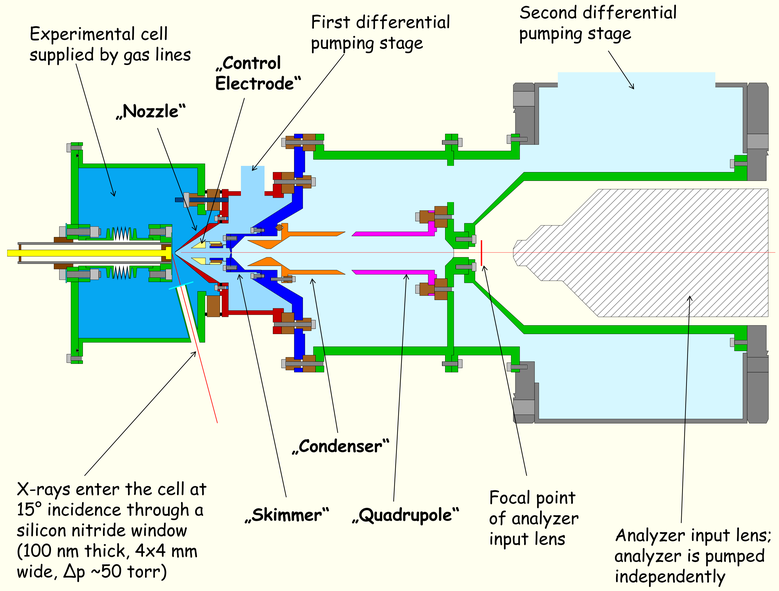
Elastic and inelastic scattering of electrons by gas molecules

LEED-type calculation of elastic scattering cross sections for Oxygen atoms

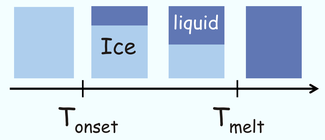
1 Torr-mm of water vapor is 3.3 monolayers



The solution: Differentially pumped electrostatic lens system

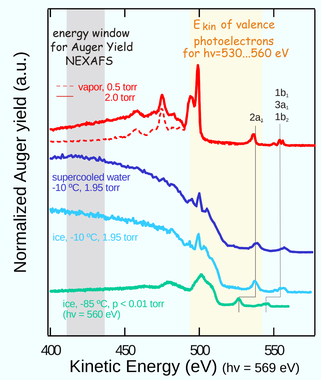


Above a certain temperature the ice surface is covered by a thin liquid film



Our goal is the investigation of the influence of hydrocarbon contamination (using XPS) on the thickness (using NEXAFS) of the liquid-like layer.

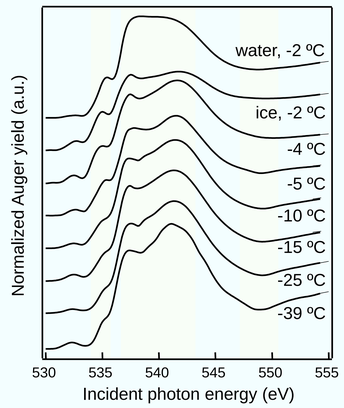
Oxygen KLL Auger spectra

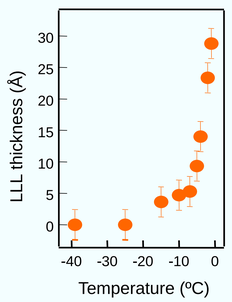


Premelting of Ice

"Clean" Ice Surface

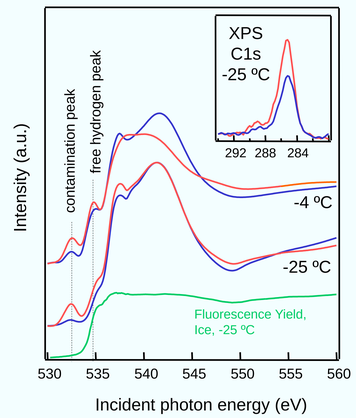
Auger yield NEXAFS spectra showing the premelting transition



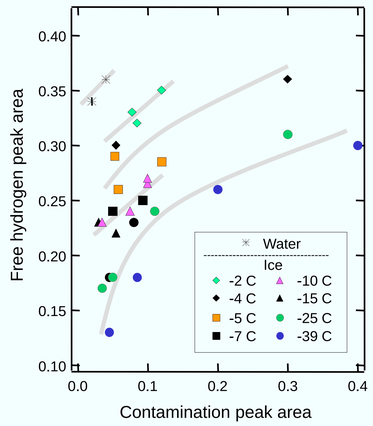


Thickness of the liquid layer on "clean" ice samples as determined from the NEXAFS spectra

Contaminated Ice Surface



Comparison of NEXFAS and XPS: At both temperatures the more contaminated ice surface shows stronger signs of premelting than the less contaminated ice surface.



Area of the free hydrogen peak (535 eV) vs. contamination peak area (532 eV).

Premelting of the ice surface thus depends strongly on both temperature and hydrocarbon contamination.

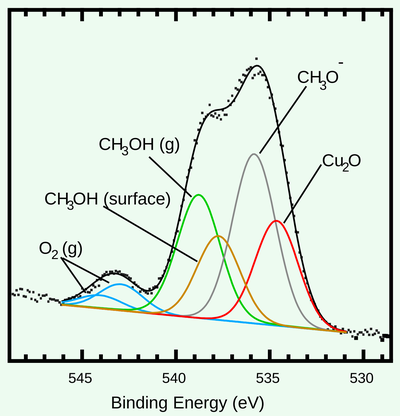
Observing Catalysts at Work

Example: oxidation of methanol over a copper catalyst.

The two main reactions are:

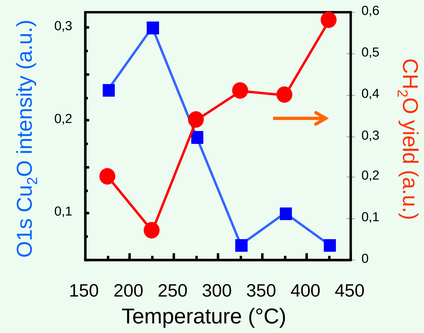
(1) $CH_3OH + \frac{1}{2}O_2 \rightarrow CH_2O + H_2O$
(2) $2CH_3OH + 3O_2 \rightarrow 2CO_2 + 4H_2O$

Reaction (1) (partial oxidation) is an important process in the chemical industry. Our goal is to identify the composition and chemical nature of the surface of the copper catalyst for formaldehyde (CH_2O) production under working conditions.



XPS O1s spectrum of a Cu foil in a gas mixture of 0.07 torr O_2 + 0.34 torr CH_3OH @ 275 °C.

Due to the work function of the sample (4.5 eV) the surface peaks are shifted towards the gas phase peaks.



Comparison of mass spec and XPS data. A more metallic (i.e., less oxidic) Cu surface and higher temperatures favor the production of formaldehyde (CH_2O).

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