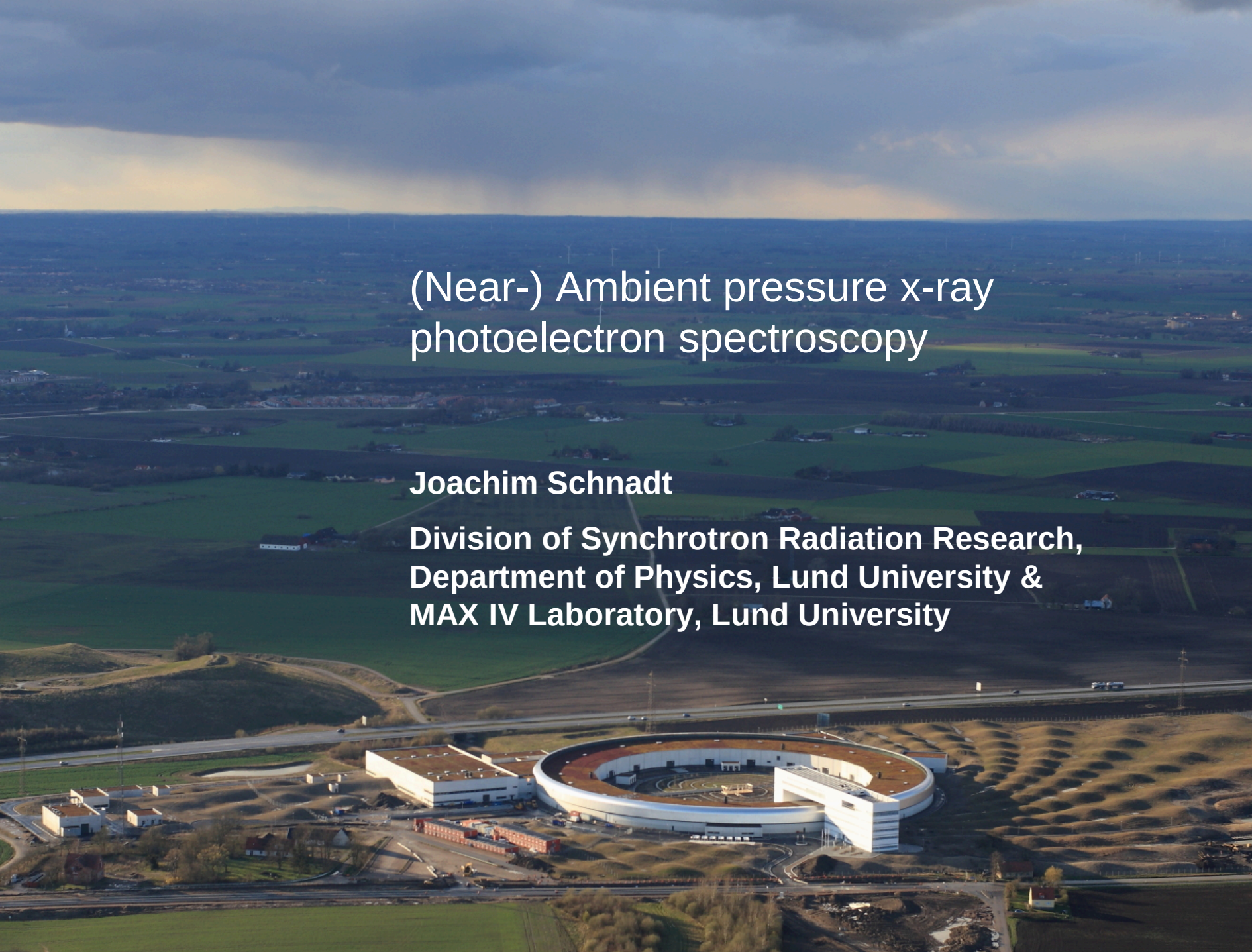

(Near-) Ambient pressure x-ray photoelectron spectroscopy

Joachim Schnadt

Division of Synchrotron Radiation Research, Department of Physics, Lund University & MAX IV Laboratory, Lund University

Outline

- **What** is Ambient pressure x-ray photoelectron spectroscopy?
- **Why** Ambient pressure x-ray photoelectron spectroscopy?
- **How** is Ambient pressure x-ray photoelectron spectroscopy done?
- **Where** can you do Ambient pressure x-ray photoelectron spectroscopy?
- Two **examples** for catalysis, surface science, and atomic layer deposition:
  (a) CO oxidation over Ir(111)
  (b) ”Live” monitoring of Atomic layer deposition: HfO_2/InAs(100)

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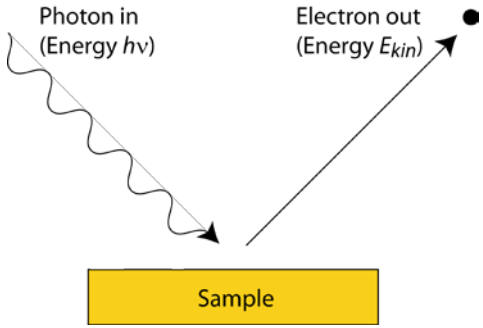
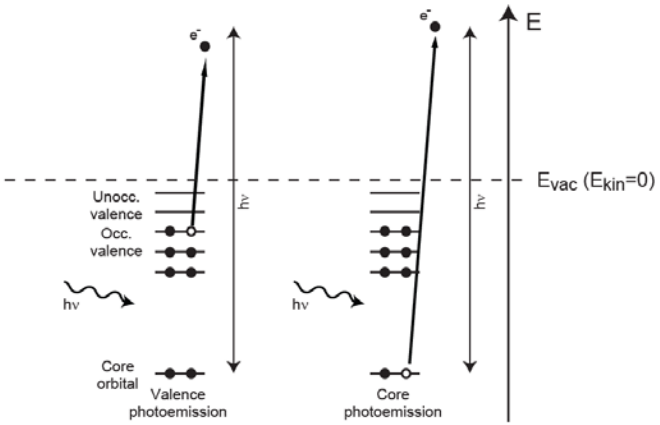
What is Ambient pressure x-ray photoelectron spectroscopy?

It's XPS!



Binding energy of electron in sample:

$$E_B = h\nu - E_{kin} (- \phi)$$



- Information on electronic structure of occupied states
- UPS: valence states
- XPS: core states
- XPS: elemental specificity +
  chemical specificity from chemical shifts
- Relationship between electronic and geometric structure
- Highly surface sensitive (~ nm)

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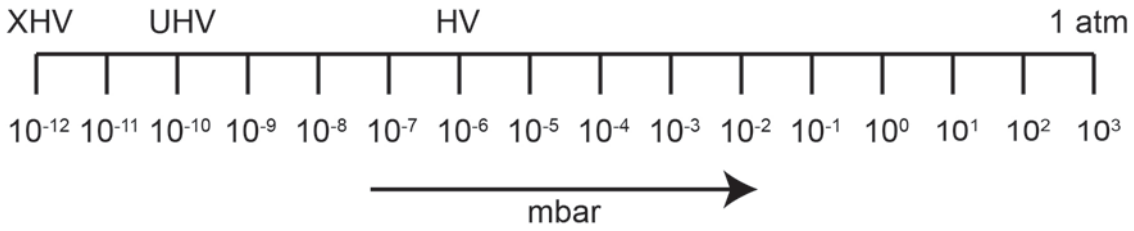
What is Ambient pressure x-ray photoelectron spectroscopy?

High pressure x-ray photoelectron spectroscopy

Near-ambient pressure x-ray photoelectron spectroscopy

Ambient pressure x-ray photoelectron spectroscopy



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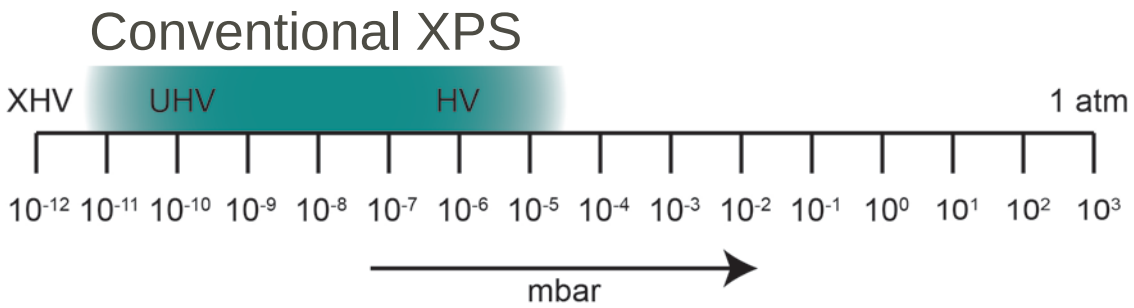
What is Ambient pressure x-ray photoelectron spectroscopy?

High pressure x-ray photoelectron spectroscopy

Near-ambient pressure x-ray photoelectron spectroscopy

Ambient pressure x-ray photoelectron spectroscopy



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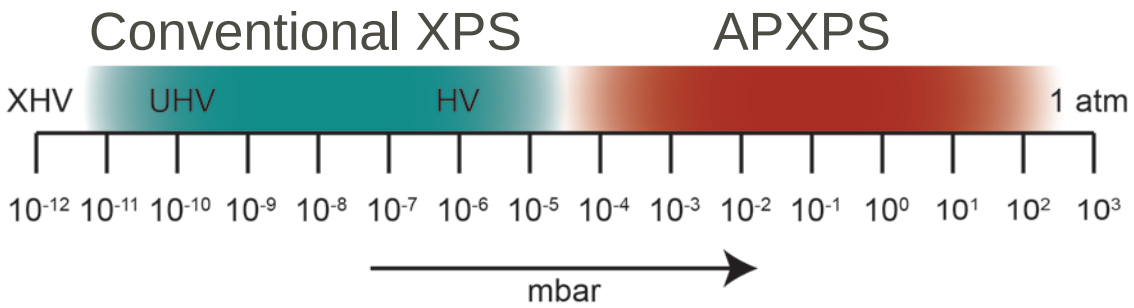
What is Ambient pressure x-ray photoelectron spectroscopy?

High pressure x-ray photoelectron spectroscopy

Near-ambient pressure x-ray photoelectron spectroscopy

Ambient pressure x-ray photoelectron spectroscopy



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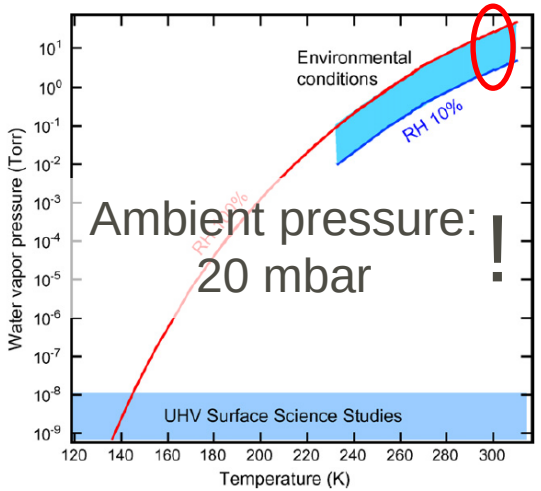
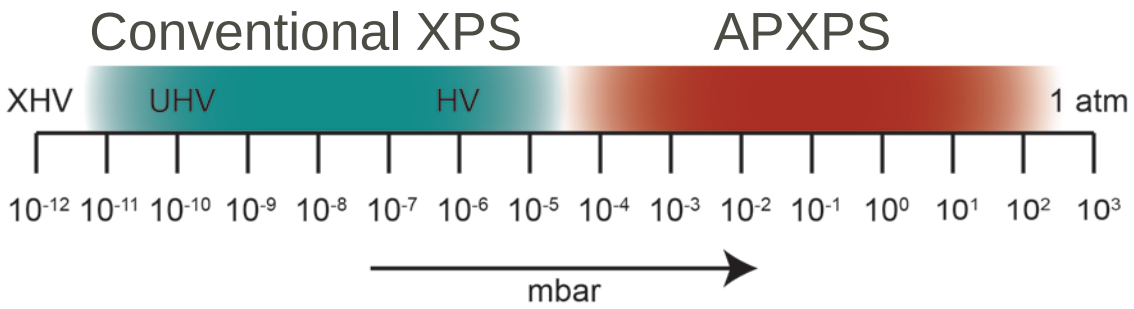
What is Ambient pressure x-ray photoelectron spectroscopy?

Ambient pressure x-ray photoelectron spectroscopy

Ambient pressure:
1 atm

?





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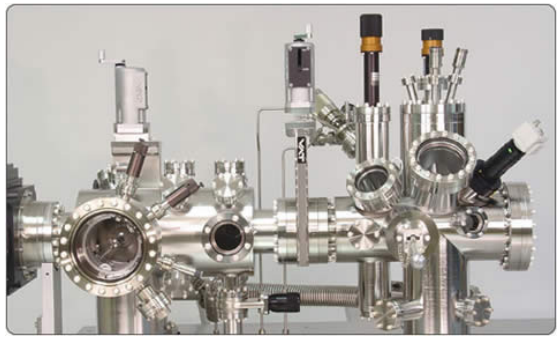
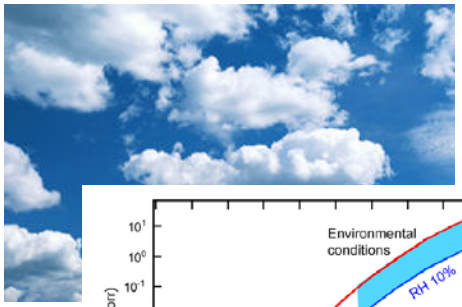
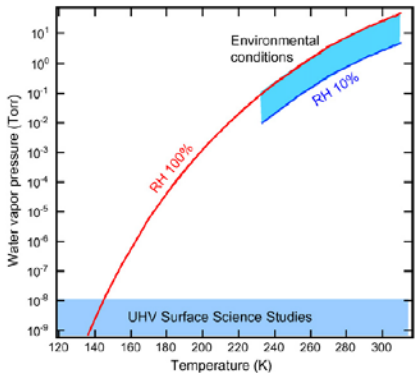
Why Ambient pressure x-ray photoelectron spectroscopy?

Pressures in conventional XPS experiments:
10^{-10} to 10^{-6} mbar

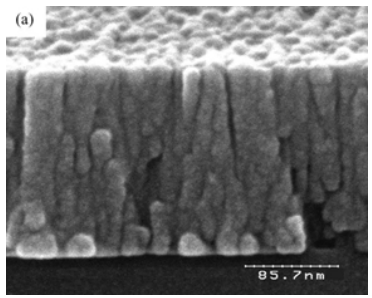






Ambient water pressure:
~20 mbar

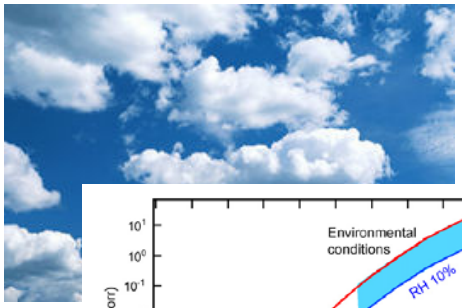
Pressure in a car catalyst:
~atm

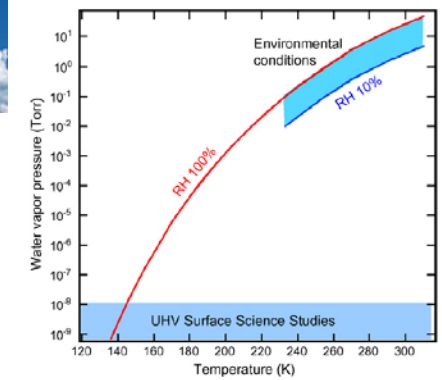


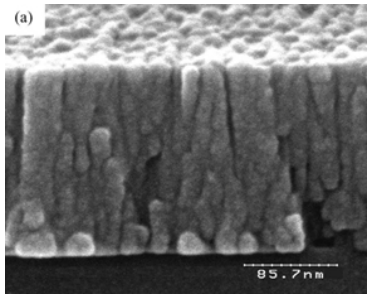
Pressures in thin film growth:
10^{-2} mbar and upwards

Pressures in typical catalytic reactors in the chemical industry:
10^{-2} mbar to hundreds of bar

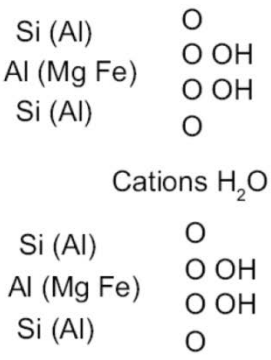
Why Ambient pressure x-ray photoelectron sepectroscopy?



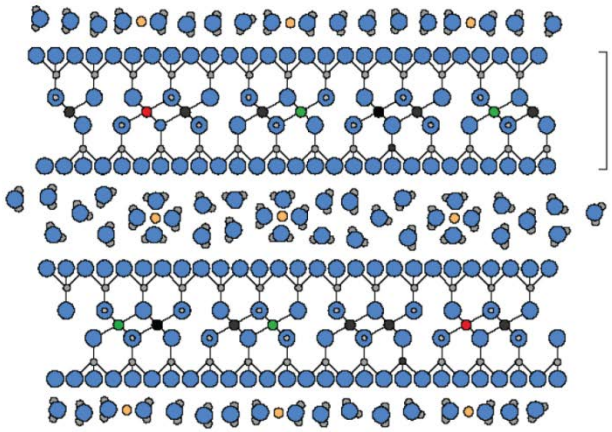




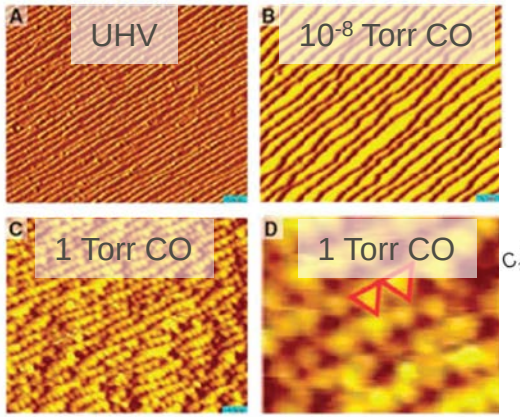
Structure!



A. Pietzsch et al.



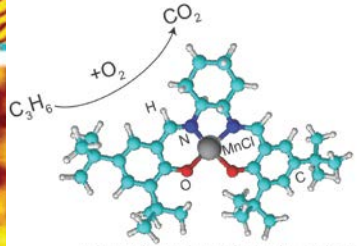
Pt(557)

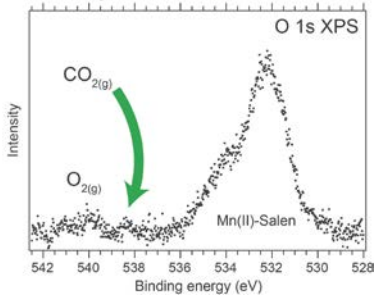


Tao et al., Science 327 (2010) 850

Structural dynamics!

Chemical reactions!





N. Johansson, J. Schnadt et al.

Why Ambient pressure x-ray photoelectron sepectroscopy?

- (Surface) Structures may differ from those observed in UHV
- Dynamic effects may play a significant, if not decisive, role
- Dynamic processes can be studied (chemical reactions)
- Materials with a high vapour pressure can be studied

- ✓ Catalysis
- ✓ Oxidiation & corrosion
- ✓ Film growth
- ✓ Electrochemistry
- ✓ Liquids and solutions
- ✓ Bio/geo samples
- ✓ …

… but … 99.9% of all XPS instruments require high vacuum or ultrahigh vacuum

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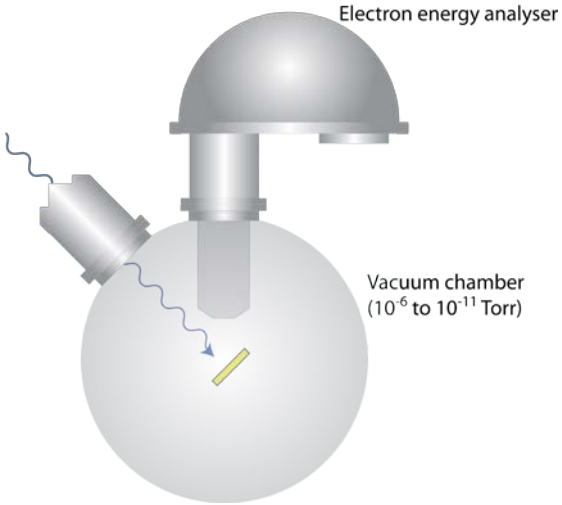
Why (ultrahigh) vacuum?



1. Control of surface state / cleanness

Kinetic gas theory:
Rate of molecules with mass *M* impinging on sample surface with area *A* at pressure *p* and temperature *T*:

$$\frac{\Delta n}{A\,\Delta t} = \sqrt{\frac{N_A}{2\,\pi\,M\,k_B\,T}}\,p$$

→ at p = 10^{-6} Torr a metal surface (sticking coefficient 1) is completely covered by gas molecules in ~1 s

→ gas contaminations down to the ppm or even ppb level (at atmospheric pressure) can lead to a ”poisoning” of the surface

At higher pressure extreme cleanliness is required if contamination by residual gases is to be avoided.

2. Detector requires vacuum

Microchannel plates in detector do not tolerate moisture and other gases when operated (~10^{-6} mbar required)

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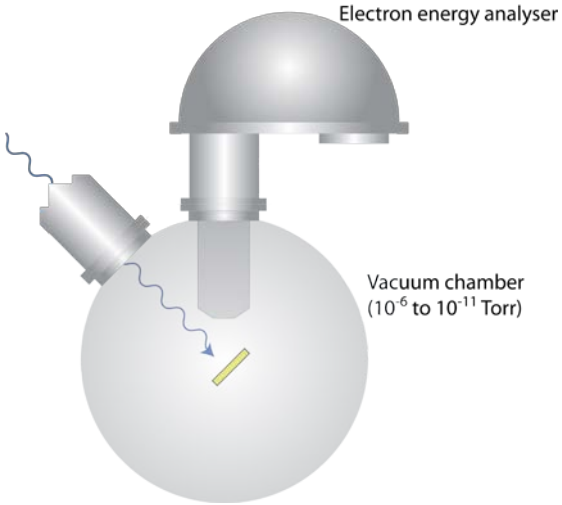
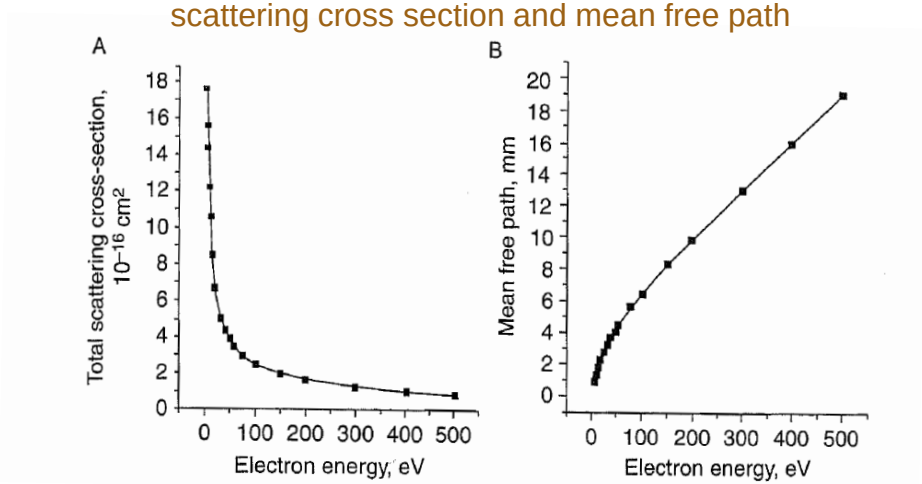
Why (ultrahigh) vacuum?



3. Limited mean free path of low-energy electrons in gases

Electron scattering by molecular hydrogen (1 mbar): scattering cross section and mean free path



from: A. Knop-Gericke et al., Adv. Catal. 54 (2009) 213

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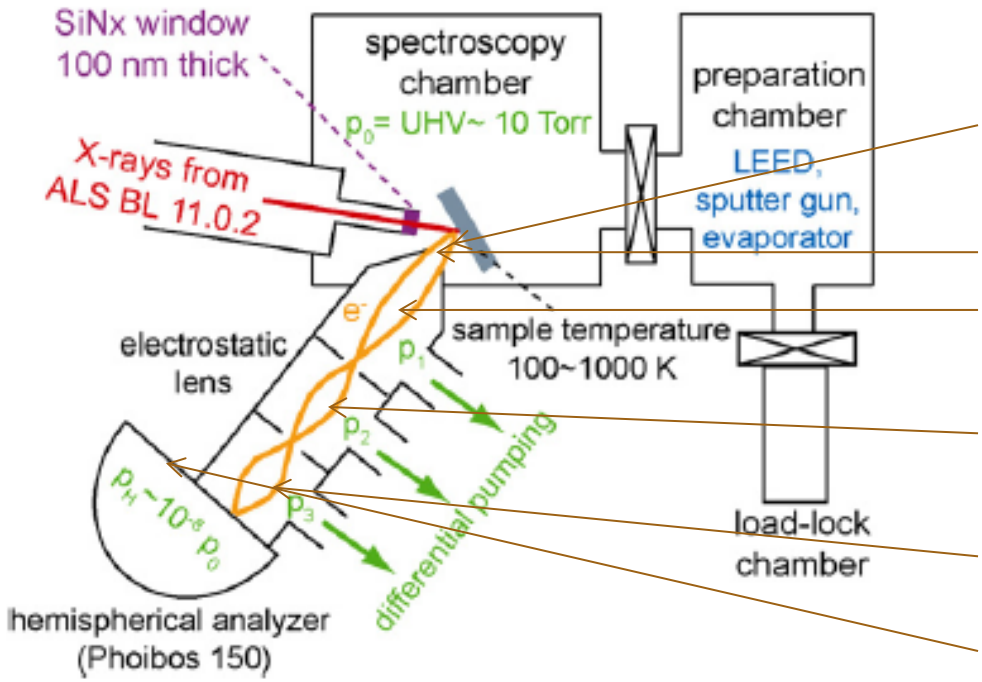
How is Ambient pressure x-ray photoelectron sepectroscopy done?



Pressure at sample:
1 mbar 1 mbar

Aperture size:
1 mm 0.5 mm

Prelens pressure:
10^{-4} – 10^{-3} mbar 10^{-5} – 10^{-4} mbar

1st stage pressure:
10^{-6} mbar 10^{-7} mbar

2nd stage pressure:
10^{-7} mbar 10^{-8} mbar

Detector pressure:
10^{-8} mbar 10^{-9} mbar

Figure 1. A schematic of the ambient pressure XPS spectrometer at ALS beamline 11.0.2.

S. Yamamoto, H. Bluhm, K. Andersson, G. Ketteler,
H. Ogasawara, M. Salmeron, A. Nilsson,
J. Phys.: Condens. Matter 20 (2008) 180425

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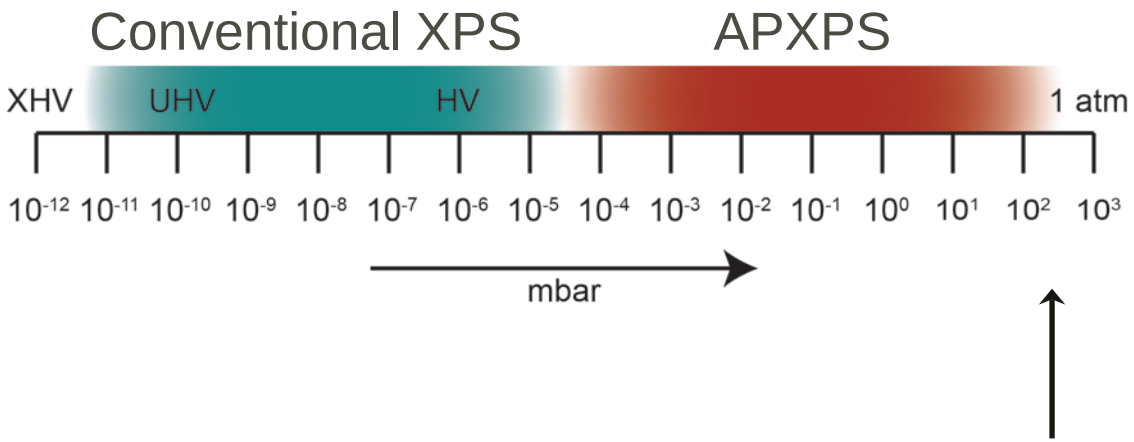
What is Ambient pressure x-ray photoelectron spectroscopy?



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How is Ambient pressure x-ray photoelectron sepectroscopy done?

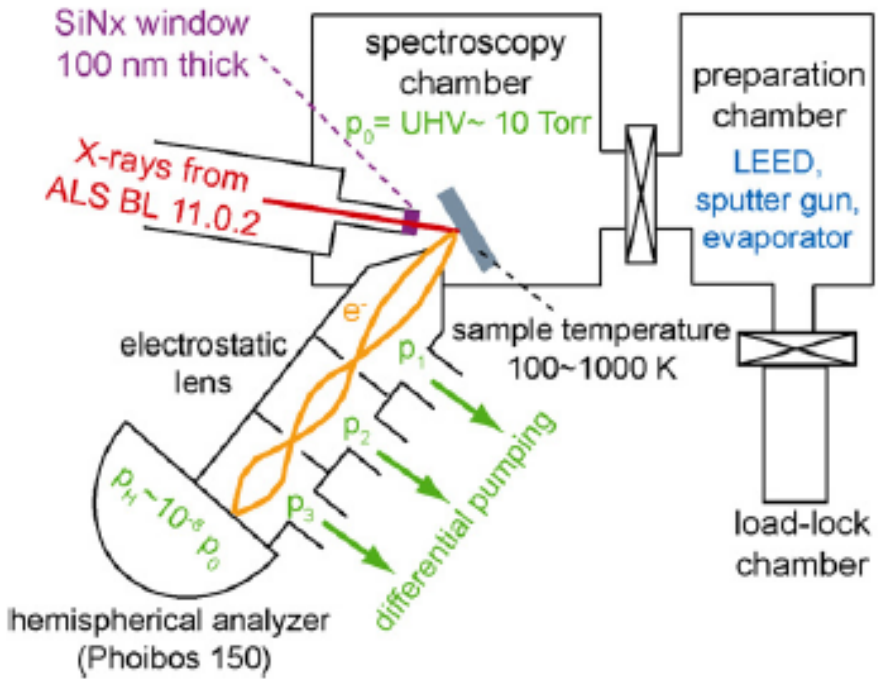

Figure 1. A schematic of the ambient pressure XPS spectrometer at ALS beamline 11.0.2.

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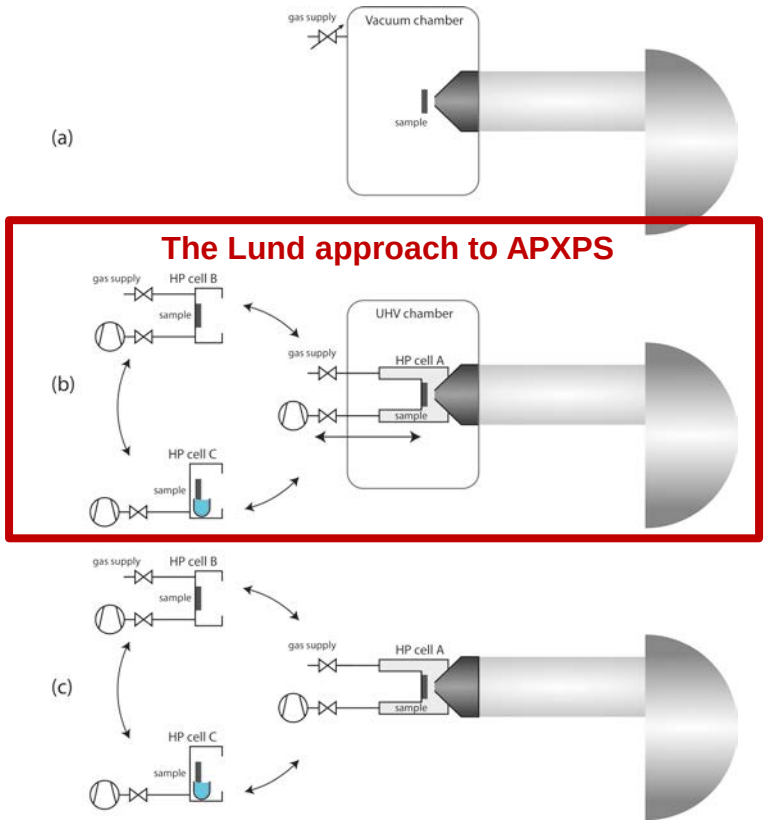
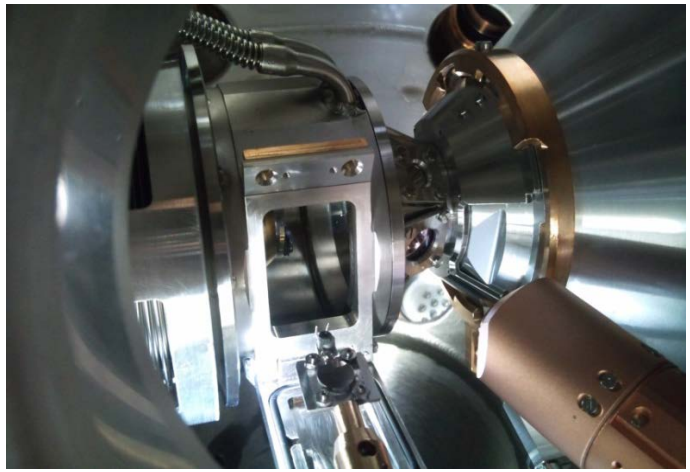


cf. D. E. Starr, Z. Liu, M. Hävecker, A. Knop-Gericke, H. Bluhm, B. Chem. Sov. Rev. 42 (2013) 5833

The Lund approach to APXPS: Ambient pressure cells at the SPECIES beamline



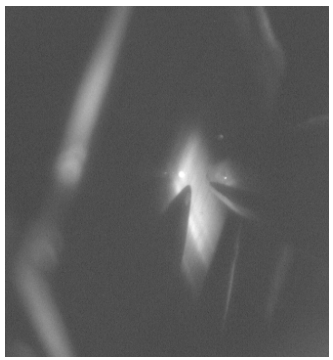
First generation Ambient pressure cell

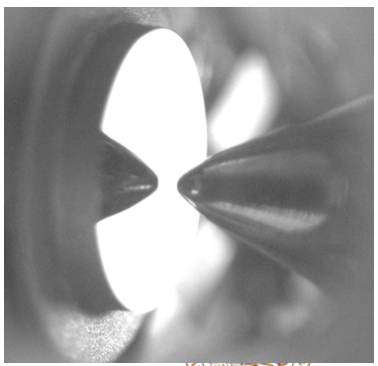
Working pressure: ~0.1 to 25 mbar
(pressure in analysis chamber during operation < 1 x 10^{-6} mbar)

Temperature range: -50 deg. C to 500 deg.

Sample can be moved during measurement (beam damage!)

Developed by SPECS Surface Nano Analysis GmbH based on the concepts and specifications developed at the MAX IV Laboratory





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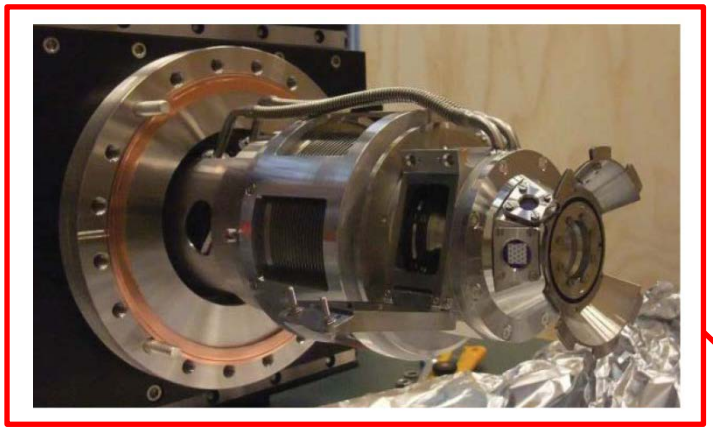
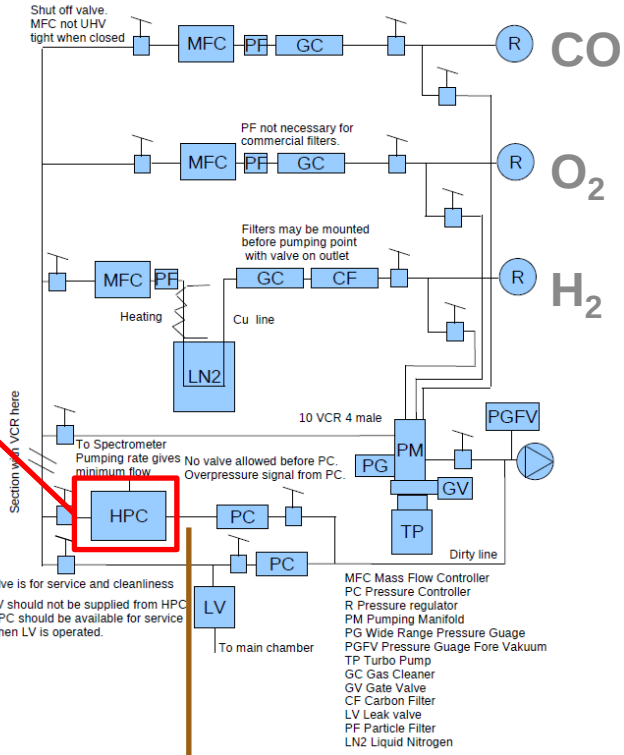
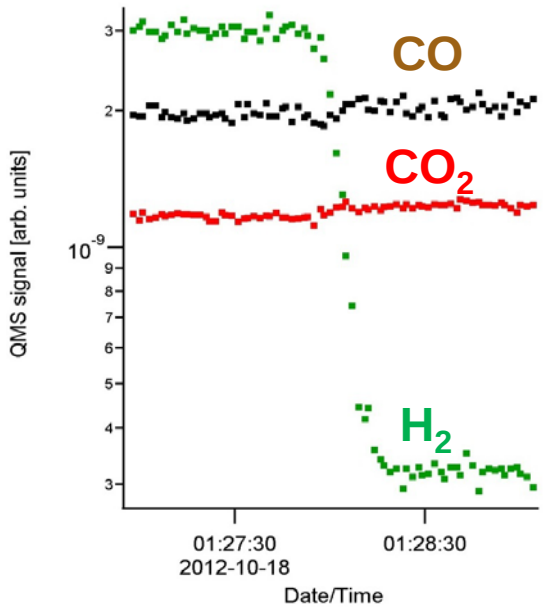
The Lund approach to APXPS: Ambient pressure cells at the SPECIES beamline







QMS

Ideal system for fast switching of gas-composition!

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Where can you do Ambient pressure x-ray photoeletron spectroscopy

+ around 15 to 20 lab instruments around the world (e.g. at Imperial College and Univ Manchester)

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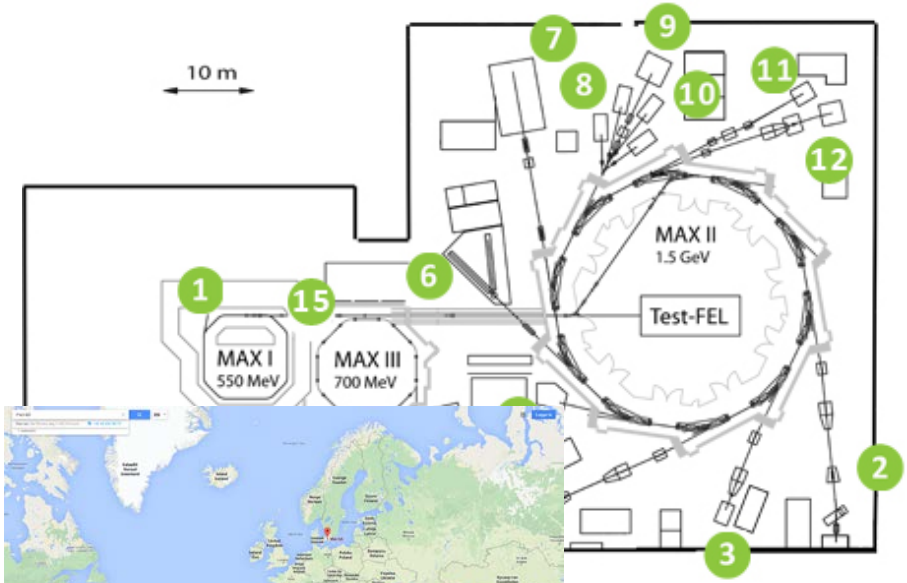
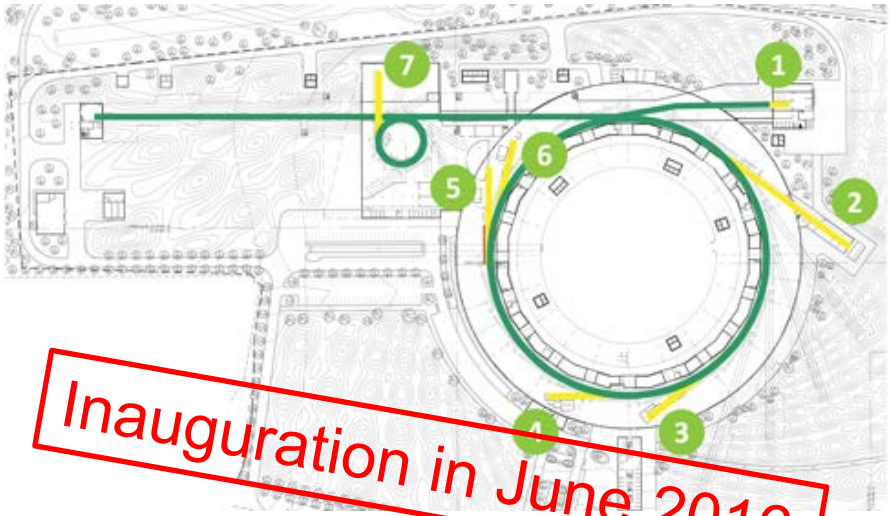
MAX IV LABORATORY =

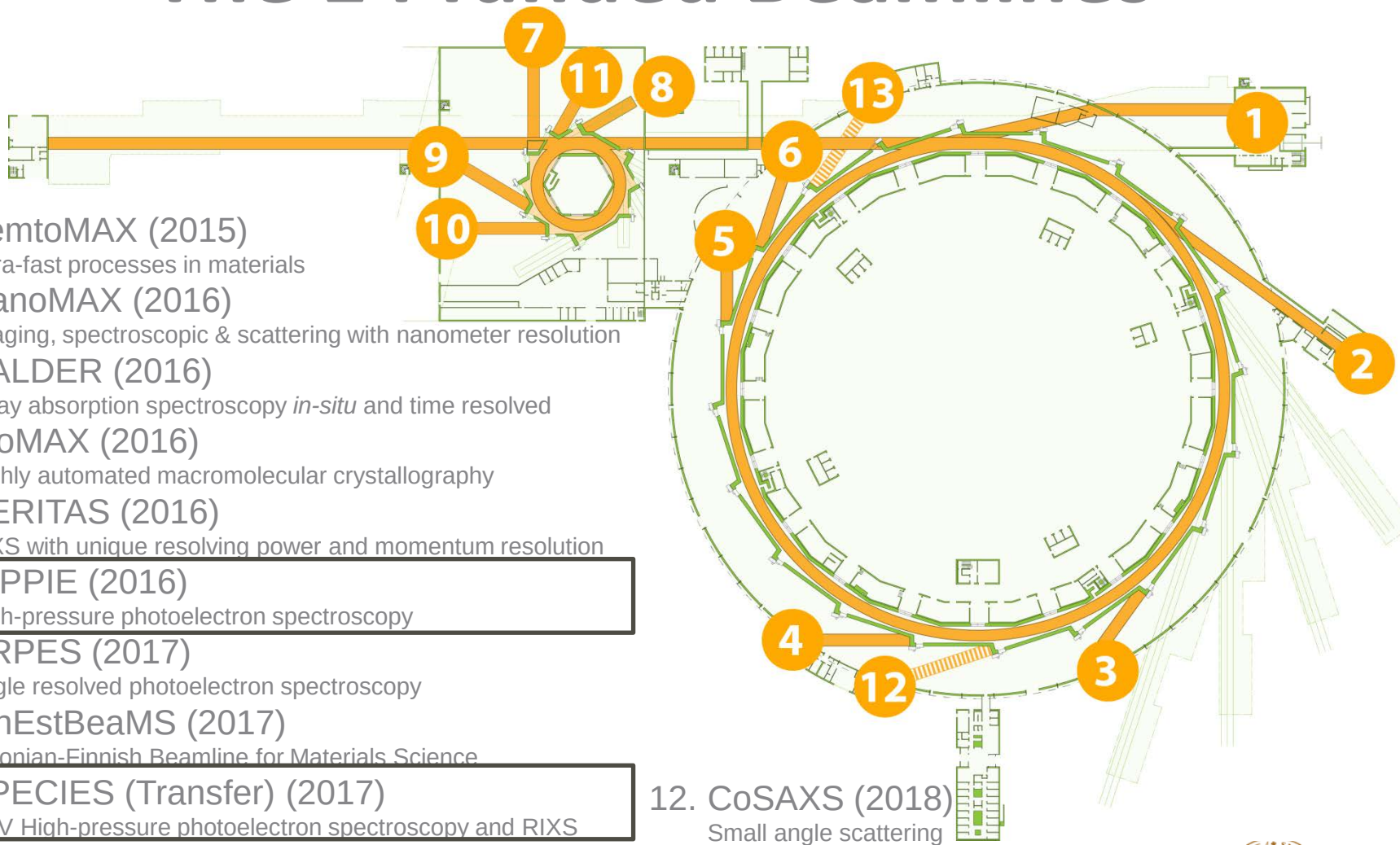
MAX-lab + MAX IV facility





Inauguration in June 2016

The 14 funded Beamlines



1. FemtoMAX (2015)
   Ultra-fast processes in materials
2. NanoMAX (2016)
   Imaging, spectroscopic & scattering with nanometer resolution
3. BALDER (2016)
   X-ray absorption spectroscopy *in-situ* and time resolved
4. BioMAX (2016)
   Highly automated macromolecular crystallography
5. VERITAS (2016)
   RIXS with unique resolving power and momentum resolution
6. HIPPIE (2016)
   High-pressure photoelectron spectroscopy
7. ARPES (2017)
   Angle resolved photoelectron spectroscopy
8. FinEstBeaMS (2017)
   Estonian-Finnish Beamline for Materials Science
9. SPECIES (Transfer) (2017)
   VUV High-pressure photoelectron spectroscopy and RIXS
10. FlexPES (Transfer) (2017)
    Photoelectron Spectroscopy and NEXAFS
11. MAXPeem (Transfer) (2017)
    Photoelectron microscopy
12. CoSAXS (2018)
    Small angle scattering
13. SoftiMAX (2018)
    Coherent Soft X-Ray Scattering, Holography…
14. DanMAX (2019)

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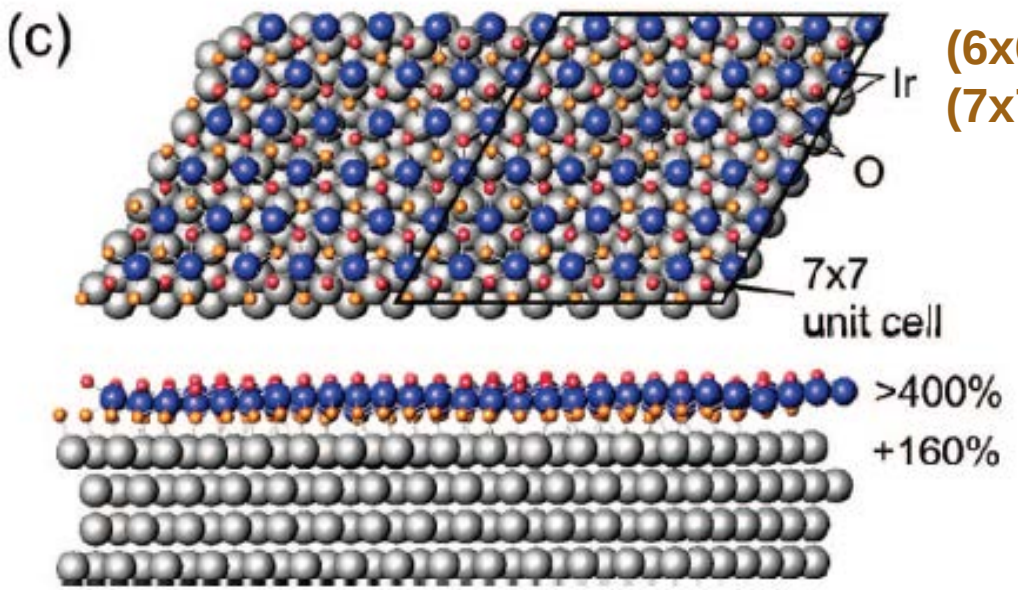
Exampel 1:
CO oxidation over Ir(111)

Motivation

TABLE 1: Summary of the Oxidation Conditions and the Resulting Phases on the Ir(111) as Observed by SXRD

T/K	P(O₂)/mbar	phase
575	10^{-6}–10^{-4}	chemisorbed O
	10^{-3}–1	O–Ir–O trilayer
	10 –100	multilayer oxide
775 (875)	10^{-5}–10^{-2}	chemisorbed O
	1	O–Ir–O trilayer
	100	bulklike IrO_2

Basic question:
What is the active phase for CO-oxidation on Ir(111)?



(6x6) IrO_2
(7x7) Ir(111)

He, Stierle, Over et al.,
J. Phys. Chem. C., 112, 11946 (2008)

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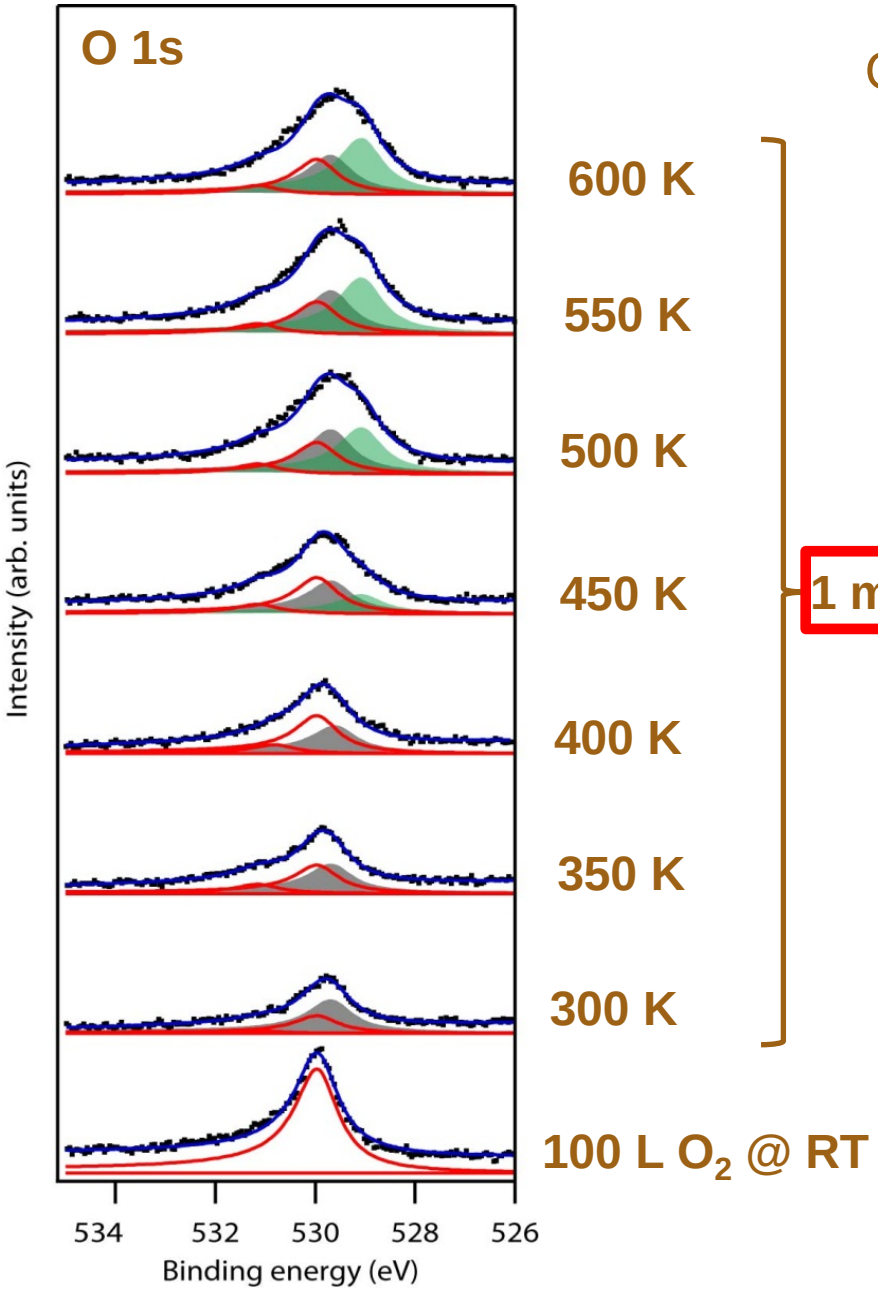
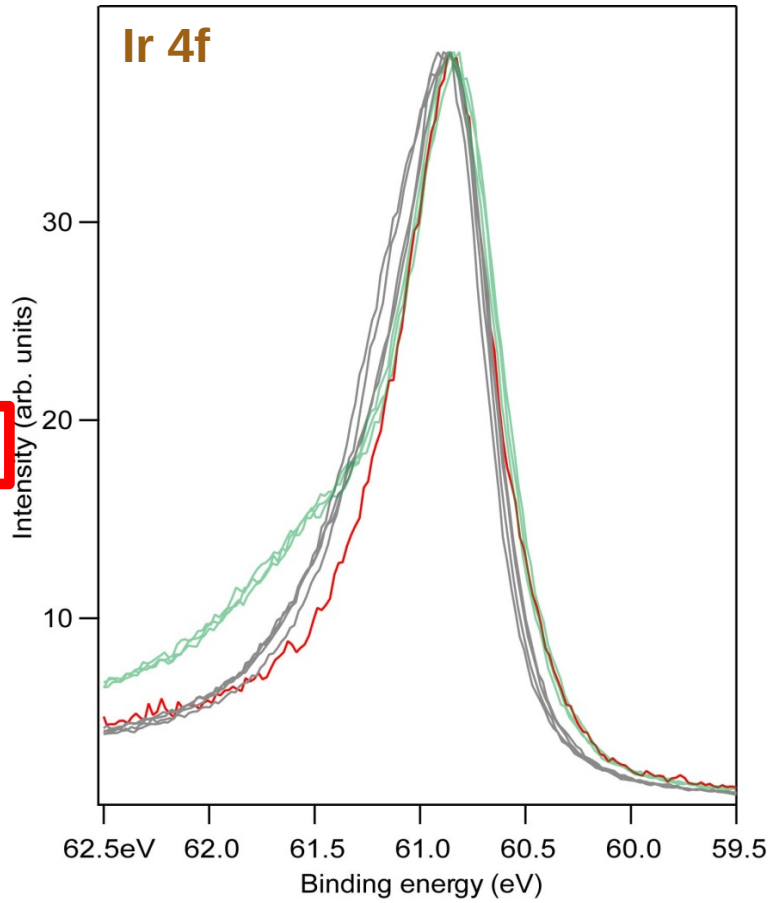
Oxidation of Ir(111)





100 L O_2 @ RT
300 K – 450 K, 1 mbar
500 K – 600 K, 1 mbar

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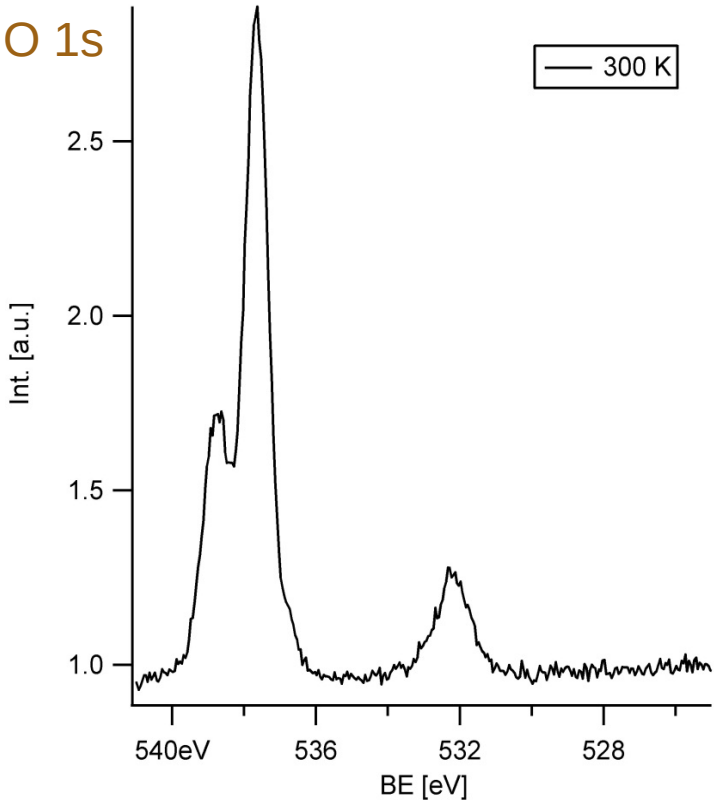
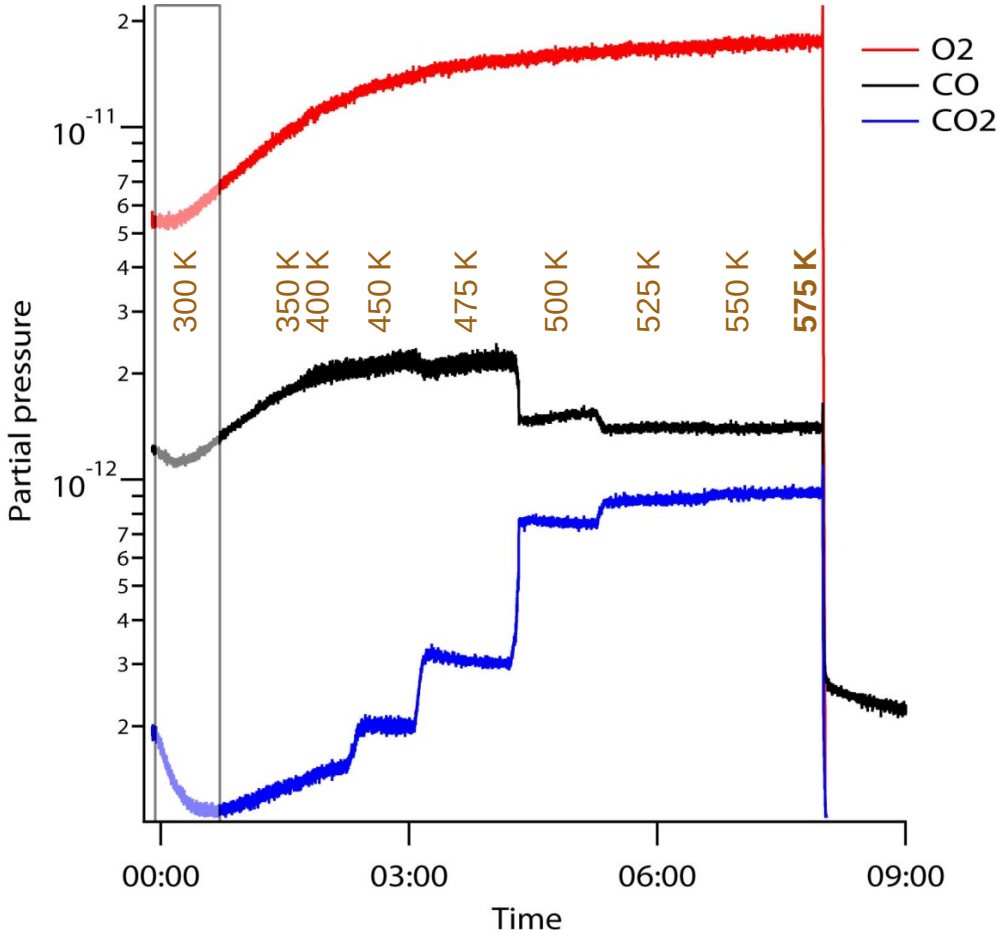
CO oxidation over Ir(111)





- CO poisoned surface (T < 450 – 475 K)
- CO and O_{atom} co-exist on the surface in the reactive phase (T = 500 K)
- CO almost dissapeared (T > 550 K)
  Mass transfer limit

P_{tot} = 0.84 mbar
$CO(10\%):O_2(90\%)$
0.6 mL/min
5.4 mL/min

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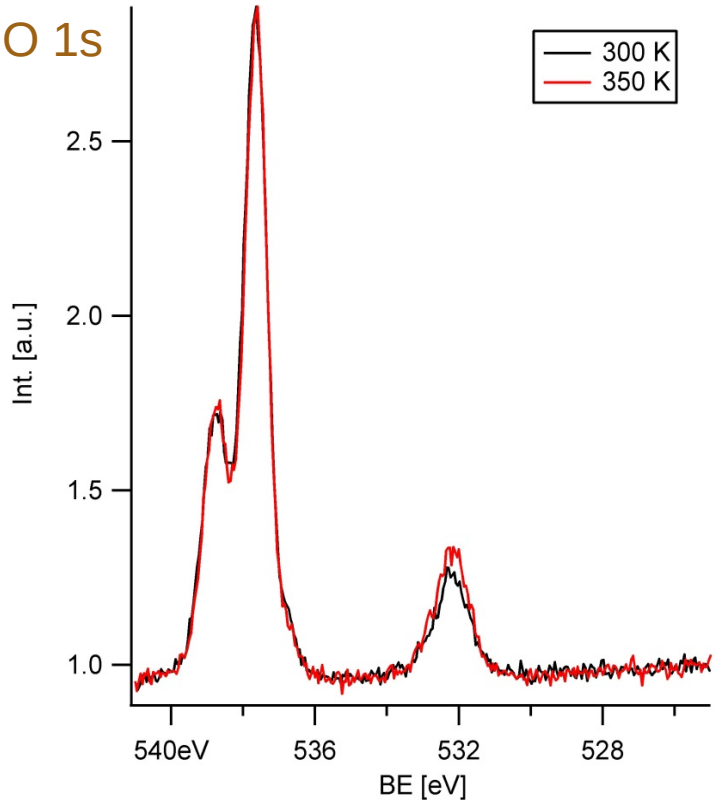
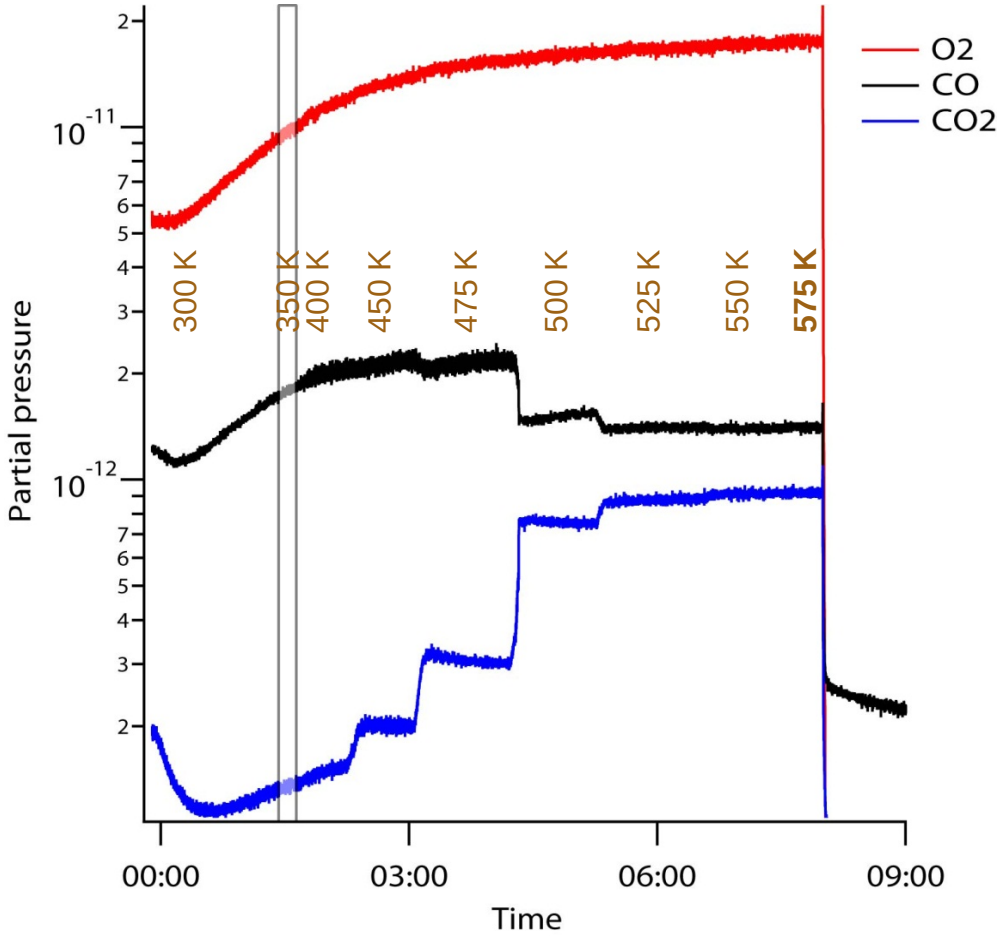
CO oxidation over Ir(111)





- CO poisoned surface (T < 450 – 475 K)
- CO and O_{atom} co-exist on the surface in the reactive phase (T = 500 K)
- CO almost dissapeared (T > 550 K)
  Mass transfer limit

P_{tot} = 0.84 mbar
$CO(10\%):O_2(90\%)$
0.6 mL/min
5.4 mL/min

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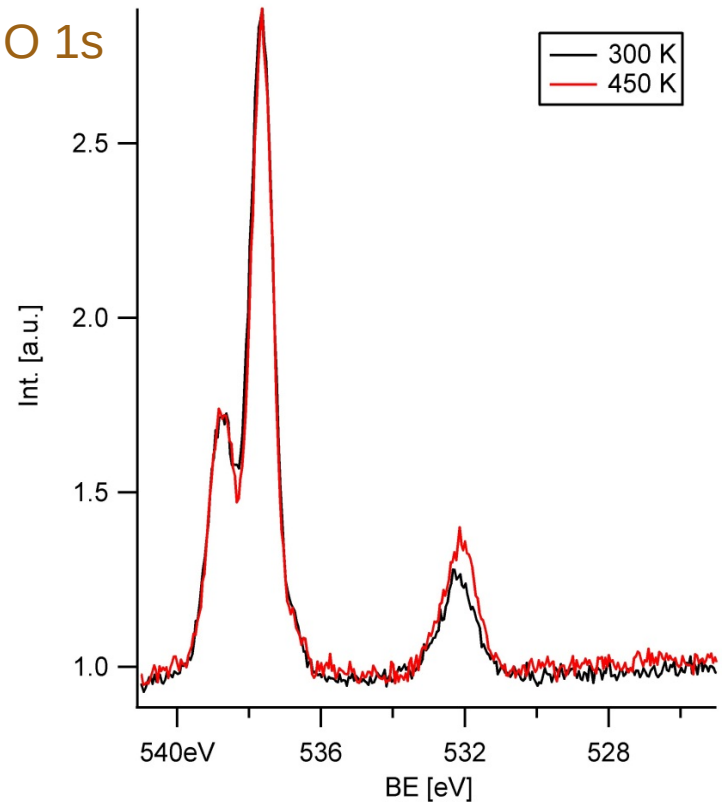
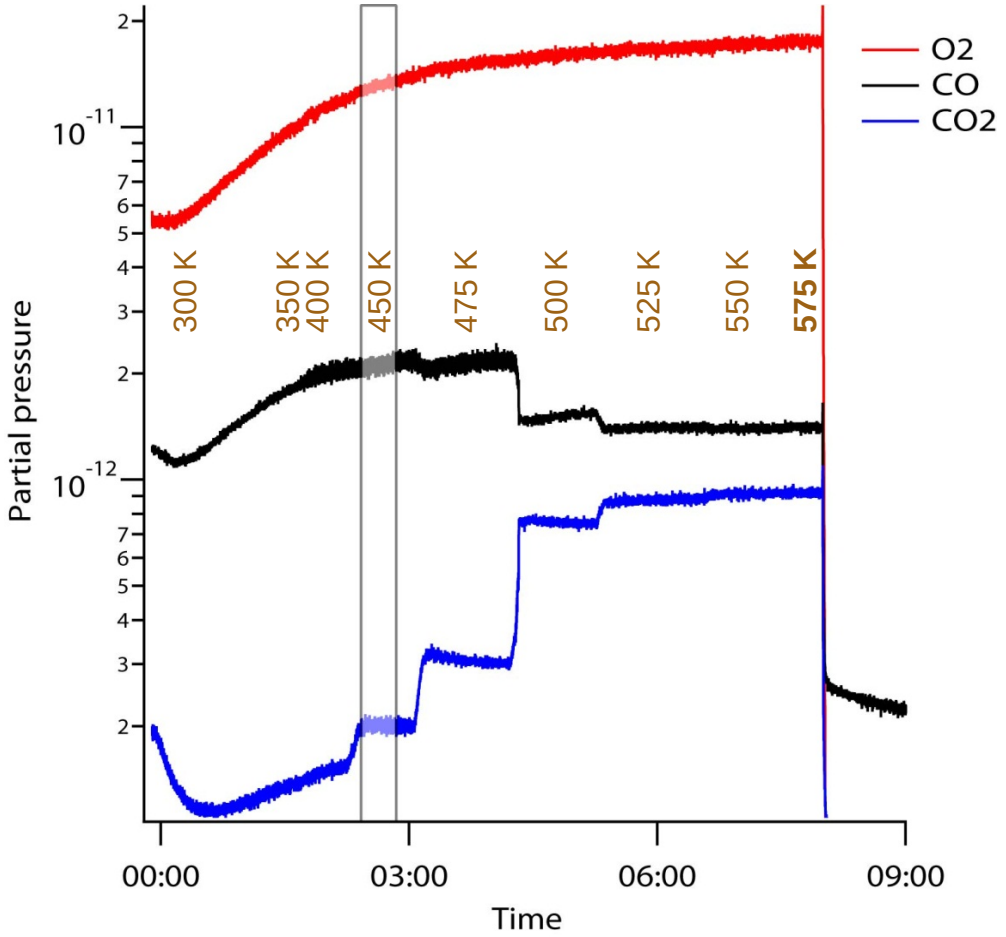
CO oxidation over Ir(111)





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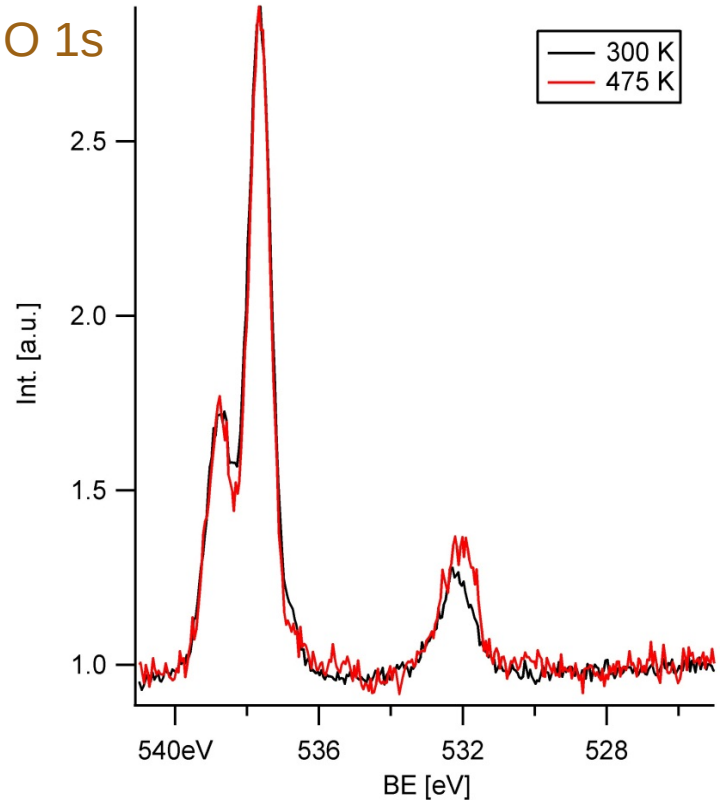

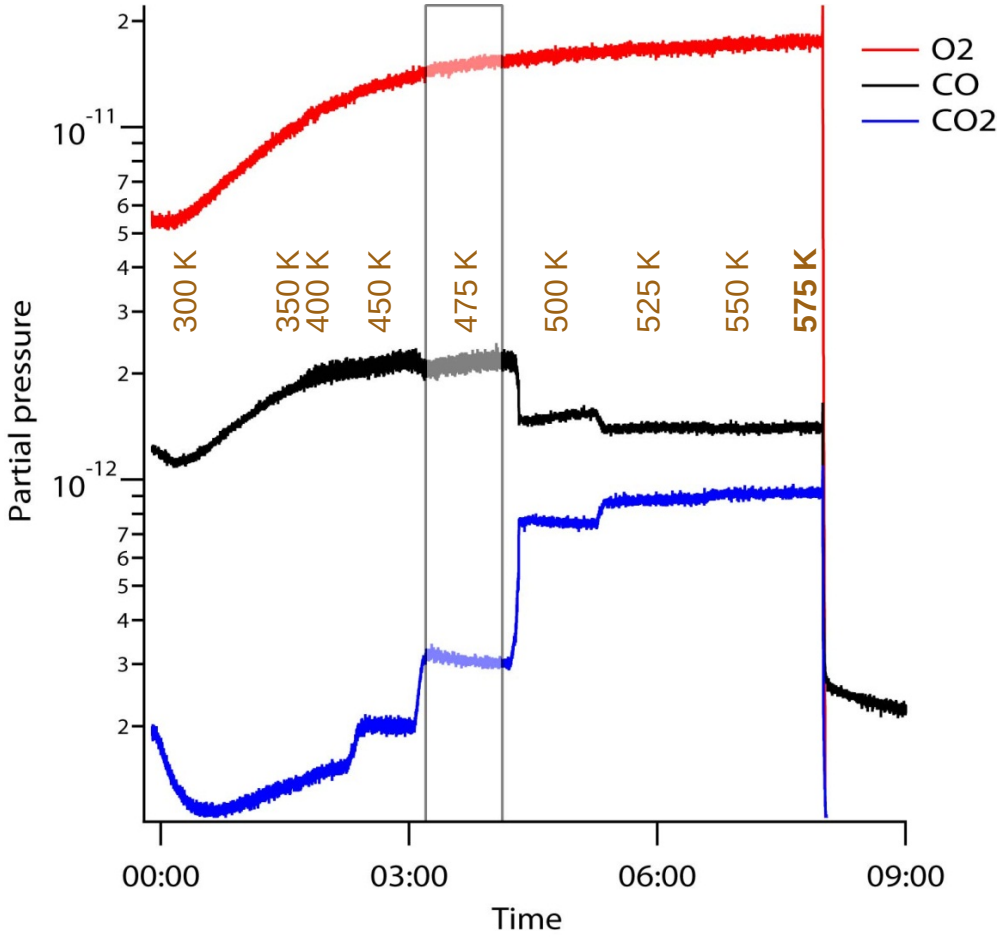

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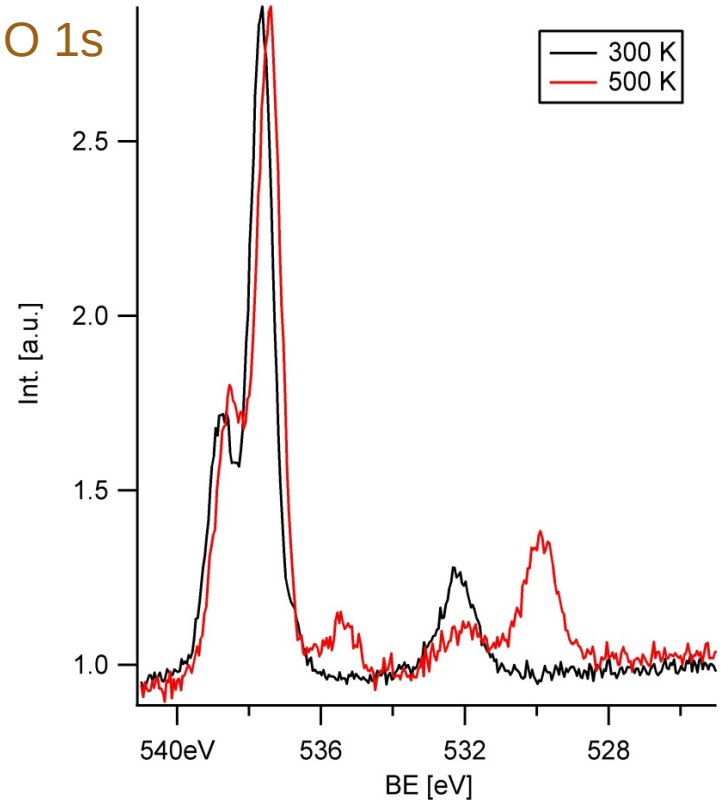

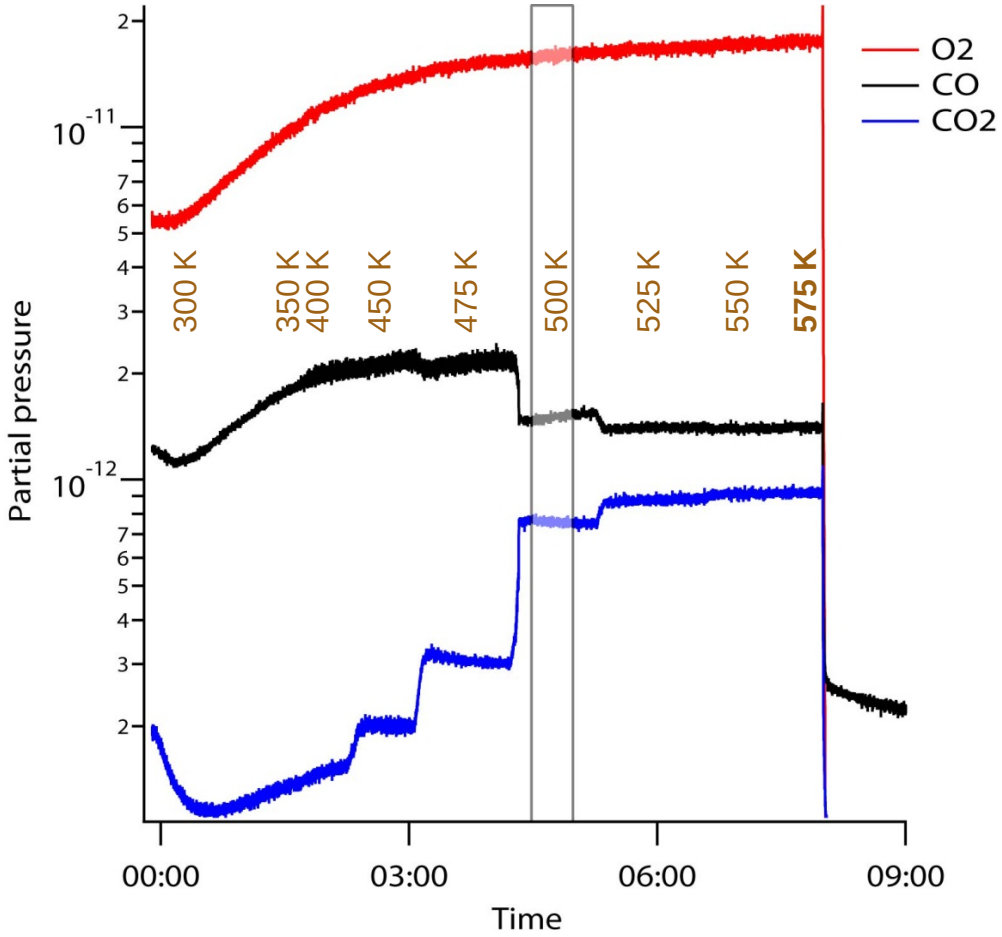

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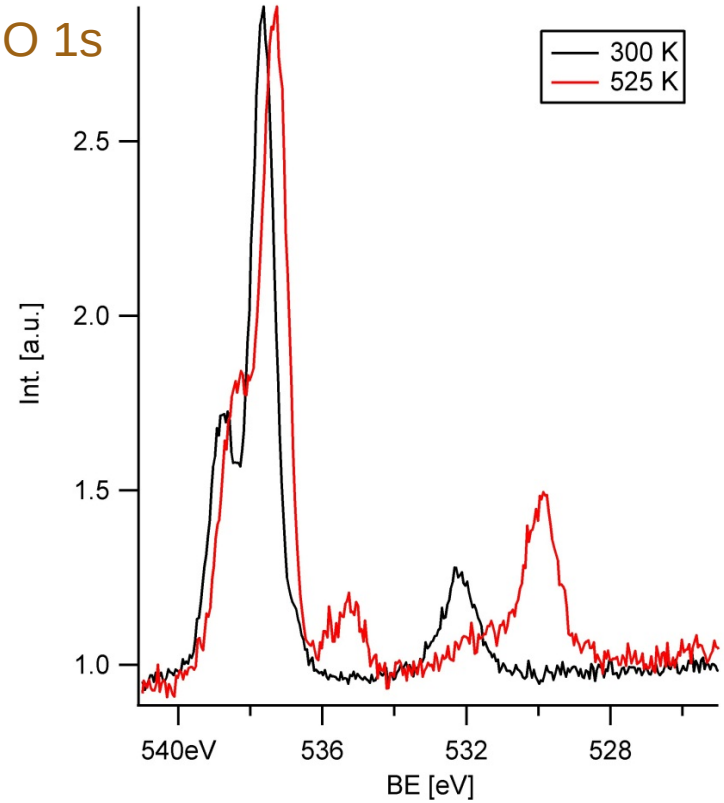

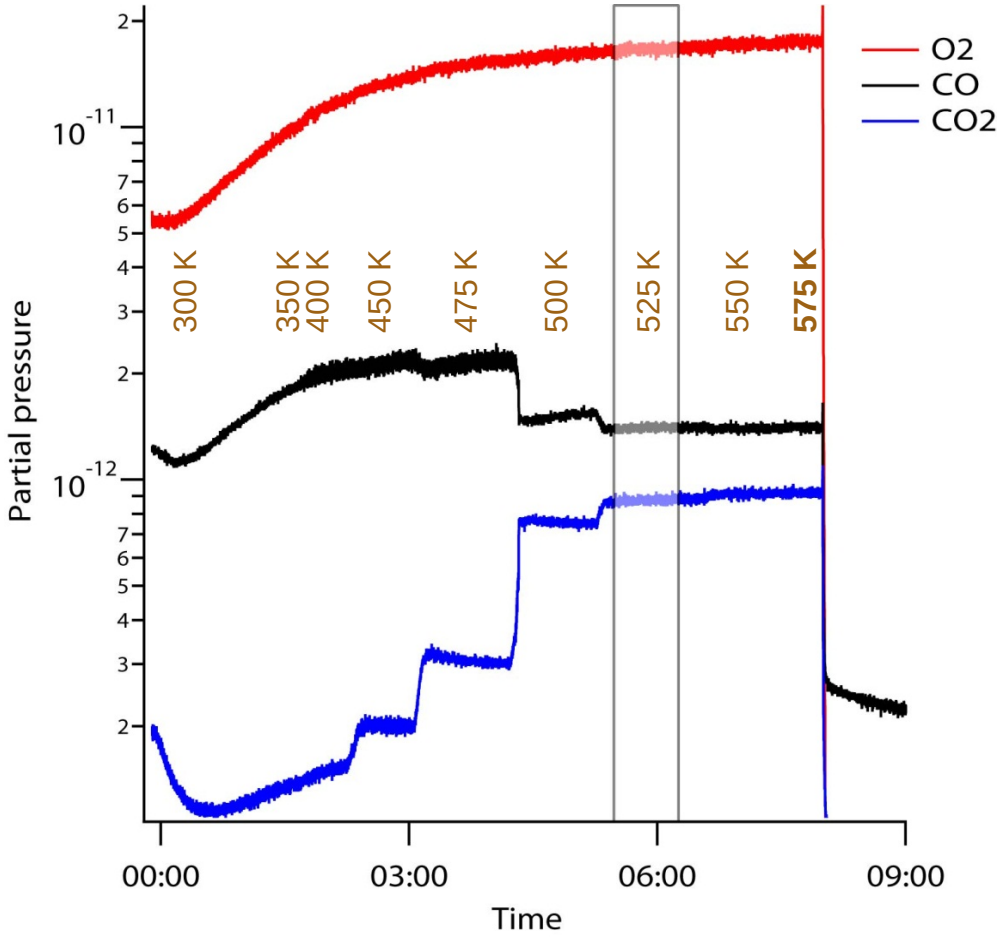

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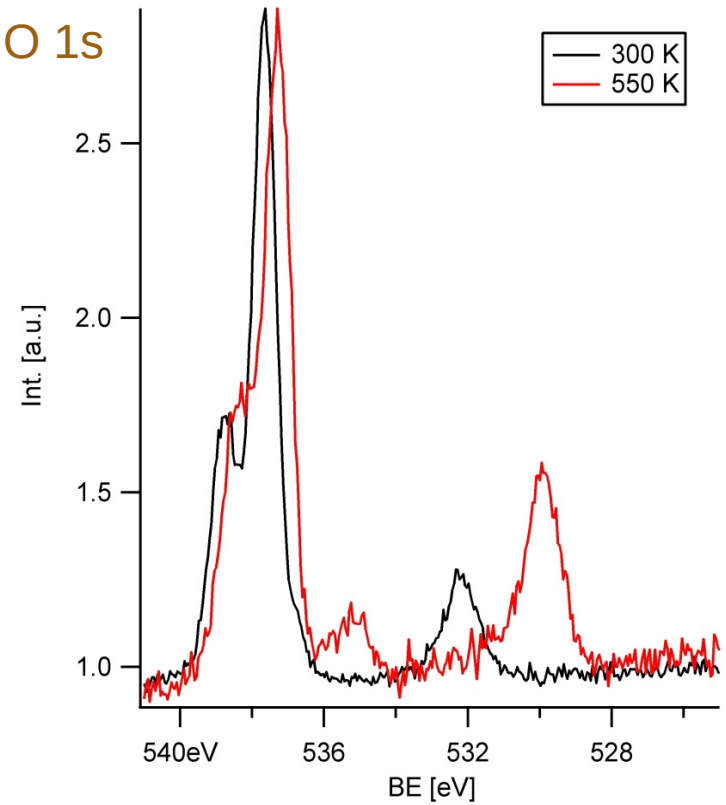

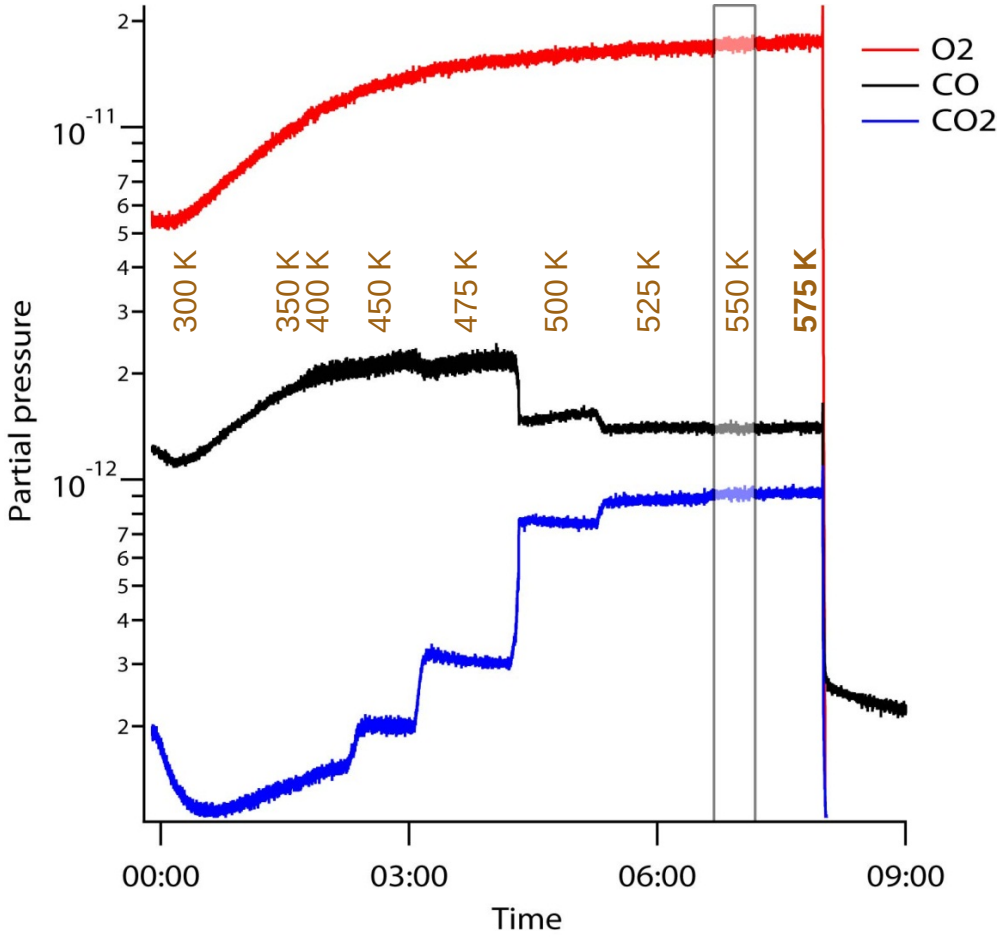

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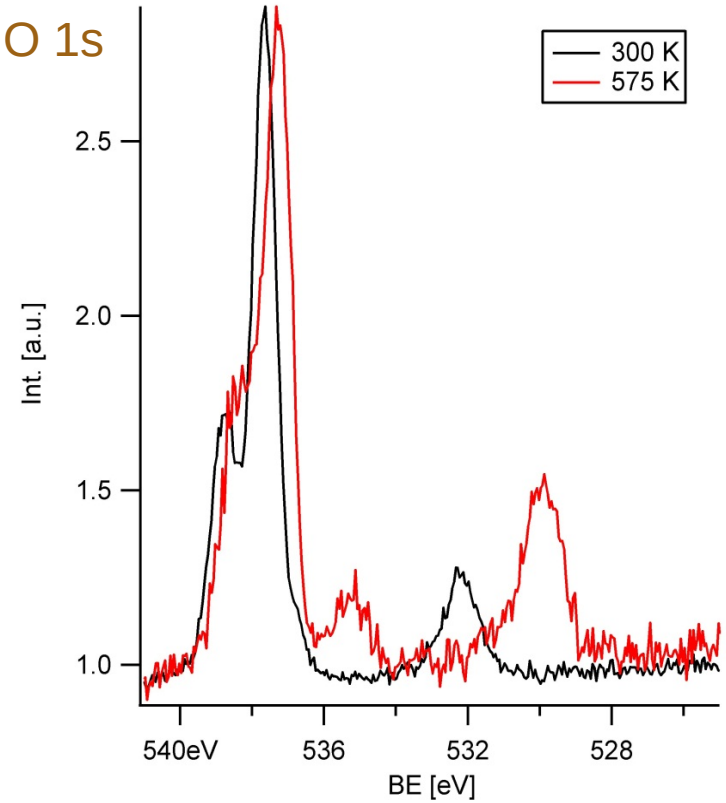

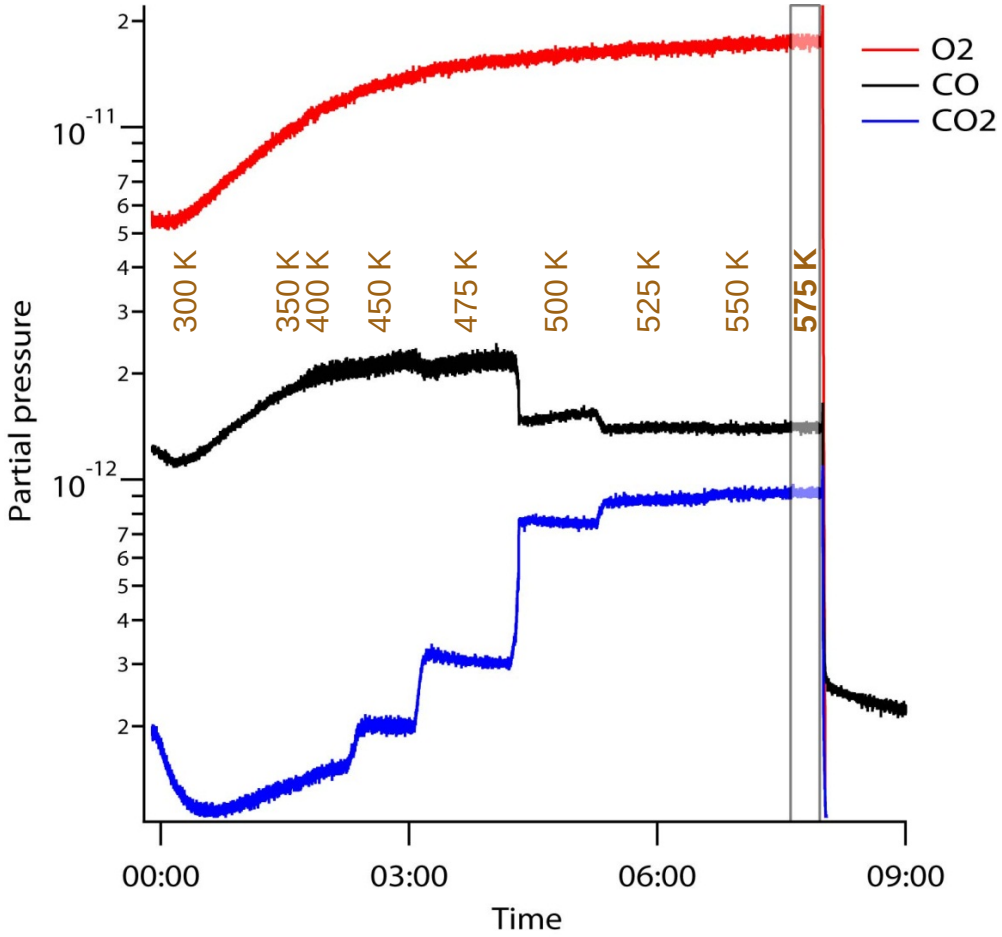

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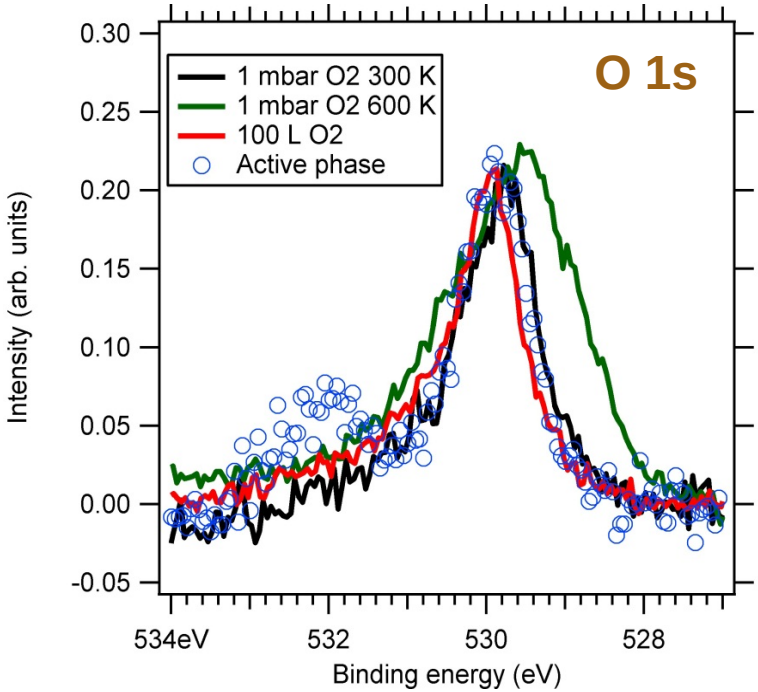
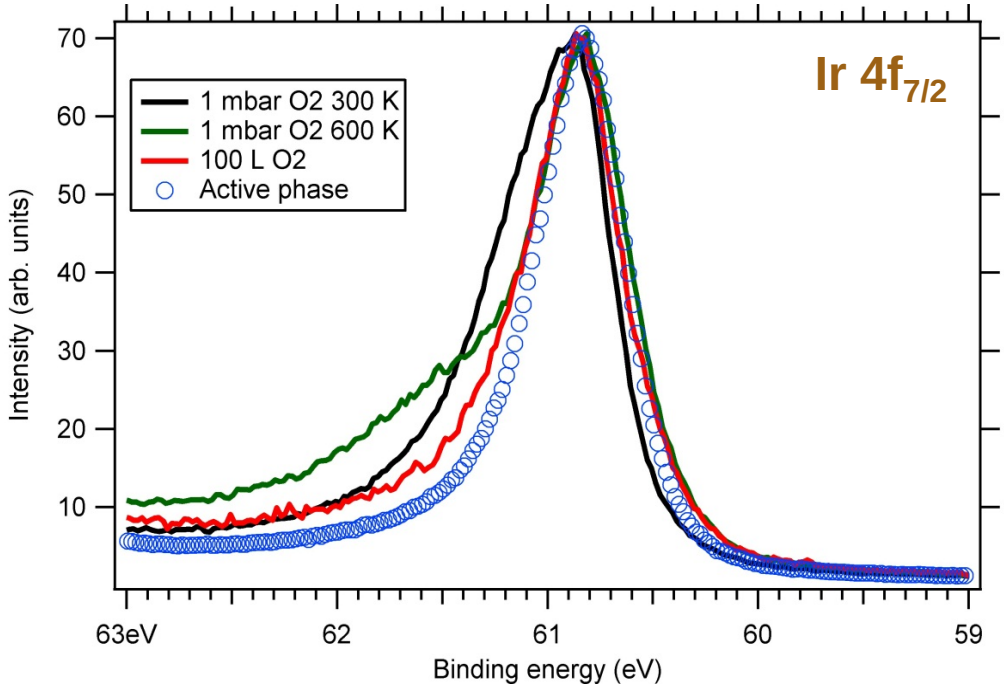
Comparison with oxidation data





The O 1s and Ir 4f spectra of the active phase are similar to the spectra of a Ir(111) surface exposed to 100 L O_2 at room temperature.

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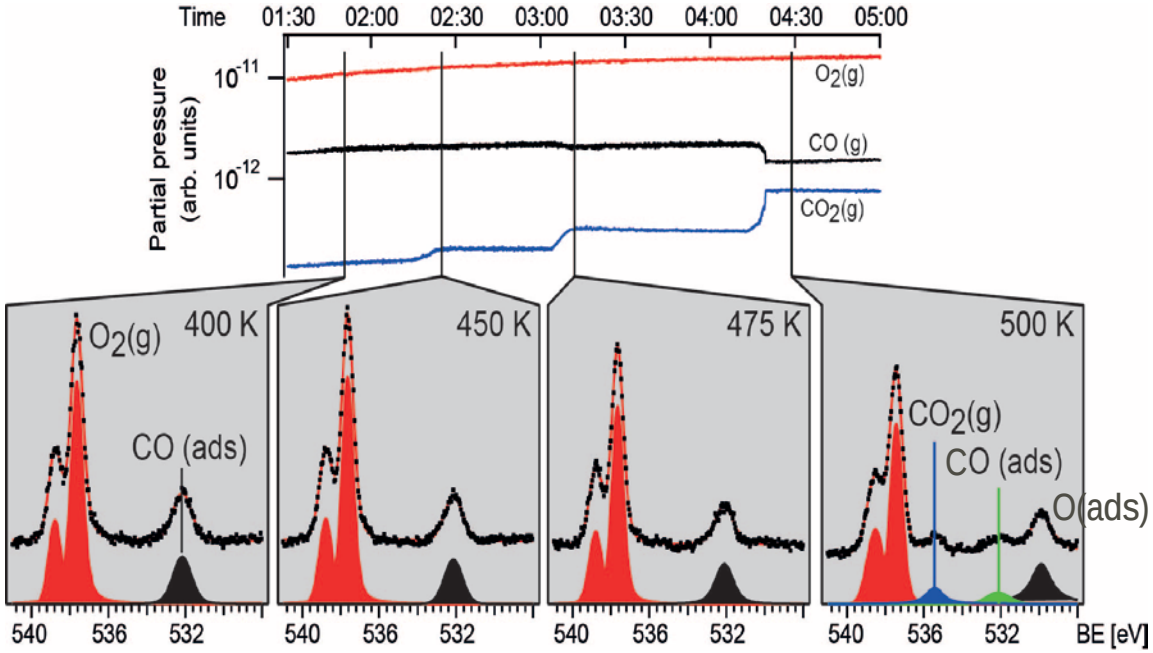
CO oxidation over Ir(111): summary



- APXPS in combination with mass spectrometry:
- Chemical reactions, surface species, and gas phase species can be observed
- Shift in gas phase peak mirrors (approximately) change of surface work function
- Here performed for plain surface – can of course also be carried out for nanoparticles

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Exampel 2:
Atomic layer deposition

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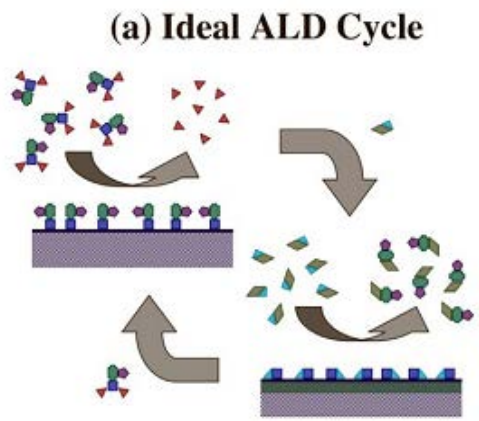
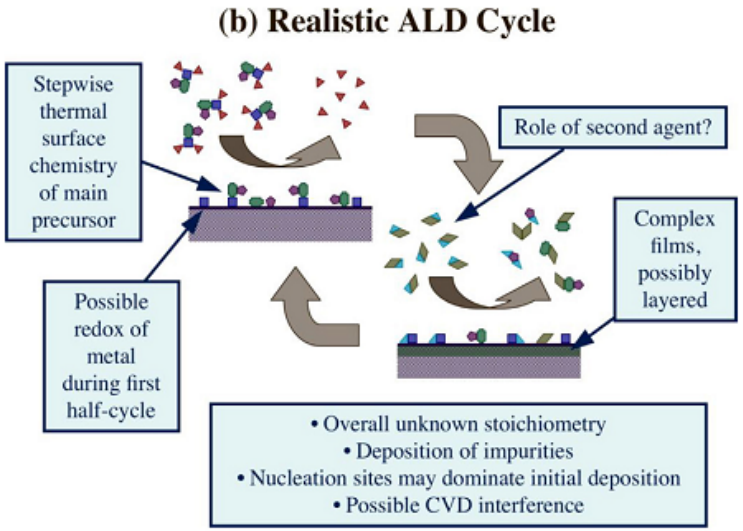
Atomic layer deposition

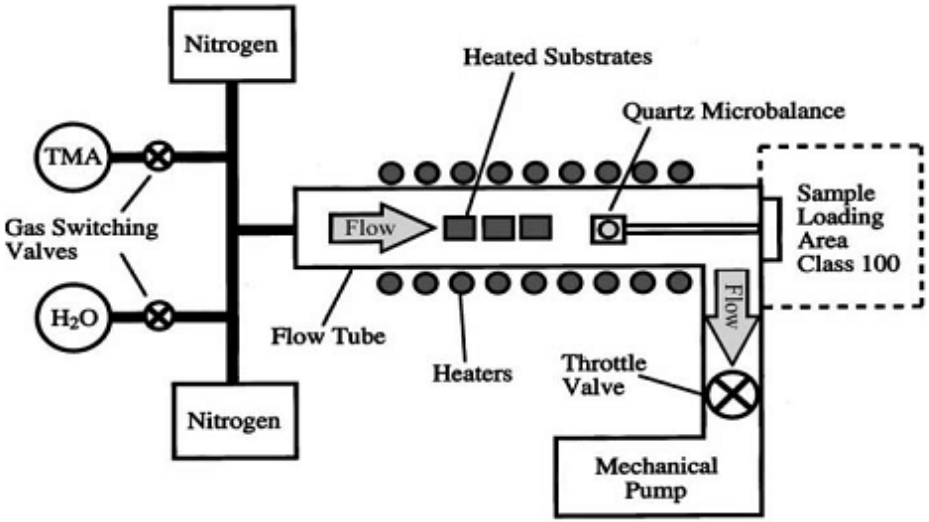


Self-limiting growth of films by alternating pressures of precursor molecules



F. Zaera, Coord. Chem. Rev. 257 (2013) 3177 – 3191.

Experimental conditions



ALD:

- 1 – 200 mbar pressure
- 1 - 2 s exposure to gas
- Purge between precursors

M. Bosi et al. Crit. Rev. Solid State Mater. Sci. 38, 203-233 (2013).

Our experiment (APXPS):

- No carrier gas
- Evacuate instead of purge
- Lower pressure (≤0.01 mbar) → slower kinetics
- Same temperatures as ALD

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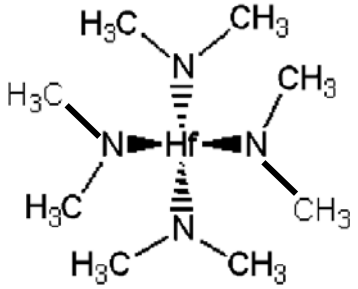
Atomic layer deposition of HfO_2 on InAs(001)

Precursors: H_2O,



tetrakis(dimethylamido) hafnium (TDMAH)

Carried out at:
Beamline I511
MAX IV Laboratory, Sweden

Substrate: InAs(001)

Pressure and temperature: ca. 10^{-2} mbar, 200 to 220 ºC

Proposed mechanism:

first half-cycle:

$$x\ (\text{-OH})_{(s)} + \text{Hf}[\text{N}(\text{CH}_3)_2]_{4(g)} \rightarrow (\text{-O-})_x\text{Hf}[\text{N}(\text{CH}_3)_2]_{4-x(s)} + x\ \text{HN}(\text{CH}_3)_{2(g)}$$

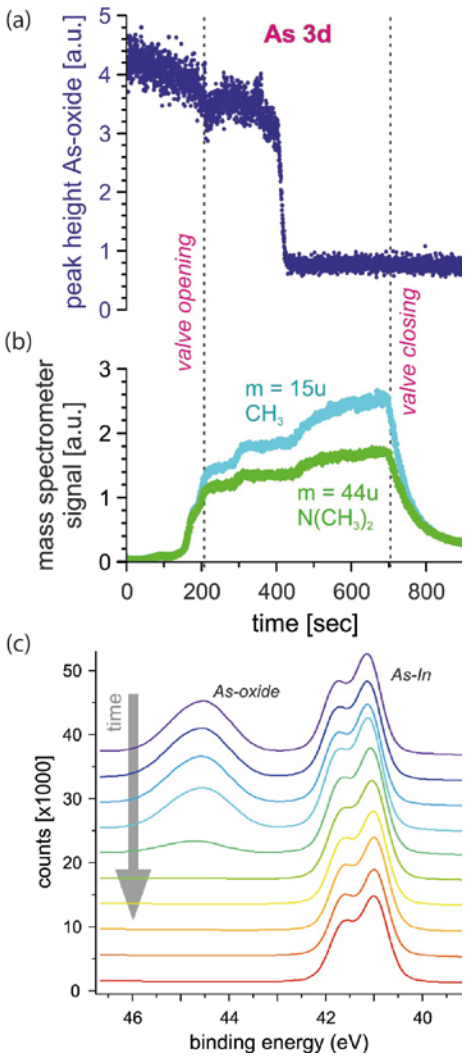
second half-cycle:

$$(\text{-O-})_x\text{Hf}[\text{N}(\text{CH}_3)_2]_{4-x(s)} + (4-x)\ \text{H}_2\text{O}_{(g)} \rightarrow (\text{-O-})_x\text{Hf}(\text{OH})_{4-x(s)} + (4-x)\ \text{HN}(\text{CH}_3)_{2(g)}$$

APXPS of HfO_2 ALD on InAs(001): real-time monitoring by APXPS and mass spectrometry

Version edited for publication on vacuum-uk.org

The full dataset presented at VS6 will be published during the next couple of months.



- **complete removal of As-Oxides**
- **formation of Hf-Oxide layer**
- **different surface species can be followed in real time**

As 3d APXPS and mass spectrometer signals during first half-cycle exposure to TDMAH

R. Timm, A. Head, S. Yngman, J. Schnadt, A. Mikkelsen et al.

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Summary

- Ambient pressure x-ray photoelectron spectroscopy: XPS at pressures in the mbar regime
- Maximum pressures (depend on instrument and system under investigation): ~0.1 mbar to 100 mbar
- Modification of instrumentation: differential pumping needed, but otherwise quite straightforward
- Opens up for new insights into e.g. structures at realistic pressures, kinetic and dynamic nature of surface processes, ”live” study of chemical processes and intermediate states, etc.

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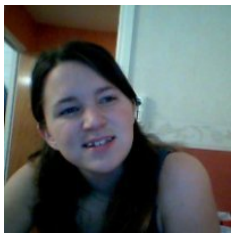
Involved people

Niclas Johansson
PhD student

Jan Knudsen
MAX IV

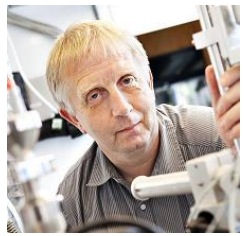
Ashley Head
Postdoc



Sofie Yngman
PhD student

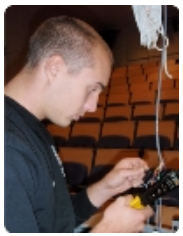
Anders Mikkelsen

Rainer Timm



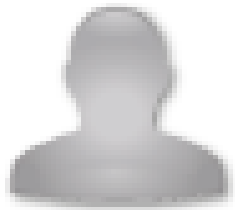
Jesper Andersen
MAX IV

Martin Hjort
PhD student

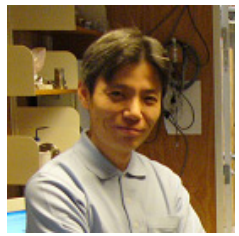


Johan Knutsson
PhD student

Alif Arman
PhD student



Yuji Monya
Keio University, JP



Hiroshi Kondoh
Keio University, JP

Funding:

Vetenskapsrådet

Knut och Alice Wallenbergs Stiftelse

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Welcome to MAX IV, SPECIES, and HIPPIE from autumn 2016/spring 2017!
www.maxiv.se