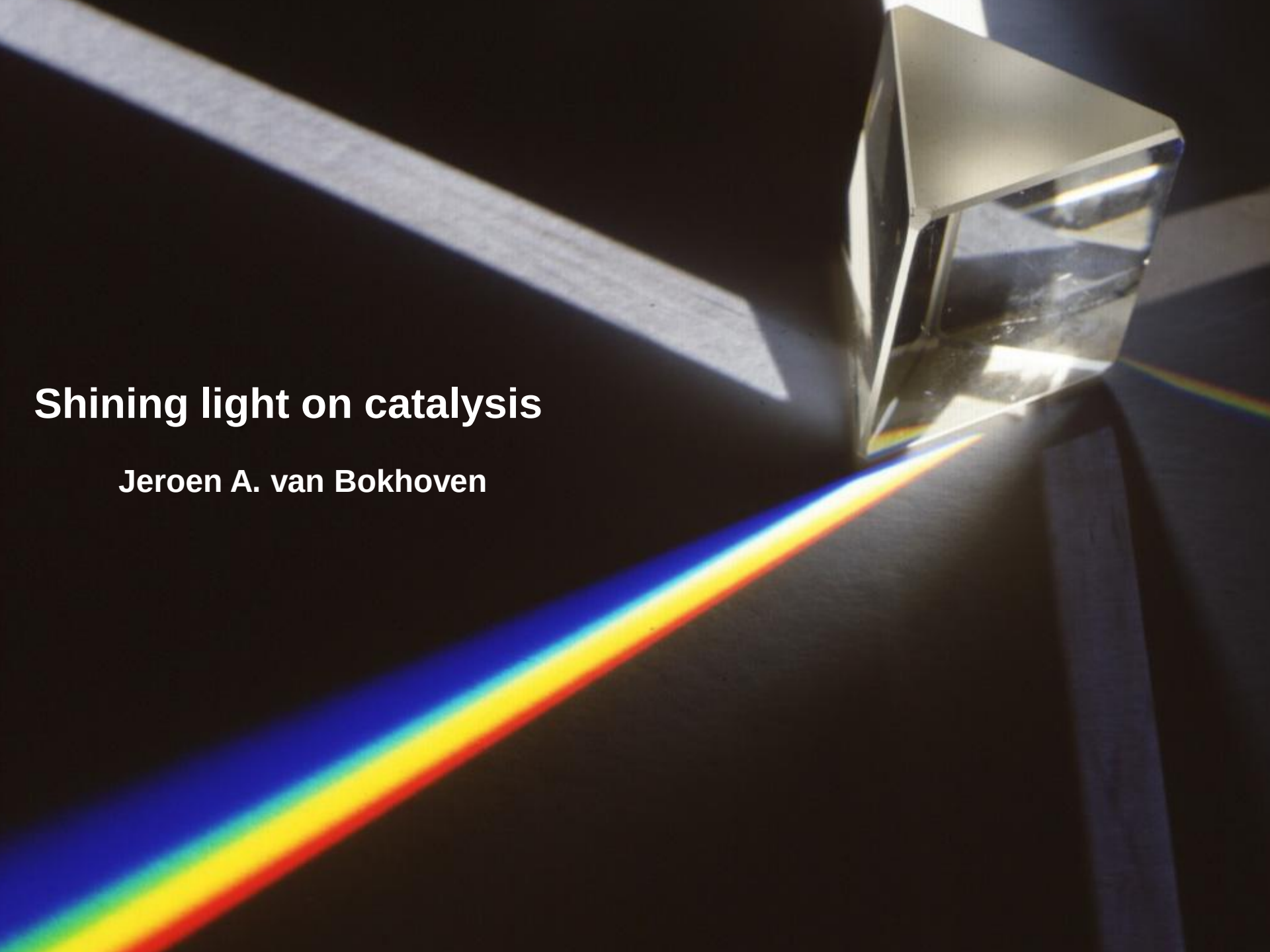


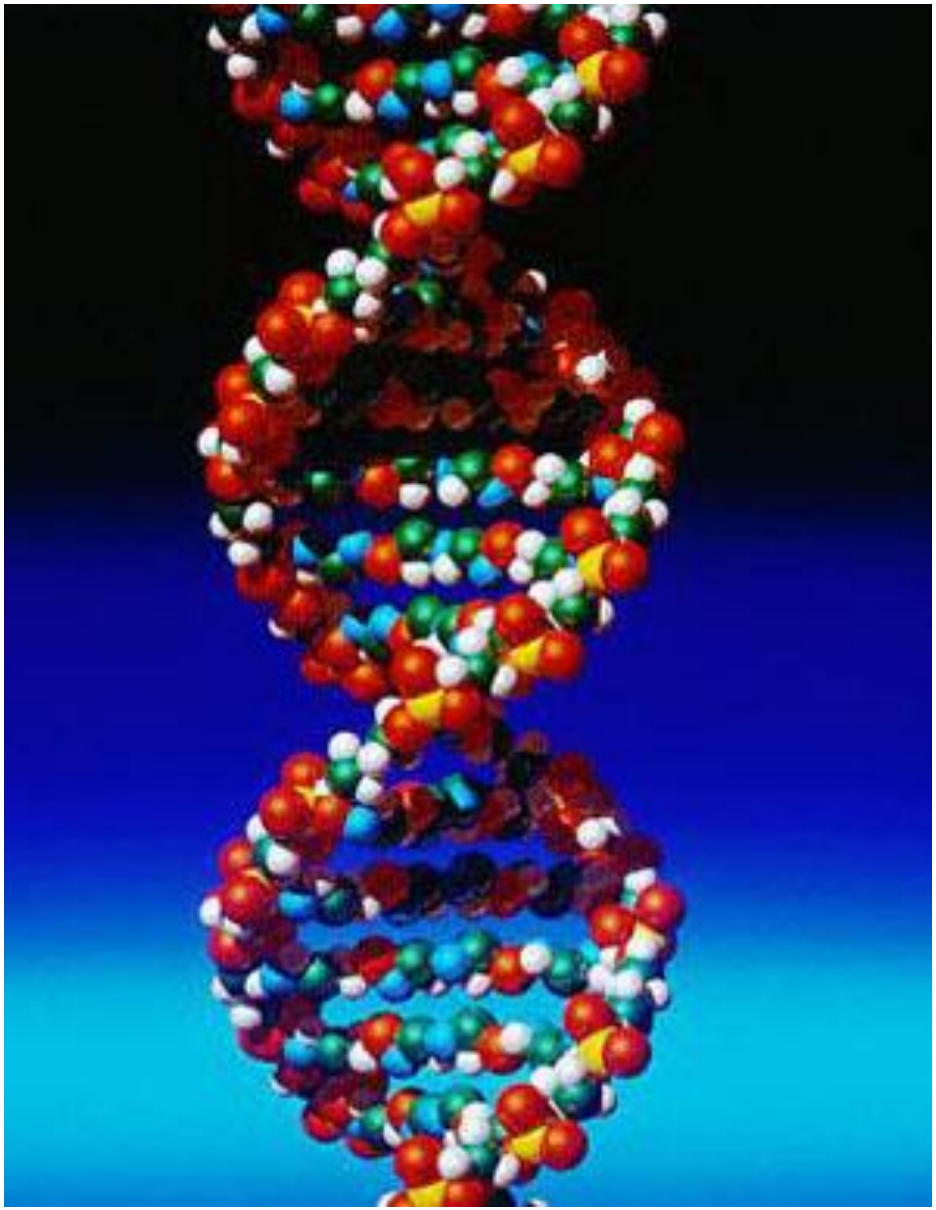
Shining light on catalysis

Jeroen A. van Bokhoven

ETH Zurich

van Bokhoven Group
Heterogeneous Catalysis

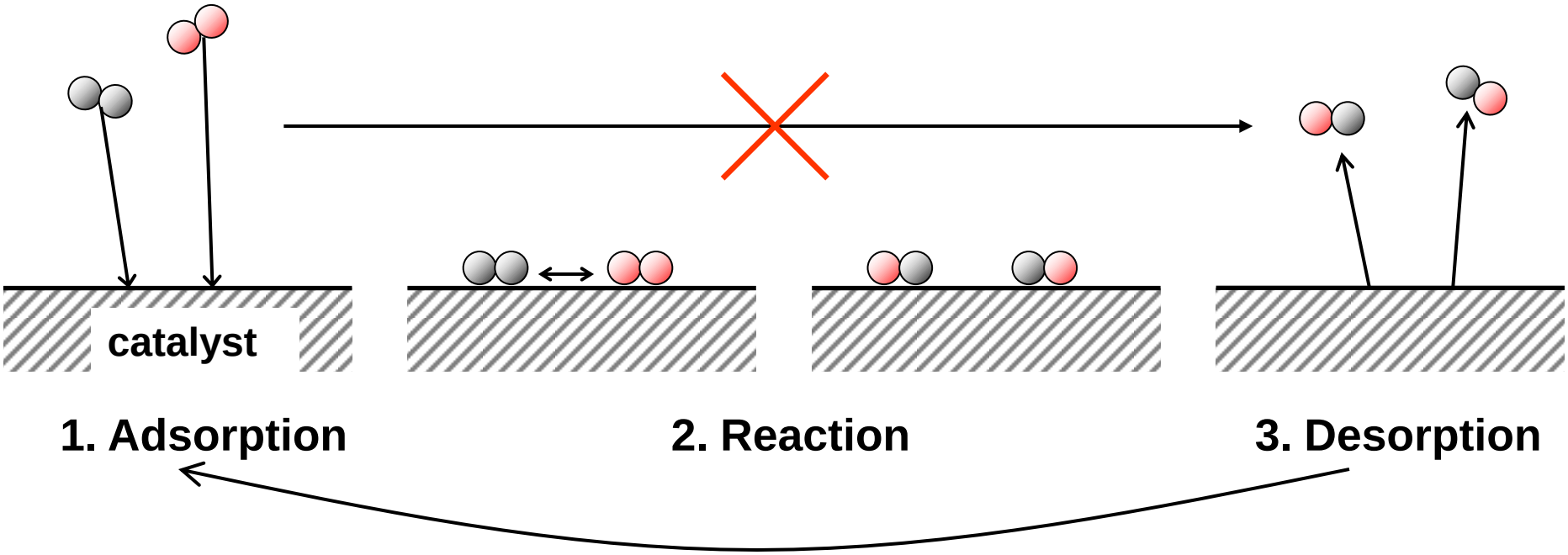
PSI Villigen



"***If you want to understand function, study structure***" (Francis Crick)

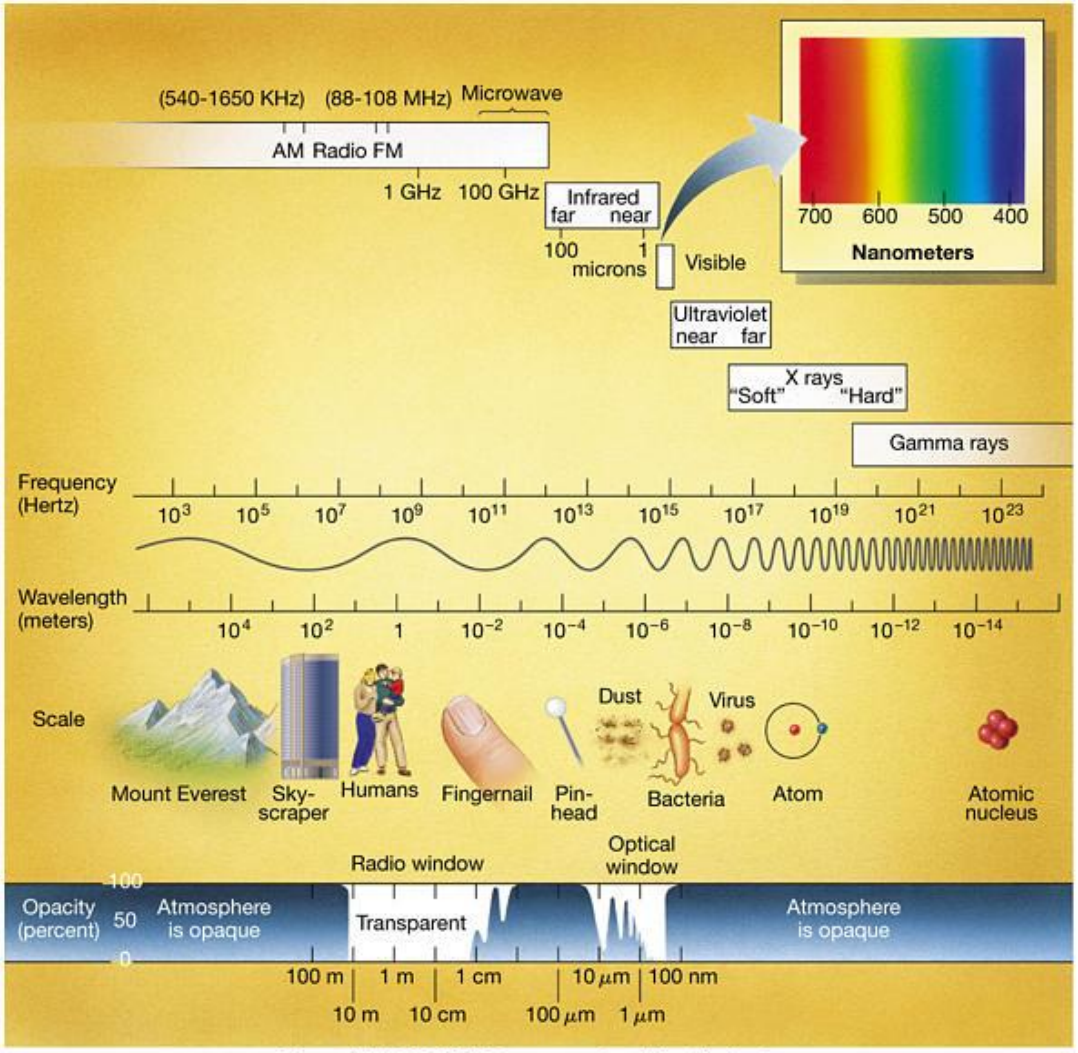
A catalyst breaks bonds ...

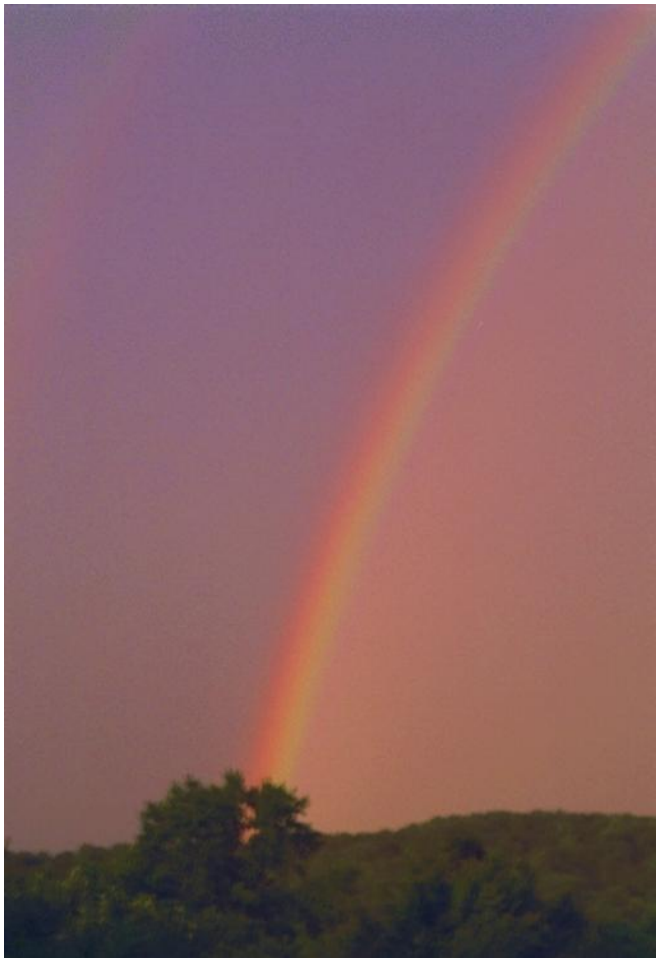
and makes bonds ...



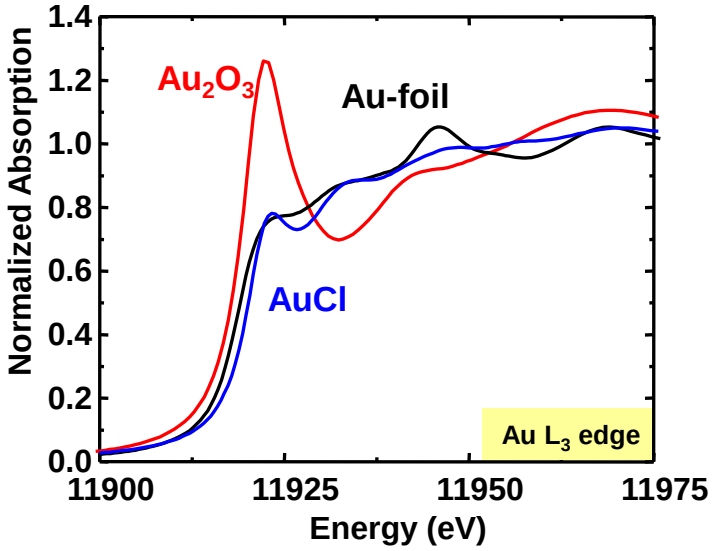
What is the structure of the active site?

Shining light on catalysis





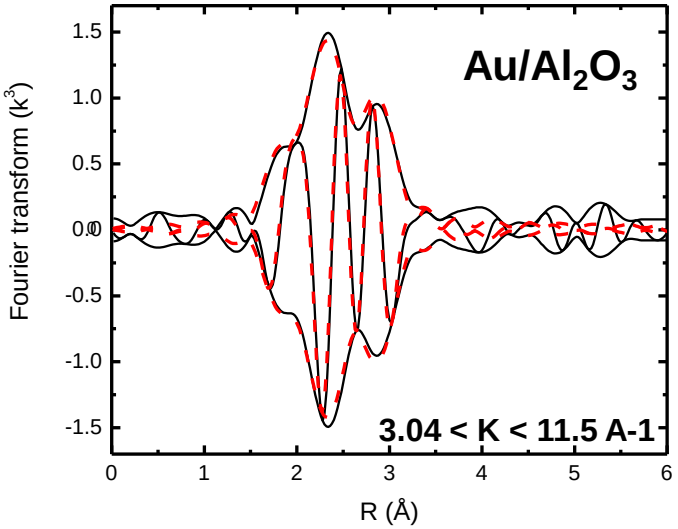
X-ray Absorption Spectroscopy



XANES: geometry
oxidation state
empty density of states

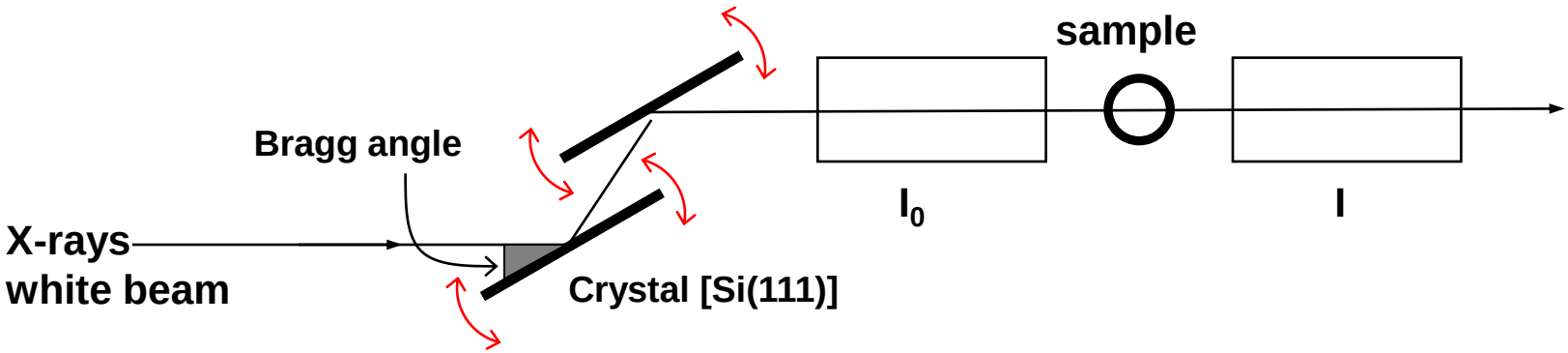
EXAFS: local structure
(particles size)

in situ / operando conditions

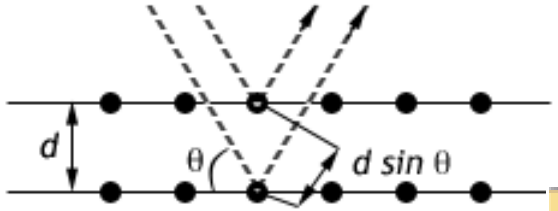


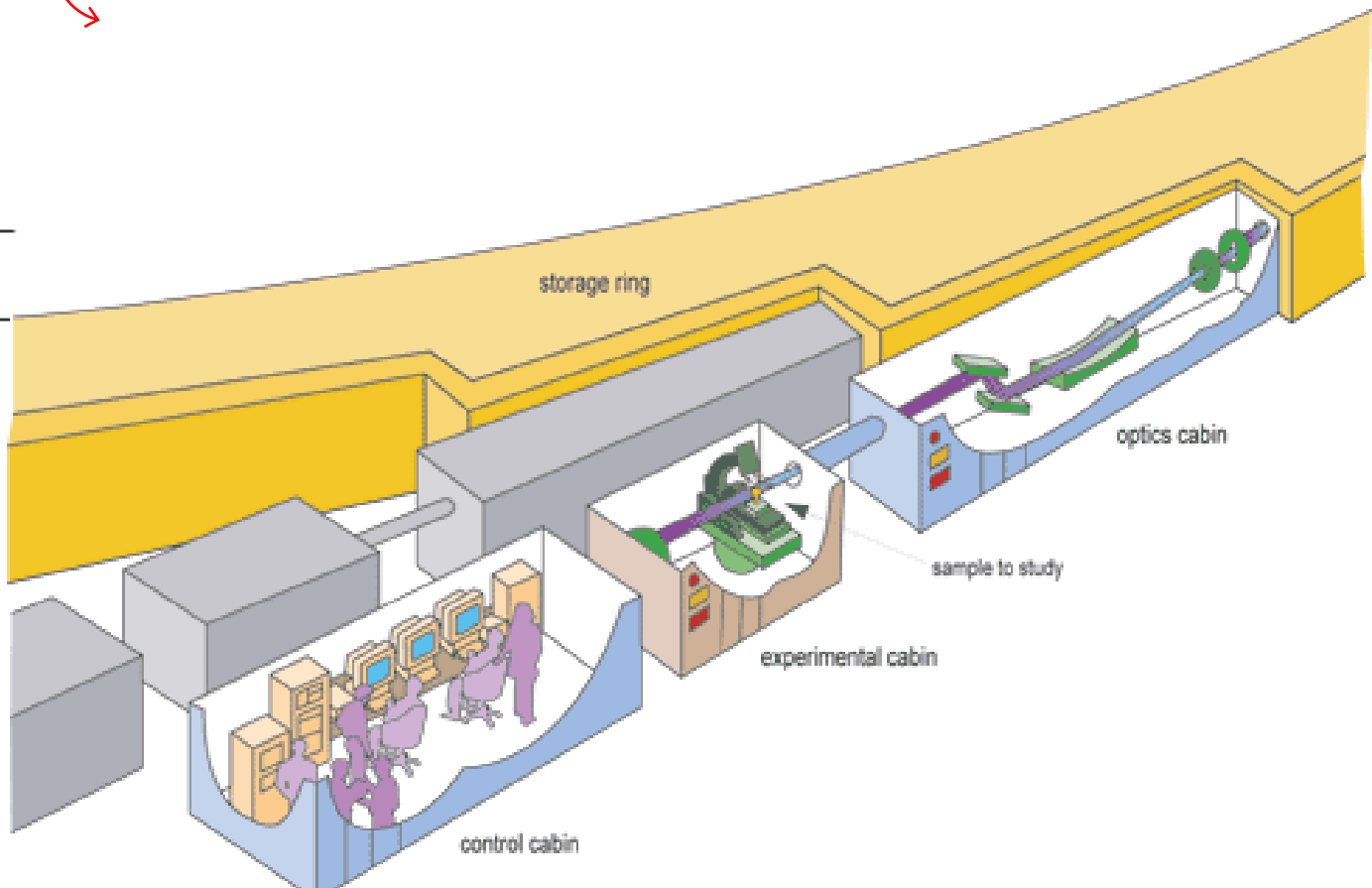
Coordination number	6.8
Au-Au distance	2.76Å
ΔDWF	0.0058
C3	9 E-6
C4	3E-6

Tuning the energy
Double crystal monochromator

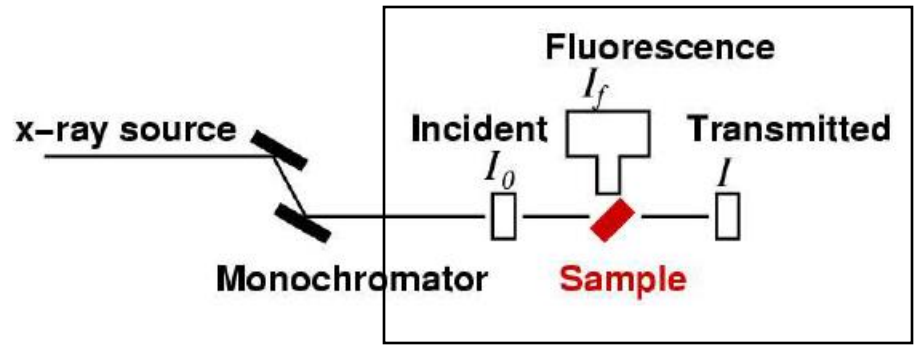


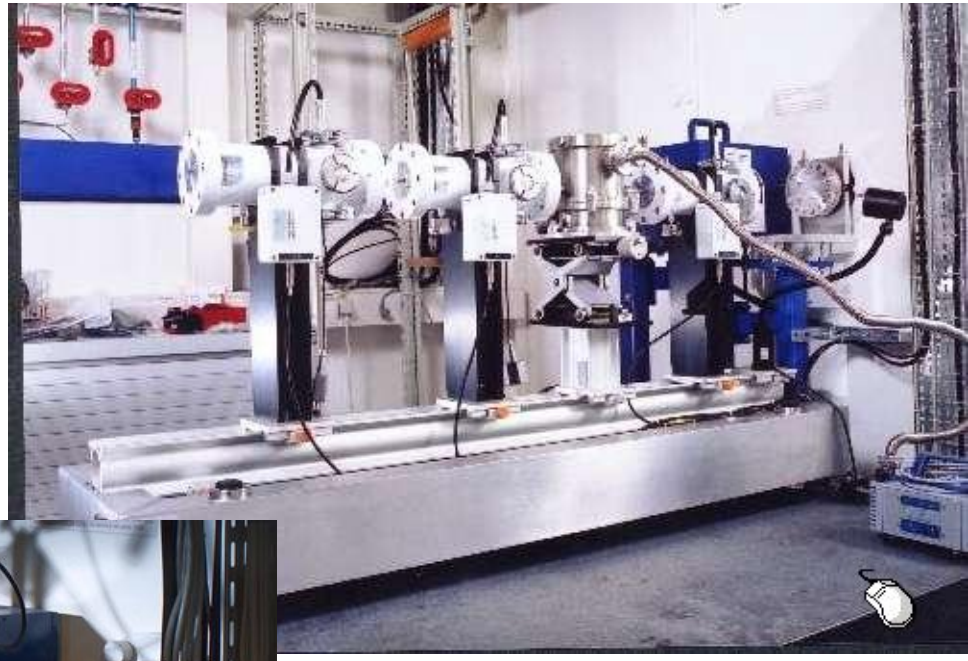
$2d \sin \theta = n\lambda$

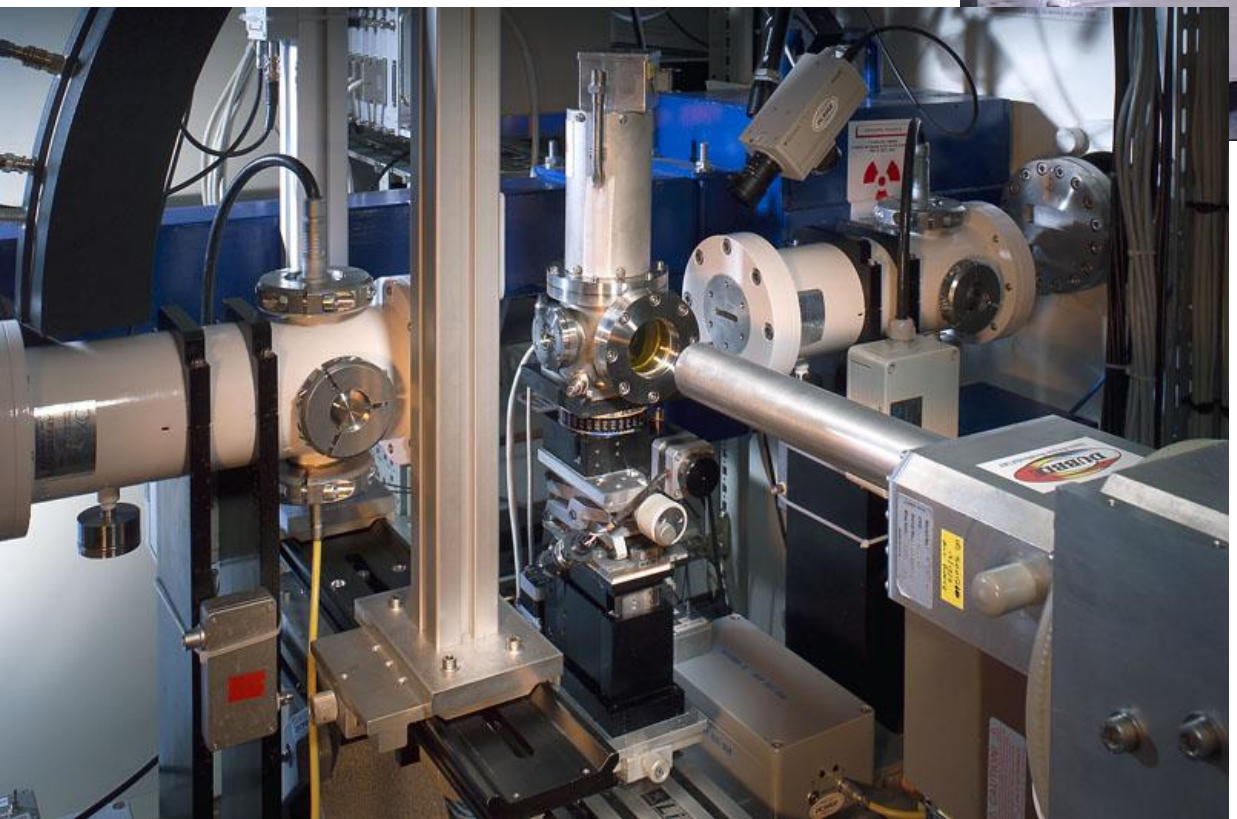




Experimental Hutch







BM26 (DUBBLE), ESRF Grenoble

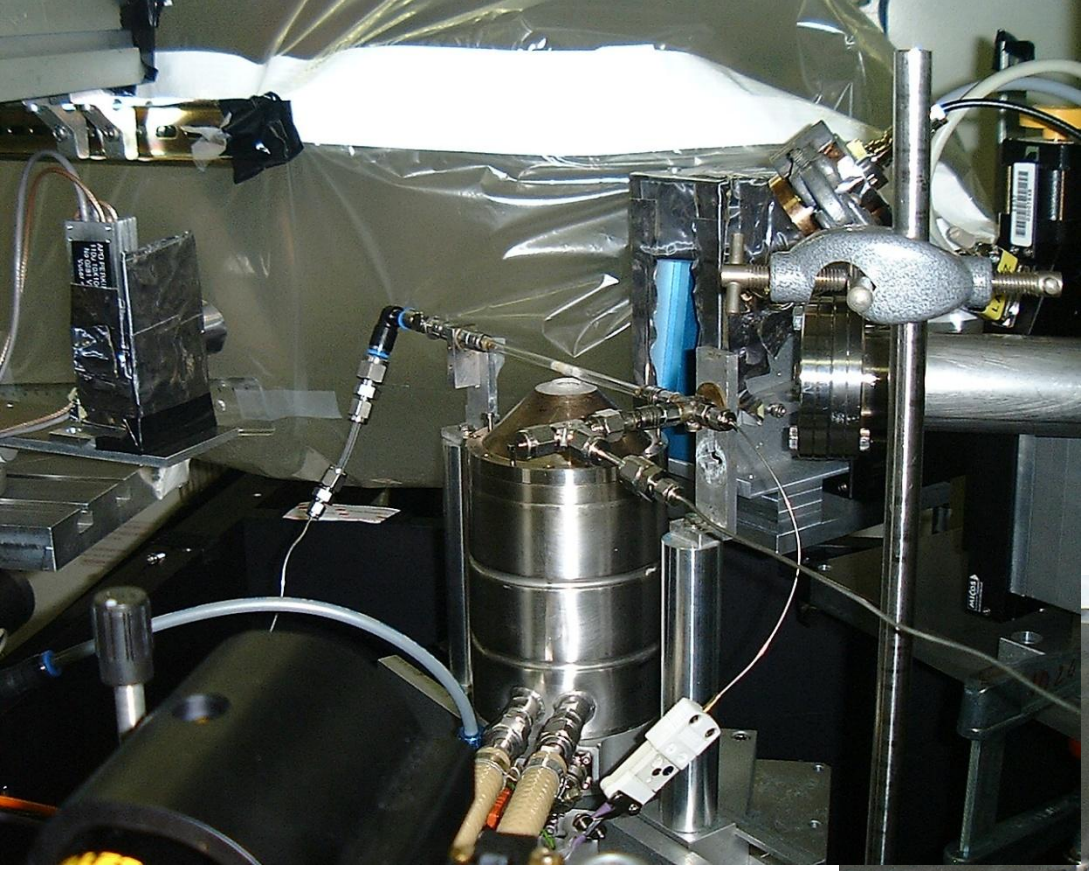
Wish list for catalysis research

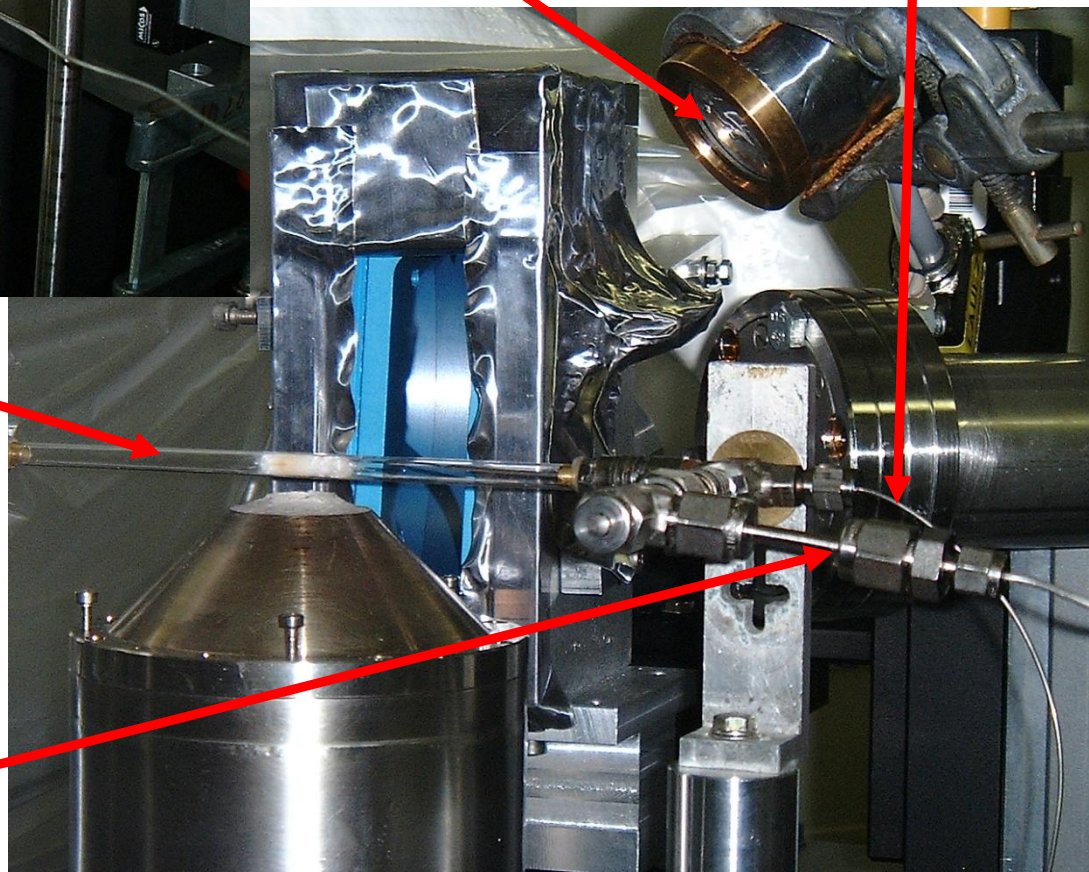
Reactors
Gas composition
On line catalyst performance (GC MS)
Sample preparation

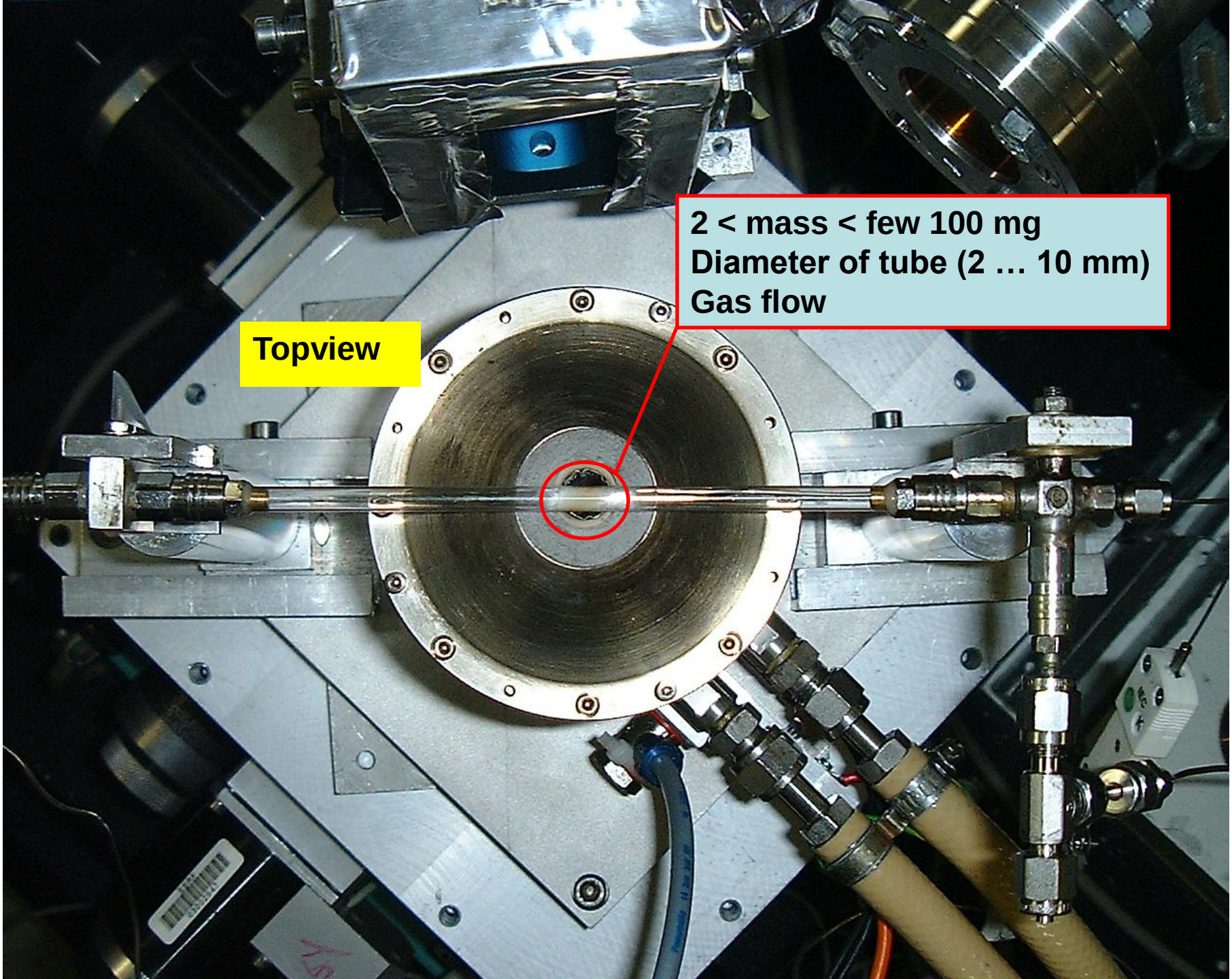
Combination of methods: XAS, XES, XRD, PDF, infrared, Raman, …

Dedicated beam line required!

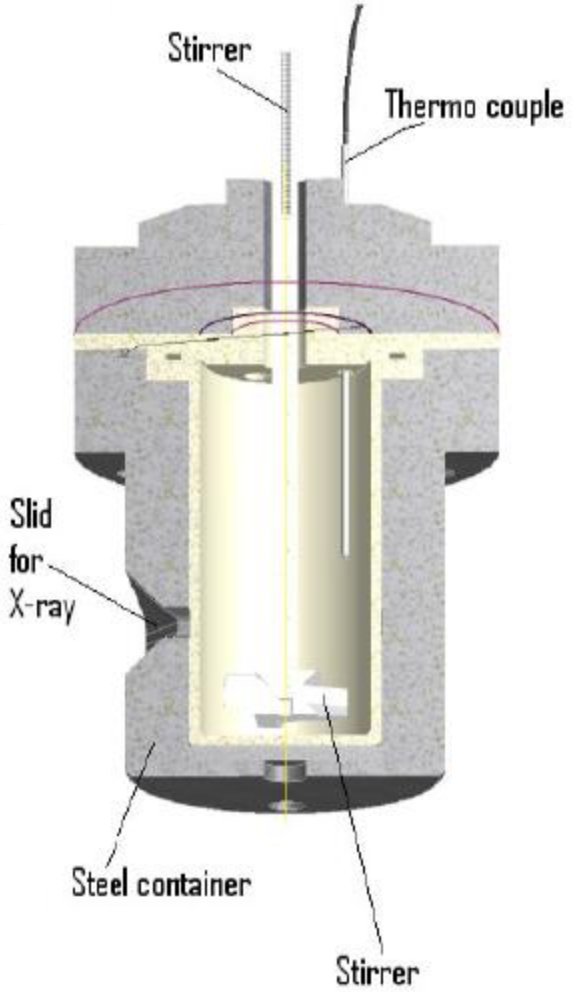
ID26, ESRF



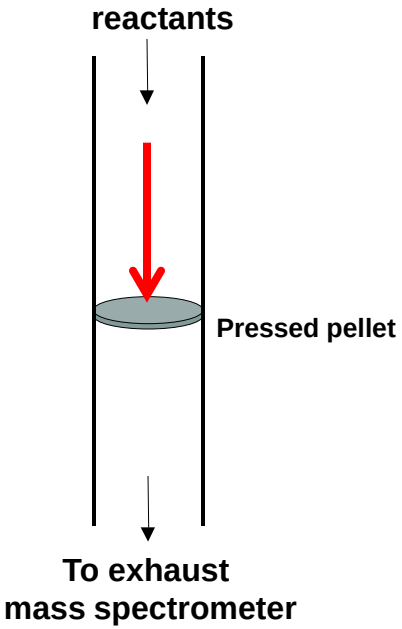

Fluorescence detector
Thermo Couple
Reactor
Exit-tube to mass spec

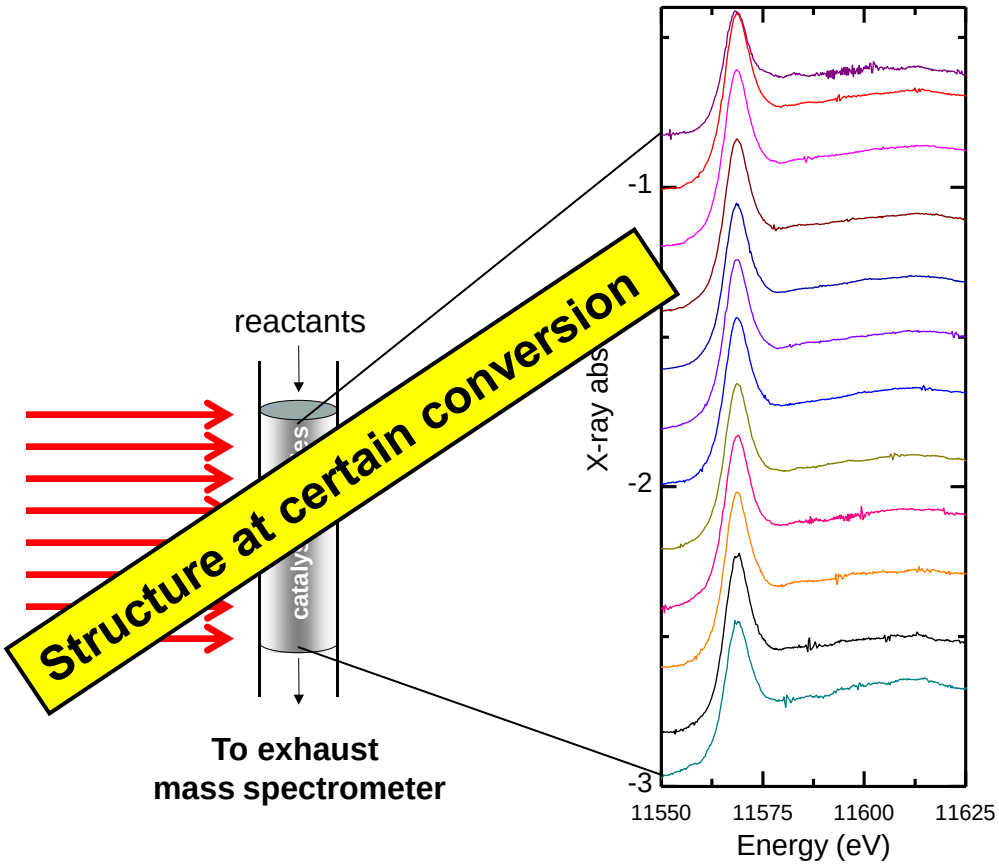

2 < mass < few 100 mg
Diameter of tube (2 … 10 mm)
Gas flow
Topview

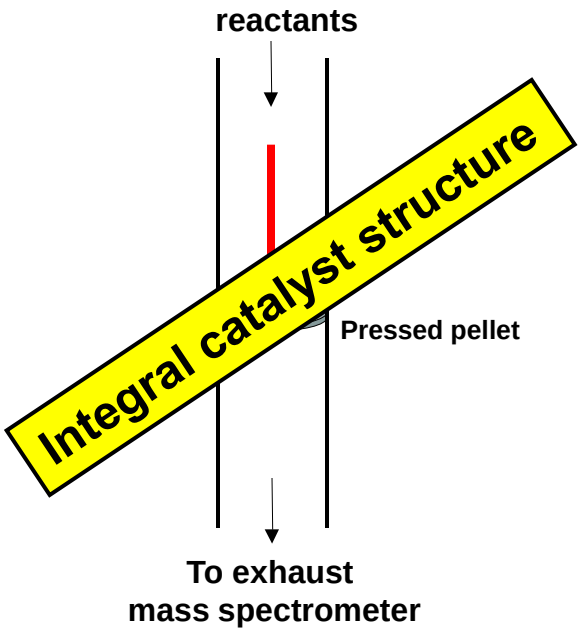
Stirred vessel
Pressurized
Solid-liquid-gas reactions



Pelletized reactor
Optimal XAS conditions







Conversion changes gas composition

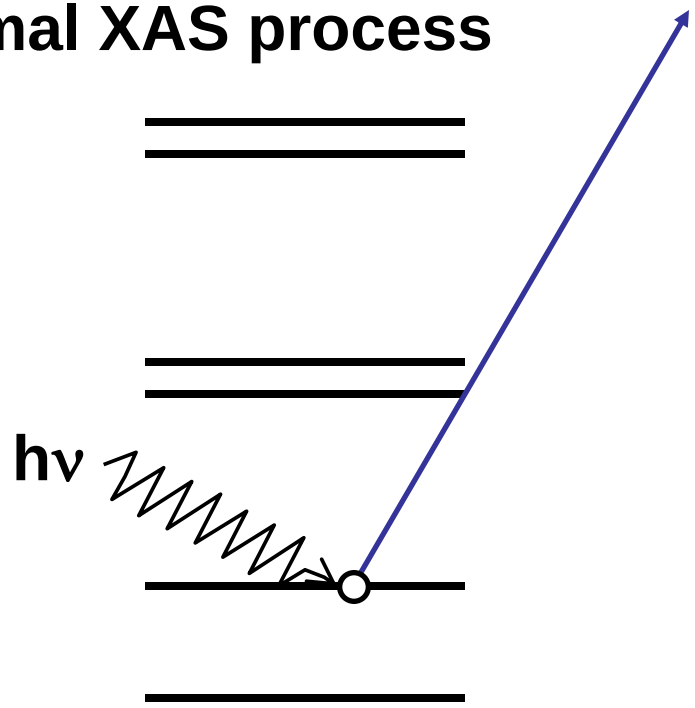
Infrastructure is essential!

Gas mixing system
Mass spectrometer
Gas chromatograph
Sample preparation

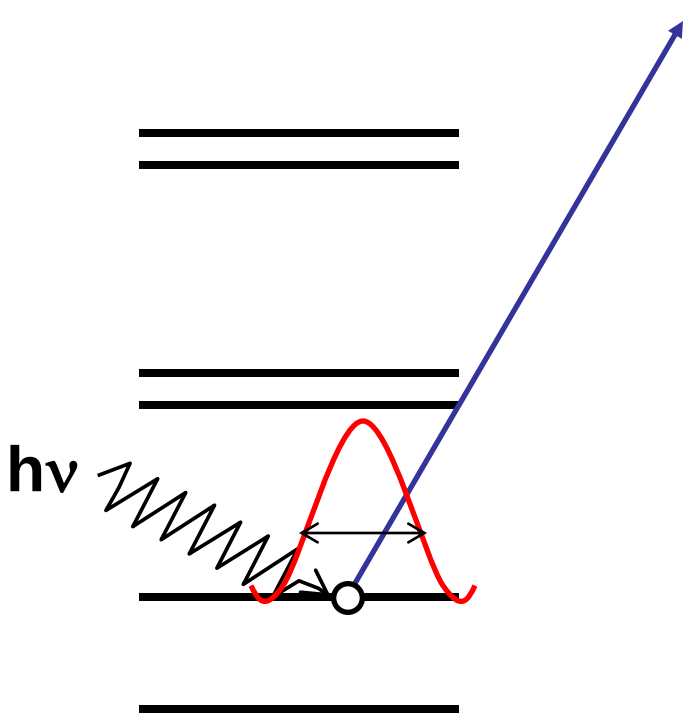
Dedicated beam line!

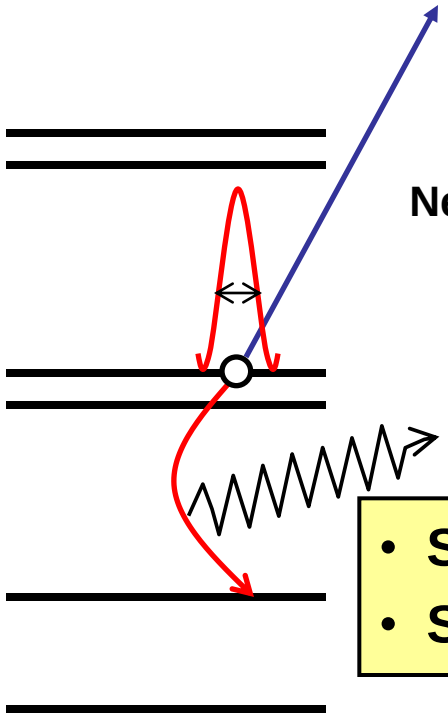
High energy resolution fluorescence detected XAS

Normal XAS process



High energy resolution fluorescence detected XAS



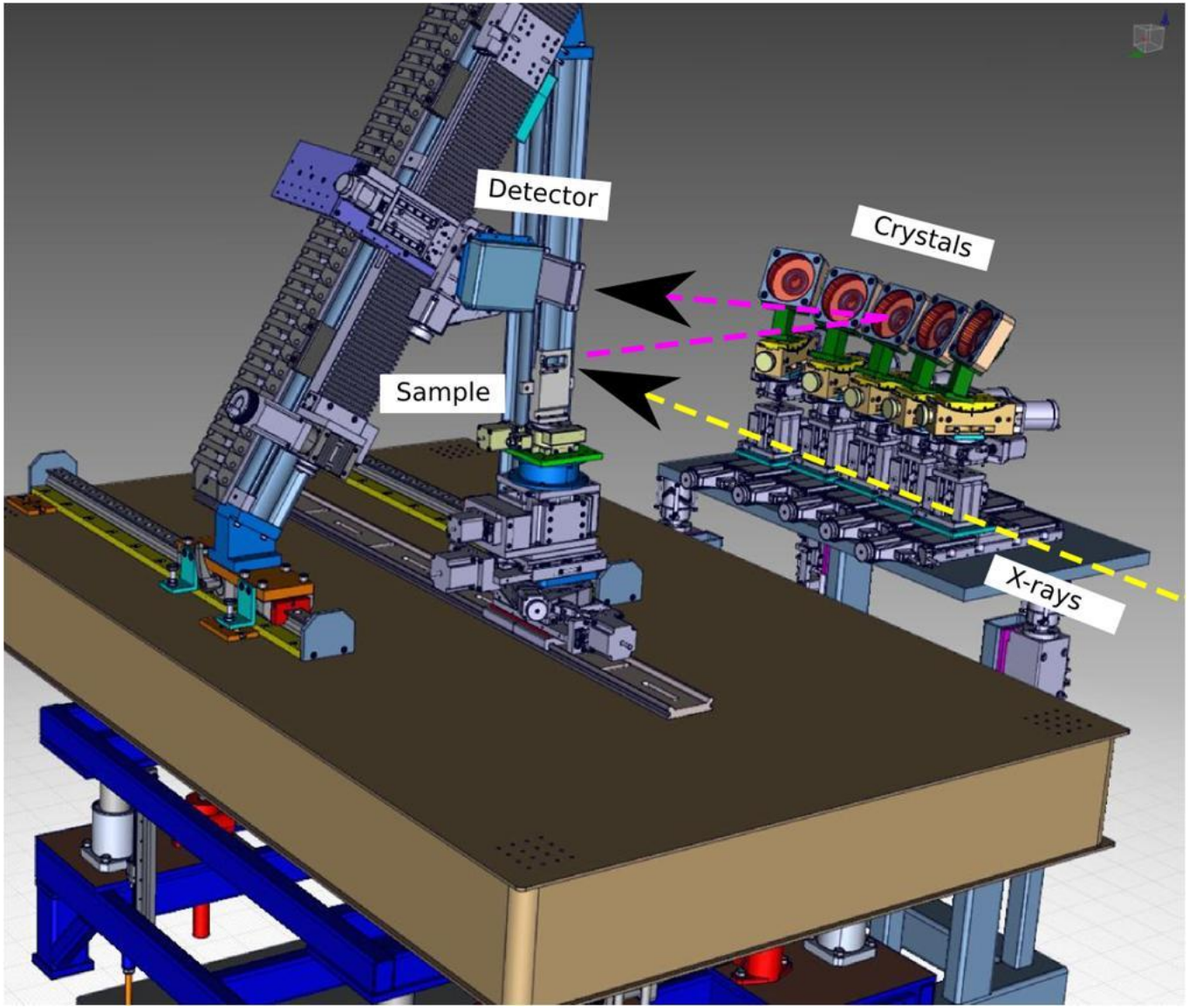


- Selective detection of h
- Spherically bent crystal

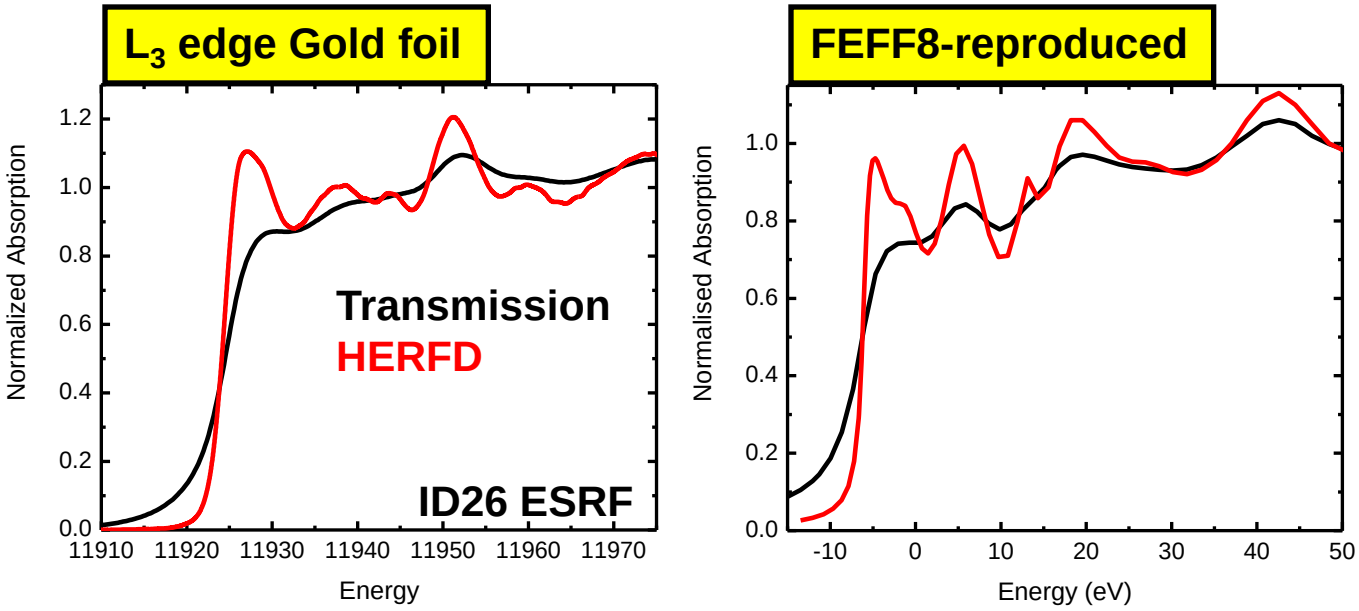
Corehole Lifetime broadening Lifetime broadening

Secondary emission spectrometer

X-ray emission spectroscopy



High energy resolution fluorescence detected XAS



Good

- **High energy-resolution**
- **Hard X-rays: in-situ**

Not so good

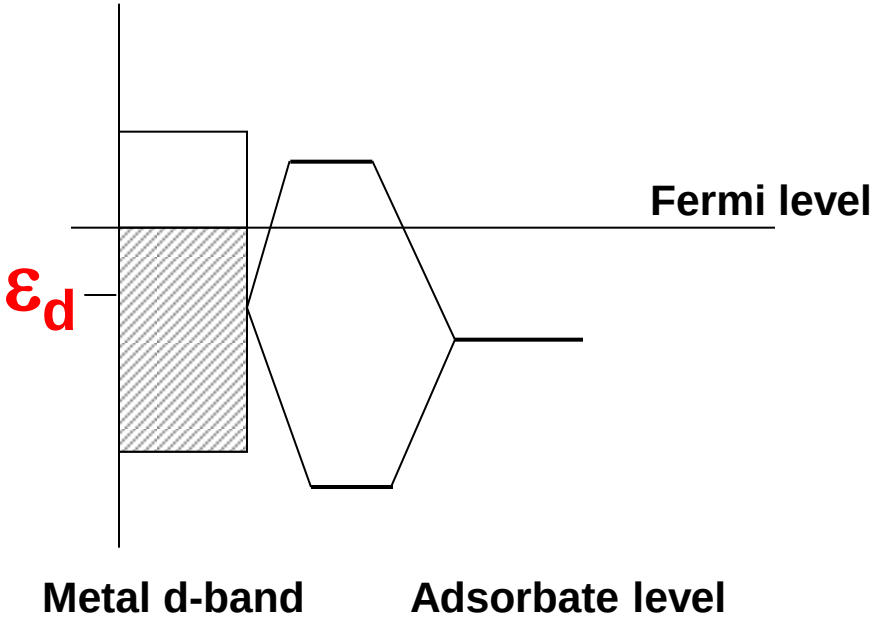
- **Low yield of good photons**

Angew. Chem. Int. Ed. 45 (2006) 4651
Rev. J. Chem Soc. (2010) accepted

Adsorption of CO on Pt/Al_2O_3

Adsorbate bonding on metals

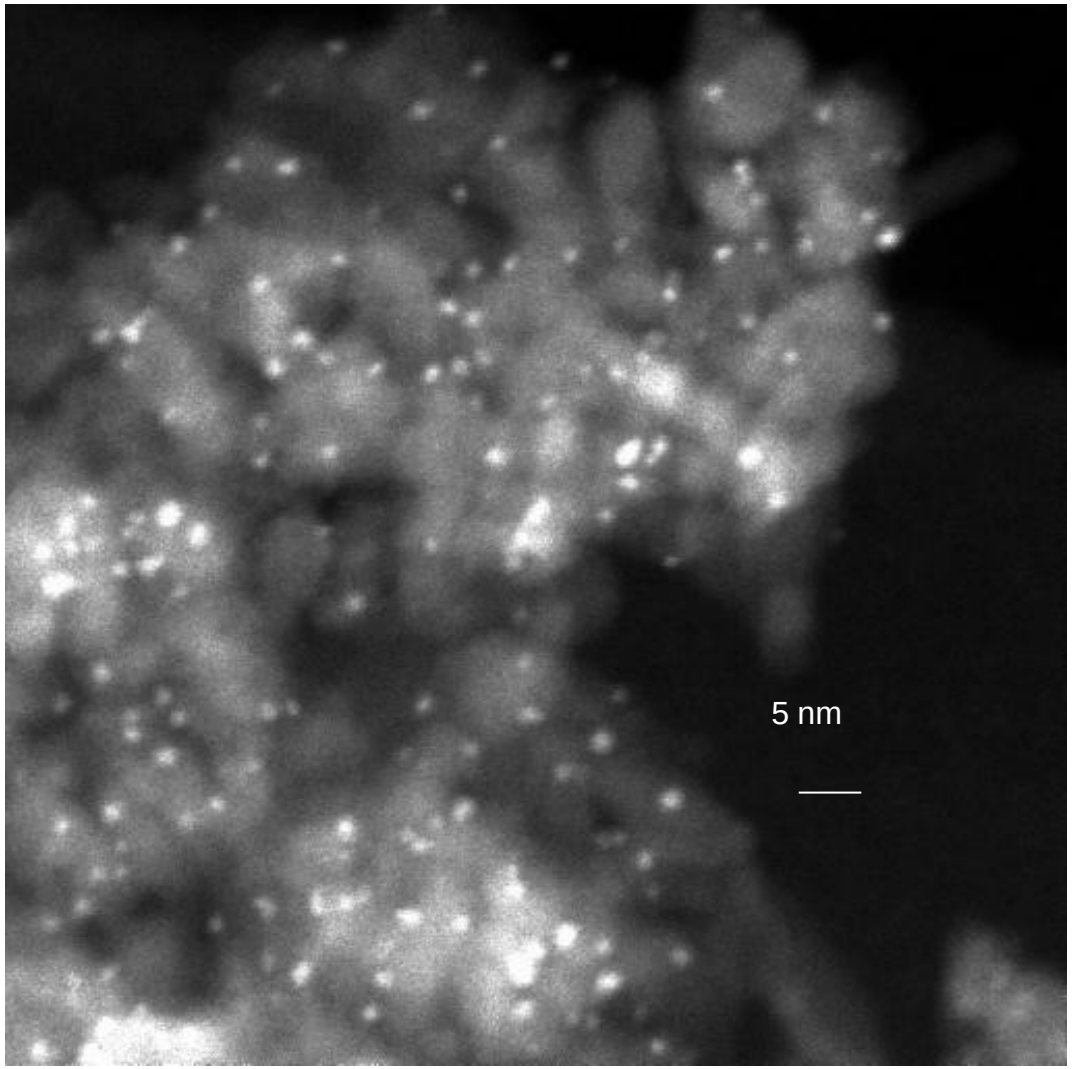
sp-interaction: broadening
d-interaction: bonding / antibonding states



Energy of d-band determines bond strength with adsorbate

Hammer and Norskøv *Nature* 1995 *376* 238

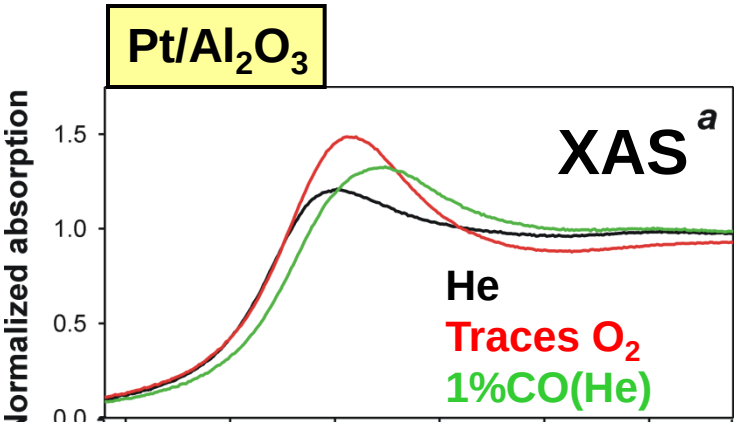
2 wt% Pt/ Al2O3



impregnation
calcination at 673 K
reduction at 723 K

1-2 nm particles

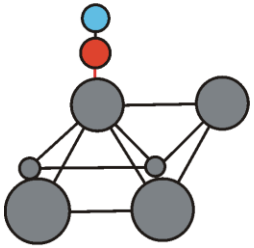
High energy resolution fluorescence detected XAS



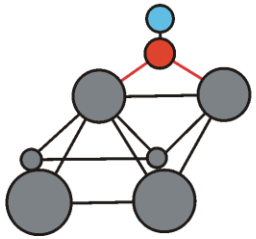
ID26, ESRF

FEFF8 simulation

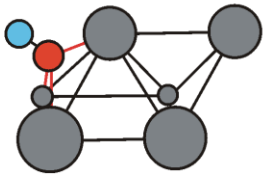
Pt_6CO atop

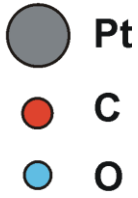


Pt_6CO bridged

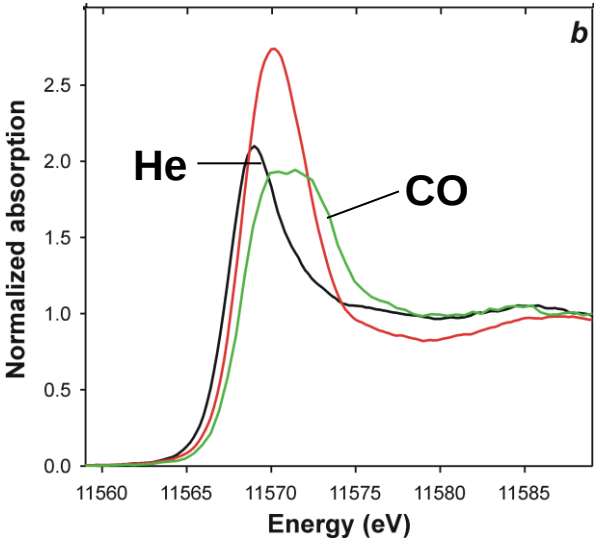


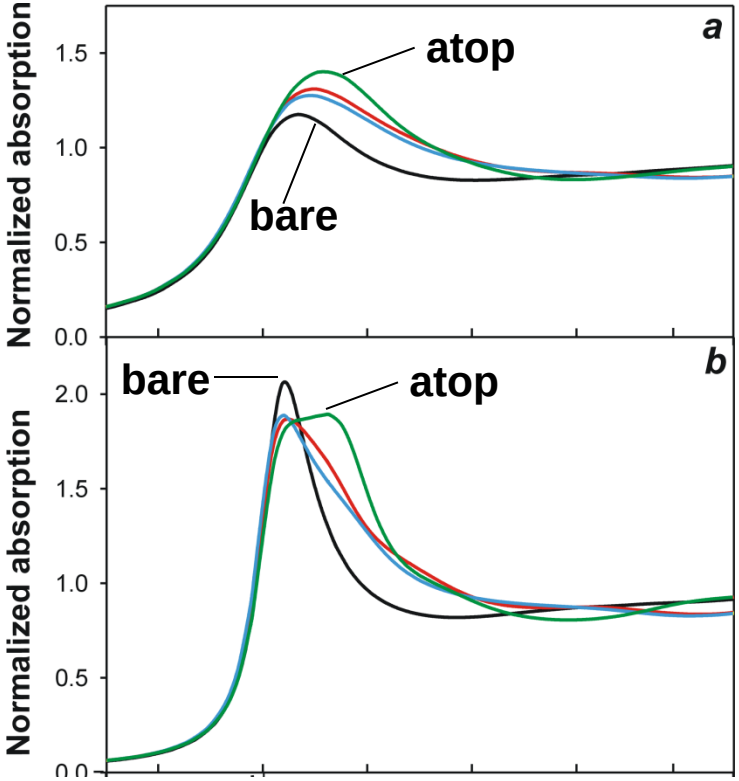
Pt_6CO face bridging





Experimental

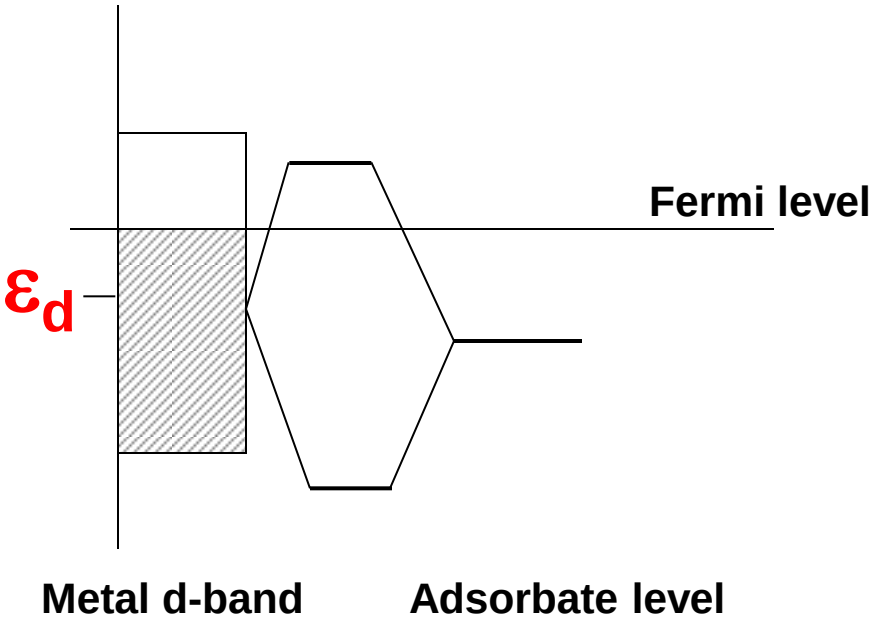


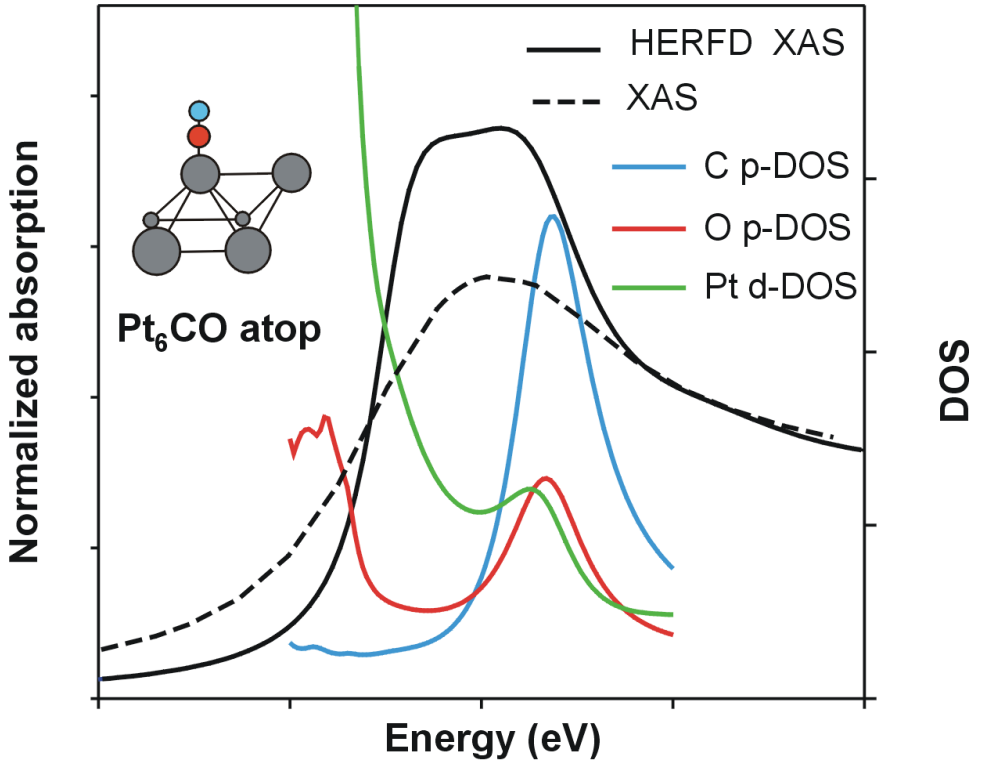


XAS

HERFD

Empty density of states



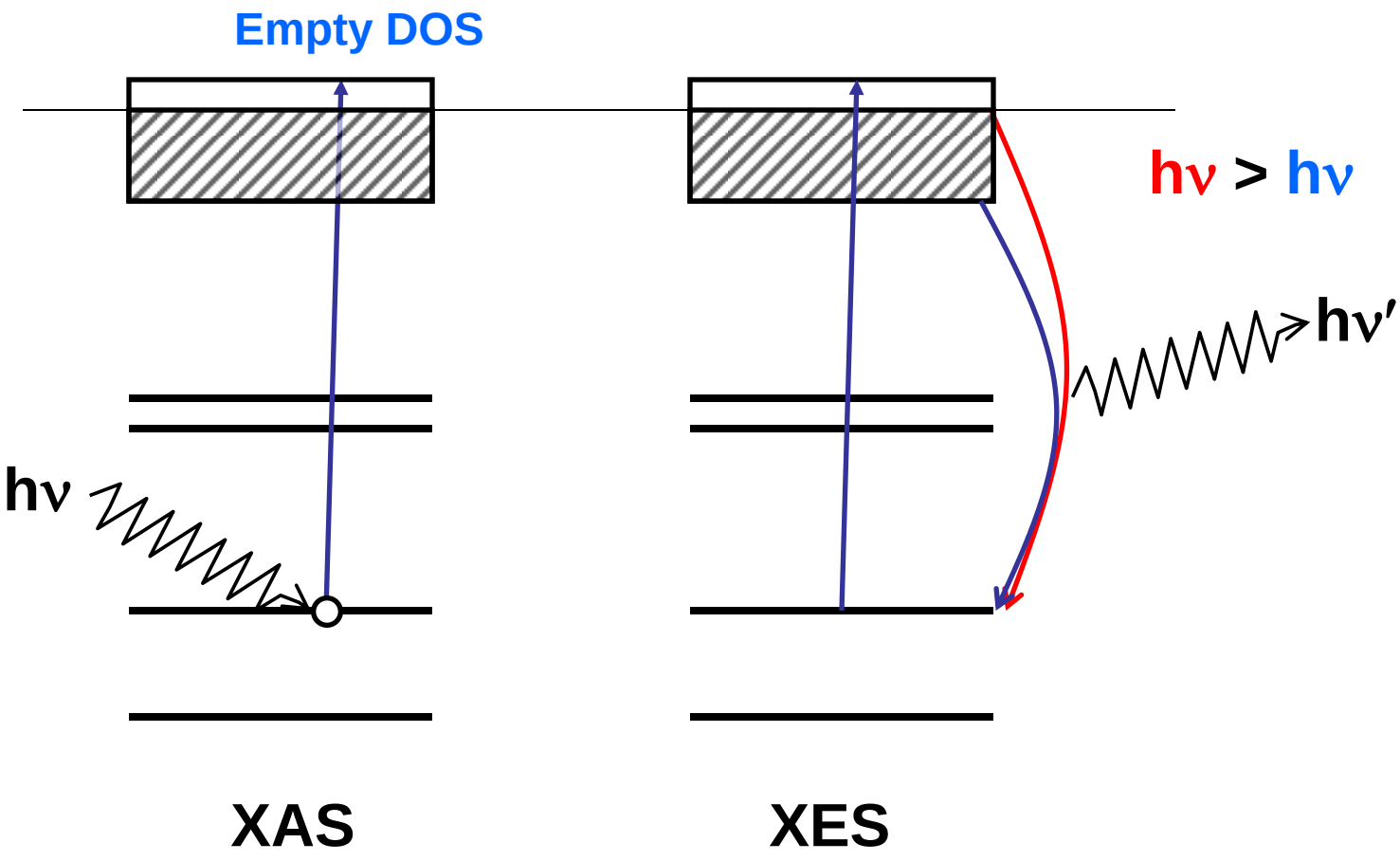


Structure of adsorption sites can be determined

FEFF8 reproduces experiment and provides LDOS

Quantification of the surface species!

J. Phys. Chem. B . 110 (2006) 16162

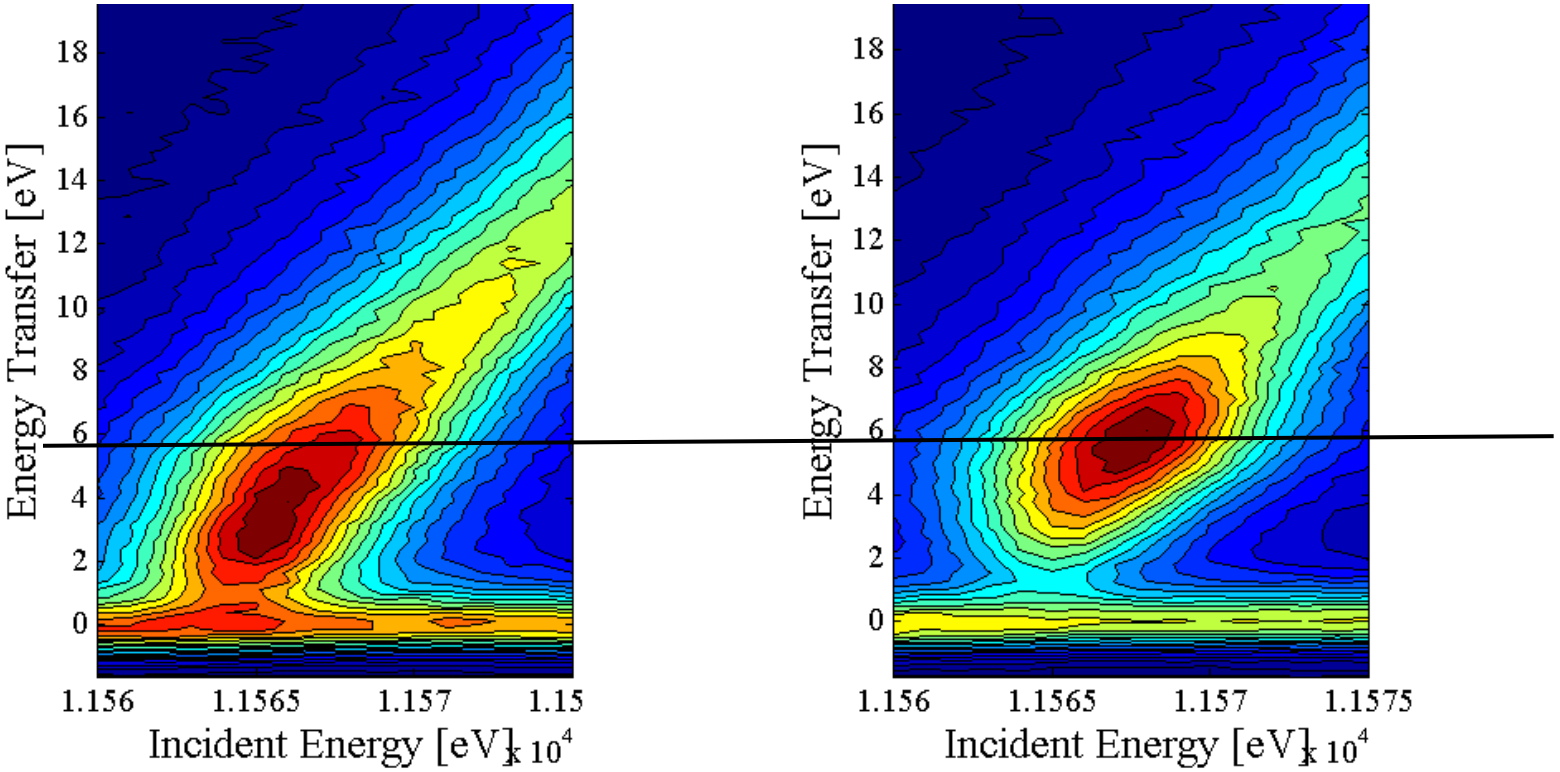


Looking at the empty and filled valence band

2pVB RIXS planes

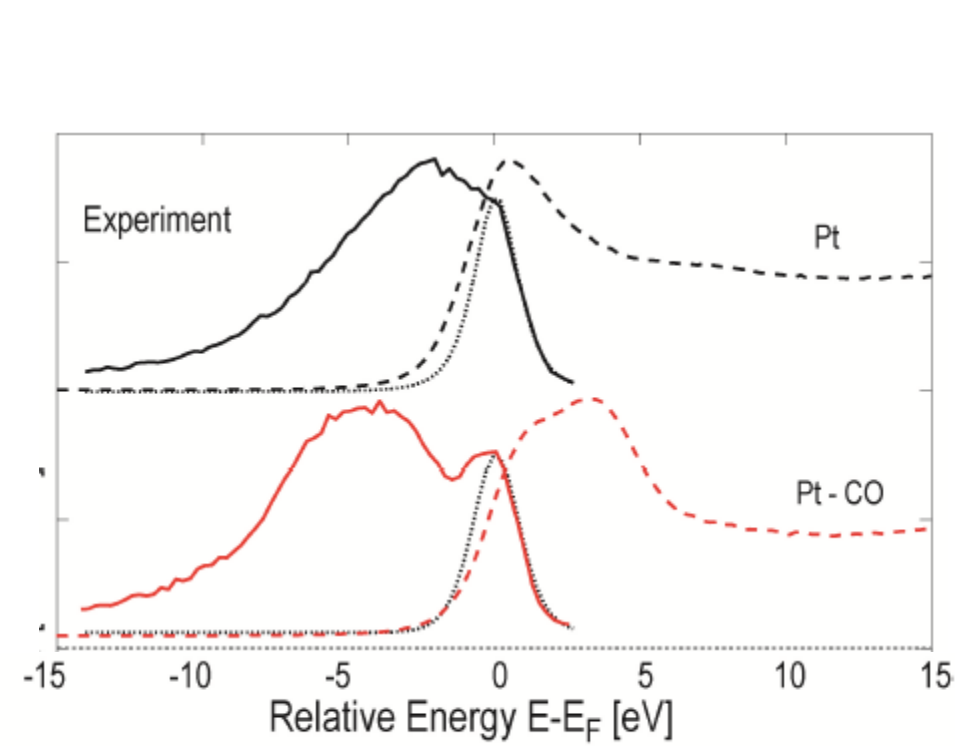
Pt/Al_2O_3

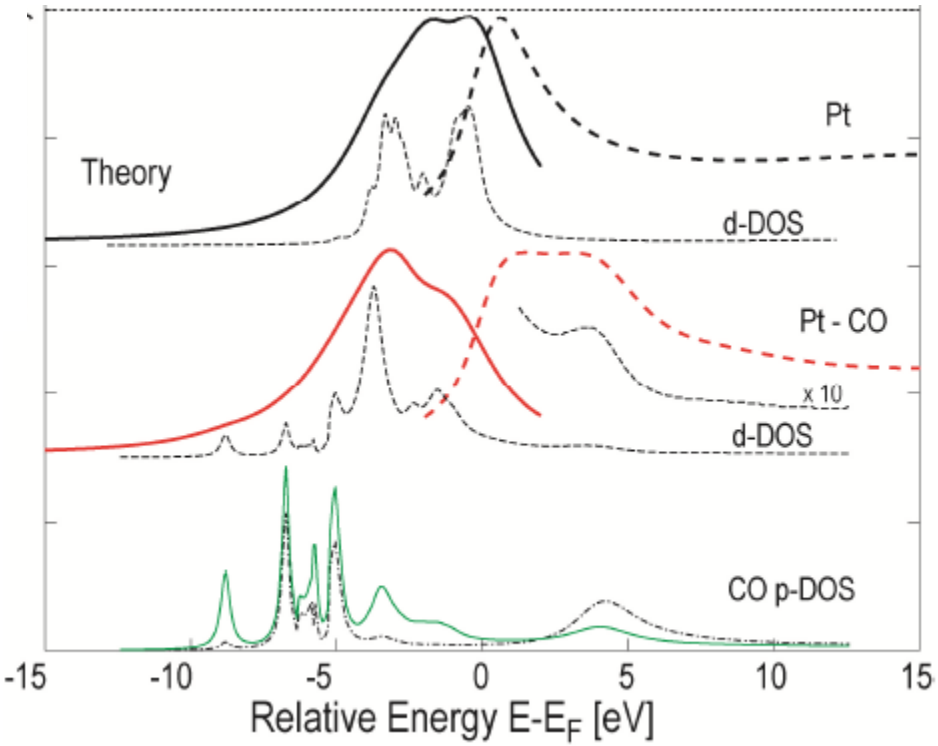
Pt/Al_2O_3 under CO



Element- and spin-specific valence band structure
Hard X-rays: in situ

JACS 132 (2010(2555


Experiment
Pt
Pt - CO
-15
-10
-5
0
5
10
15
Relative Energy E-E$_F$ [eV]

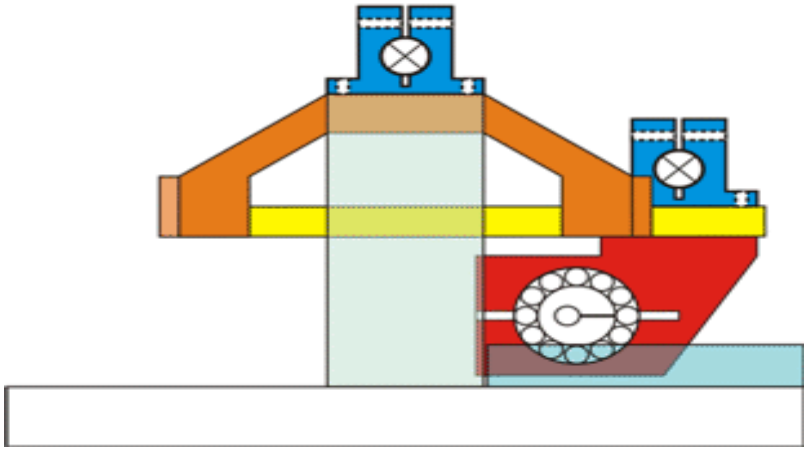

Theory
Pt
d-DOS
Pt - CO
x 10
d-DOS
CO p-DOS
-15
-10
-5
0
5
10
15
Relative Energy E-E$_F$ [eV]

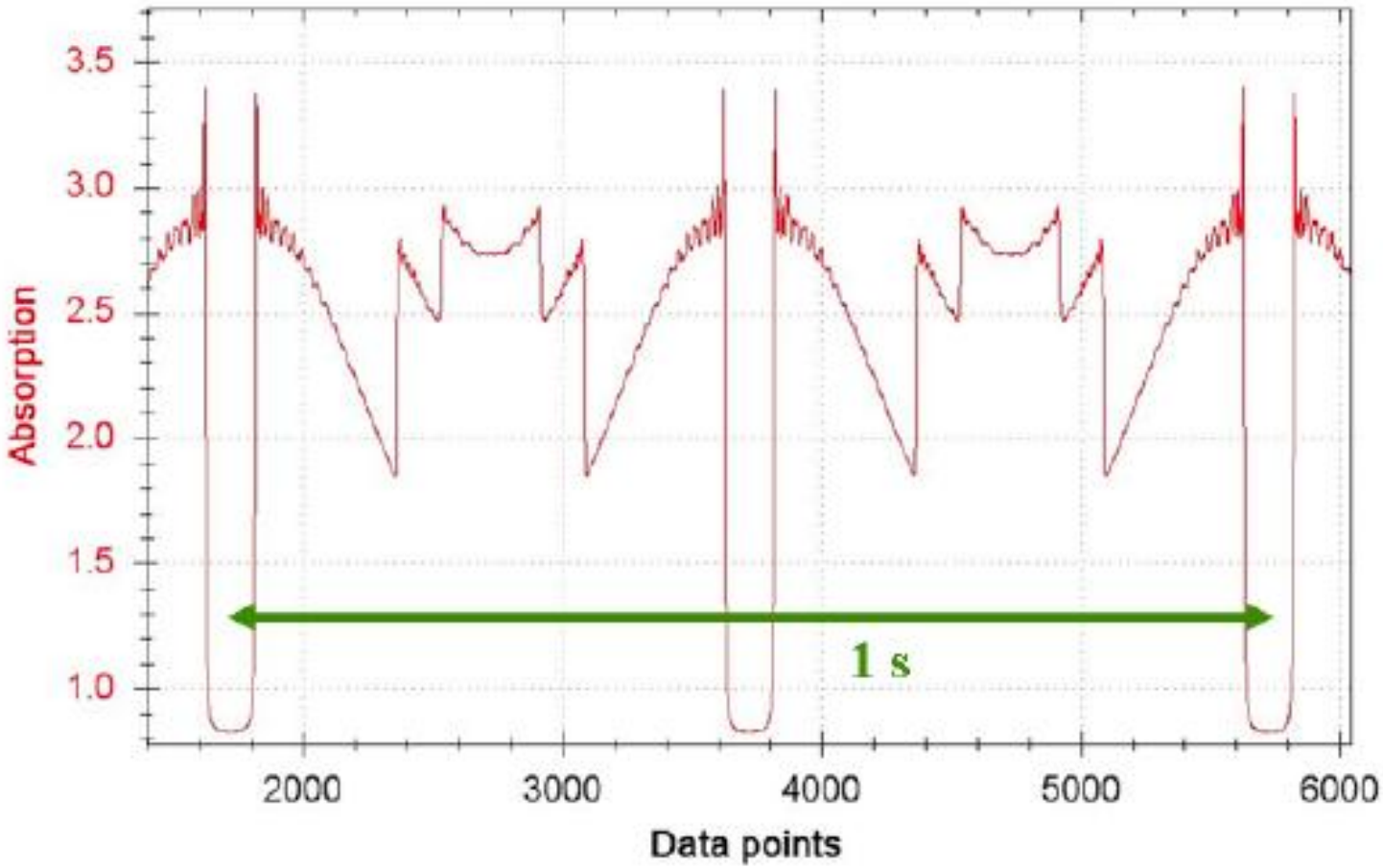
Time resolved structure

Qexafs signals

Pt foil

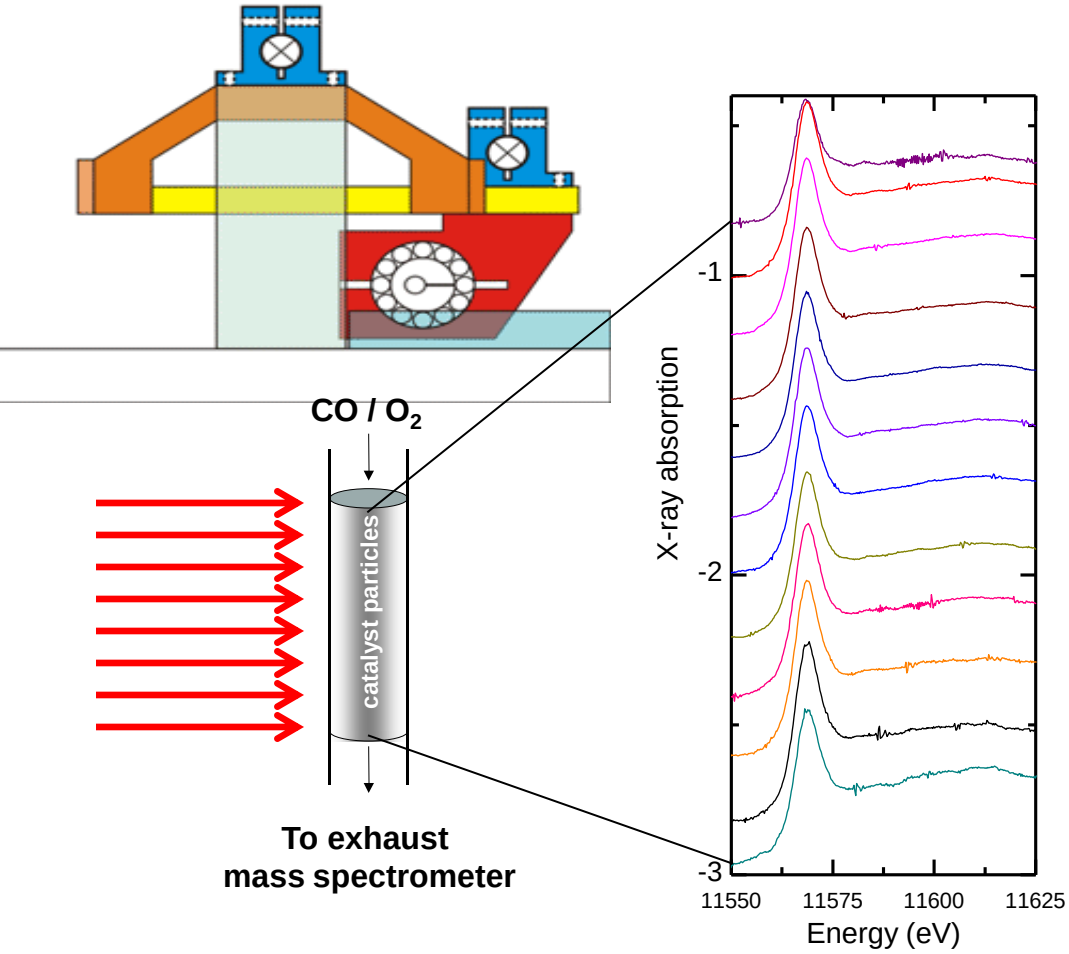
L_3, L_2, L_1 edges





SuperXAS: QEXAFS

monitoring oscillating reactions



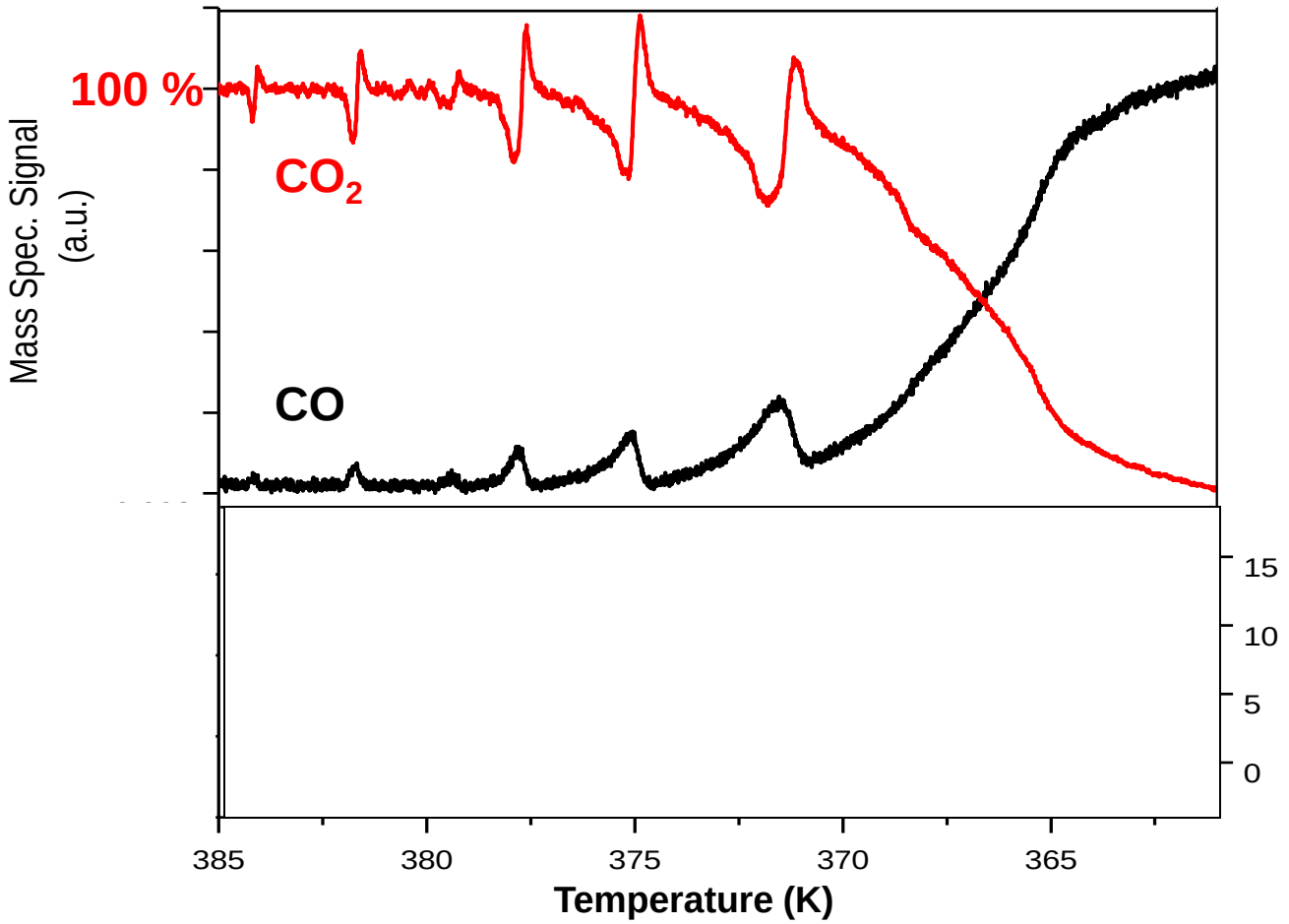
Full XANES and EXAFS:
electronic and geometric structures

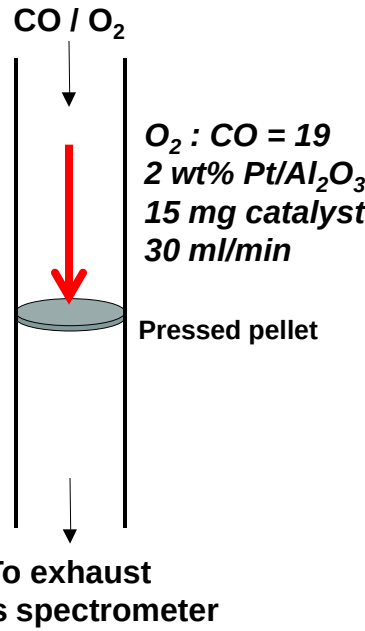
Spectral repetition 2 Hz

Spot size
100 μm x 1000 μm

Oscillating reactions

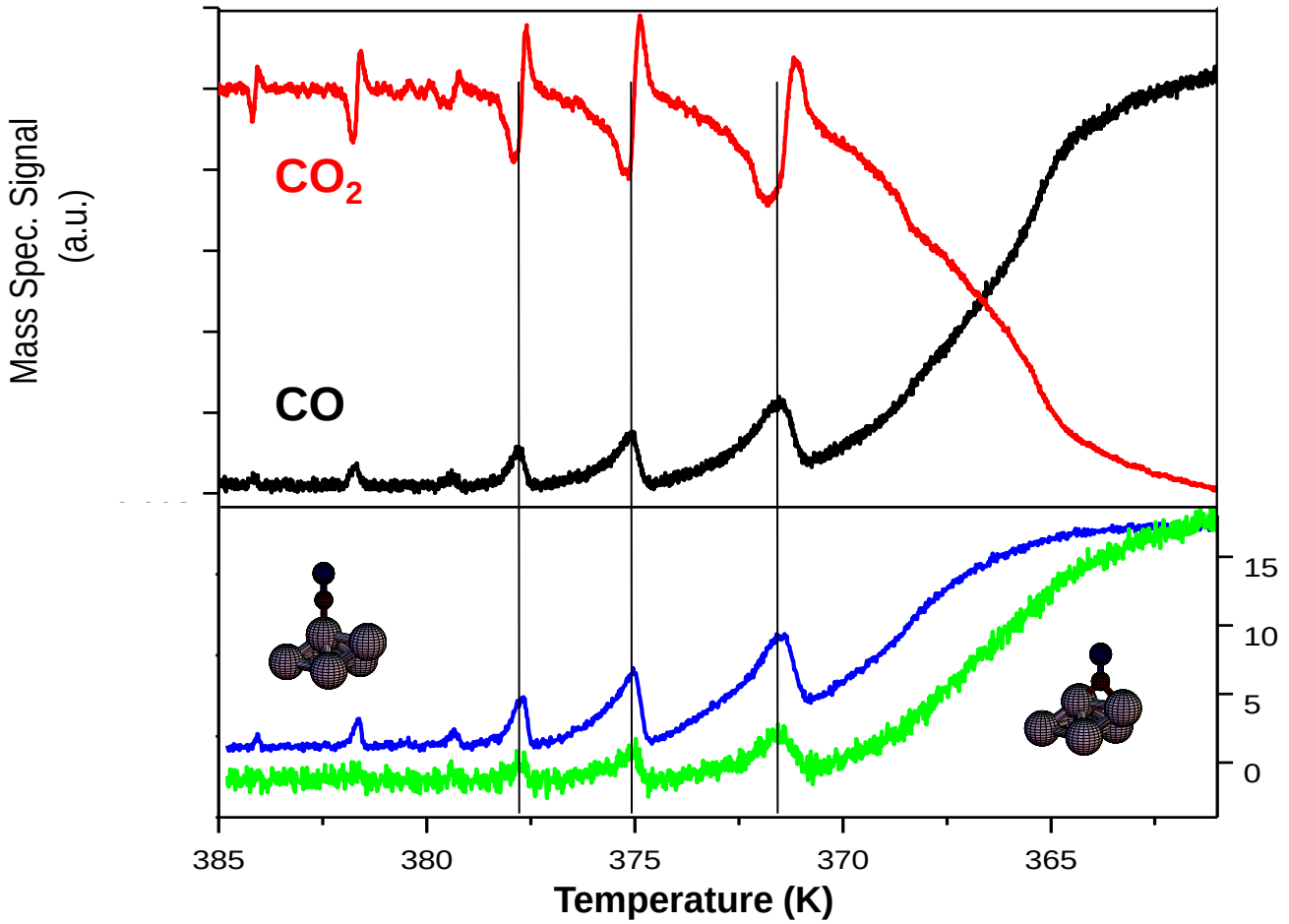
$CO + O_2 \rightarrow CO_2$



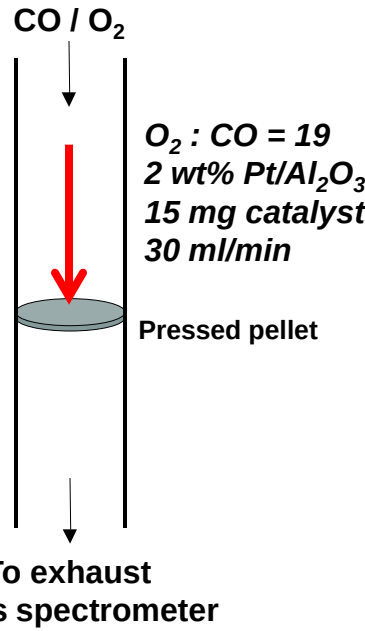


Oscillating reactions

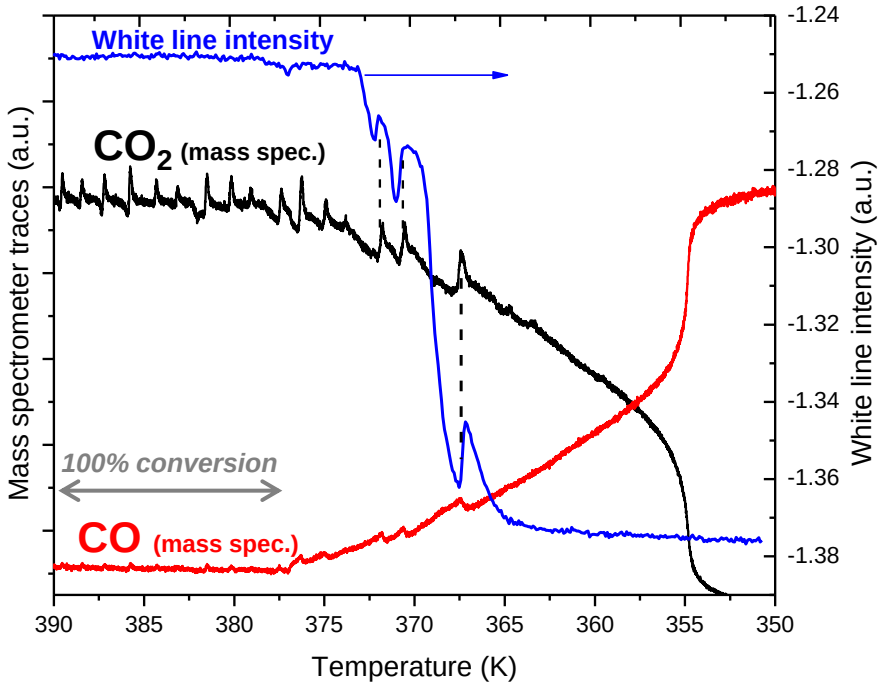
$CO + O_2 \rightarrow CO_2$

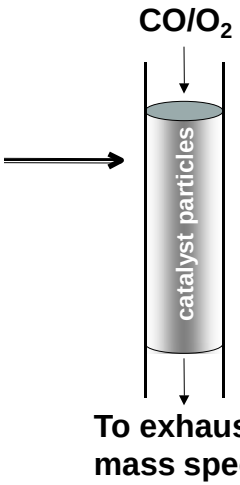


CO storage
CO poisoning

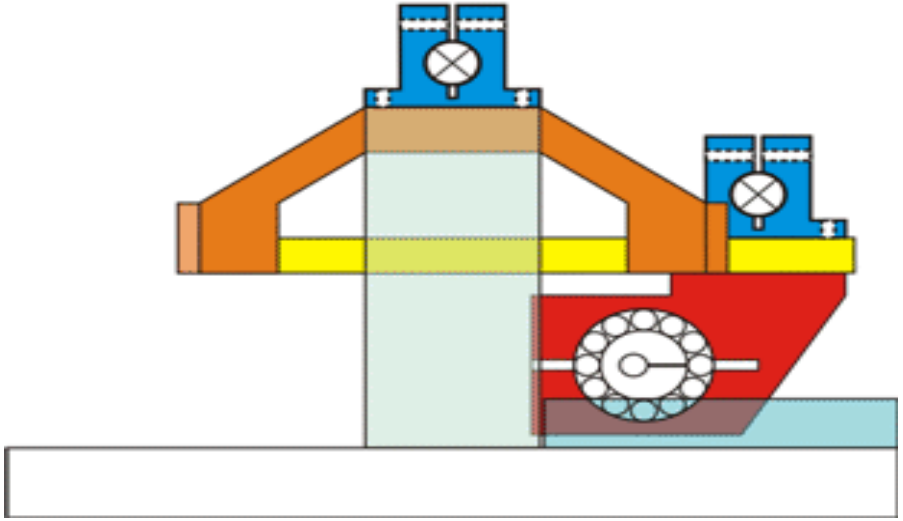


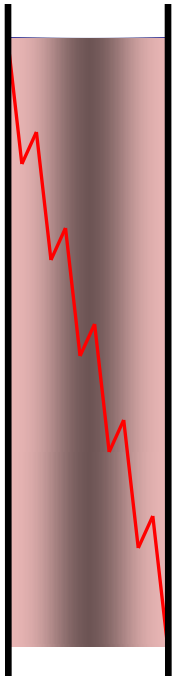
Time and space dependent catalyst structure



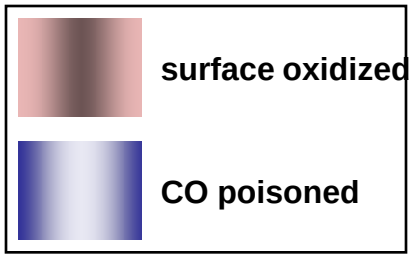


Position in reactor (mm)	Conversion (%)
Top	94
1.0	74
2.5	36
4.5	30

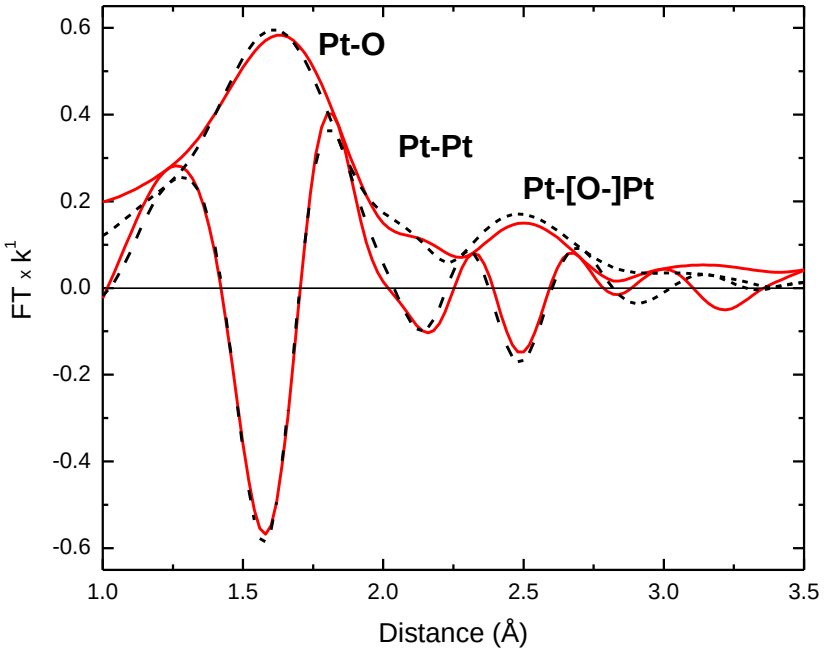




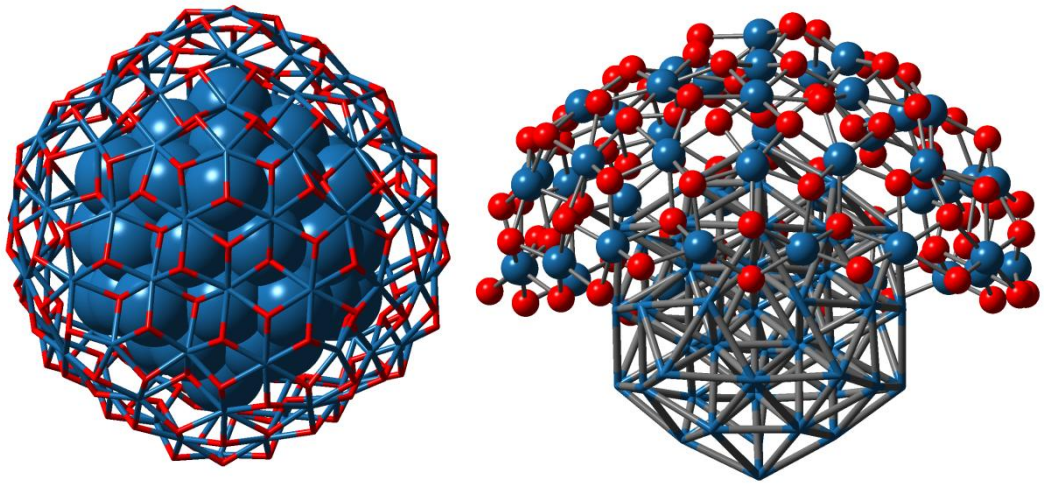
Decreasing conversion



Structure of the oxide?



		CN	DWF	R	Eo
Surface oxidized	Pt-Pt	5.4	0.0091	2.59	7.6
	Pt-O	2.9	0.0014	1.99	3.4
	Pt[-O]-Pt	3.1	0.0150	3.09	-1.6



Current limit:
100 ms 2wt% Pt/Al_2O_3

Oxide layer based on: Hammer *Phys. Rev. Lett.* 93 (2004) 146104

conclusion

What can XAS do for catalysis?

Local geometric structure dynamic! quantitative! *Averaged* structure
Electronic structure filled and unfilled states

In situ conditions **essential**
Time resolution sub second
Space resolution (sub-)micrometer, confocal, tomographic, 3D structure!

Instrumentation development photons in - photons out
X-ray emission spectroscopy new opportunities: valence band, site selective XAS, X-ray Raman scattering

Combining complementary methods