



*Structure of heterogeneous catalysts using X-ray absorption spectroscopy*

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# Abbreviations

XAS

X-ray Absorption Spectroscopy

EXAFS

Extended X-ray Absorption Fine-Structure

XANES

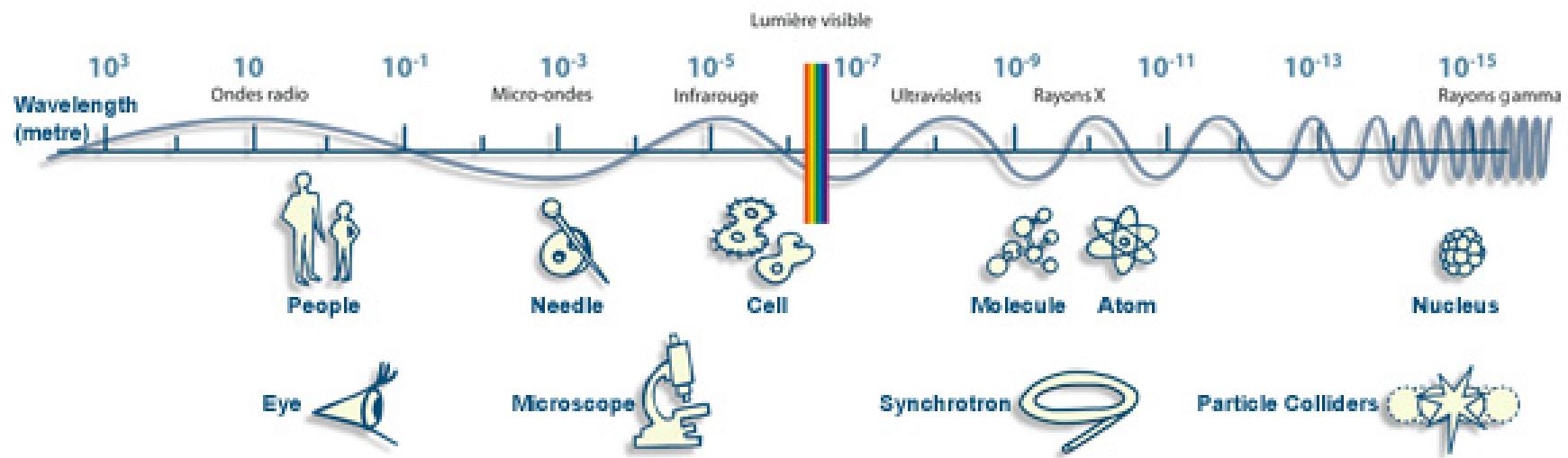
X-ray Absorption Near-Edge Structure

NEXAFS

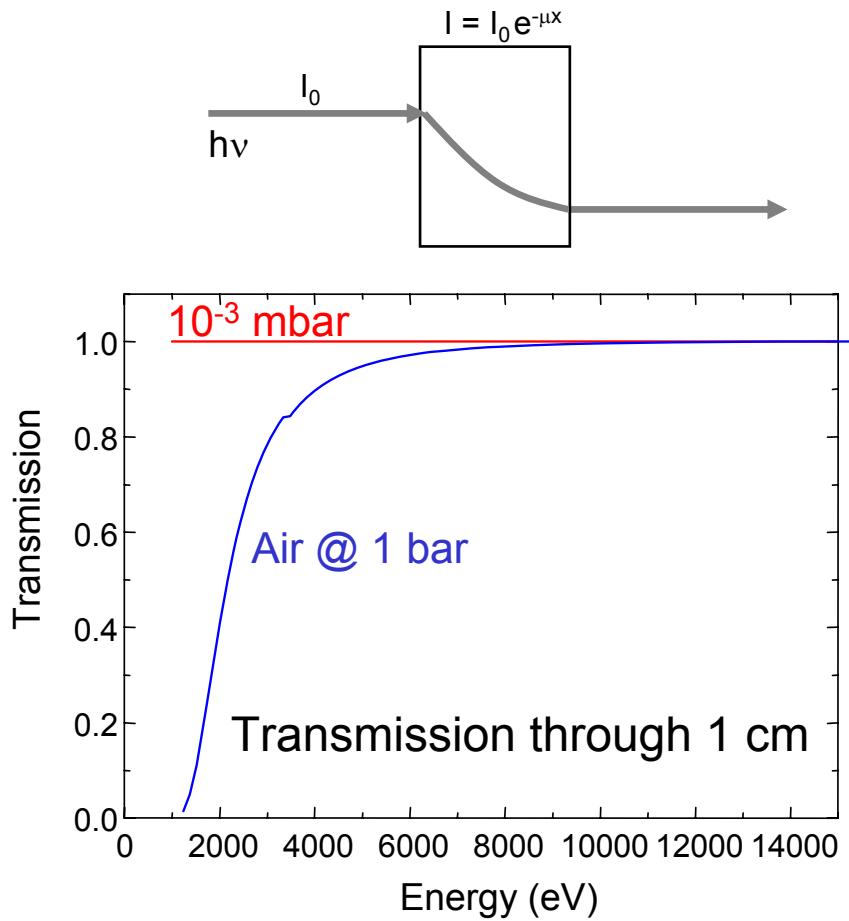
Near-Edge X-ray Absorption Fine Structure



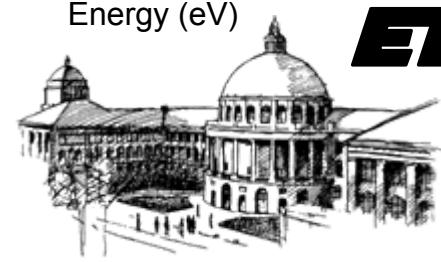
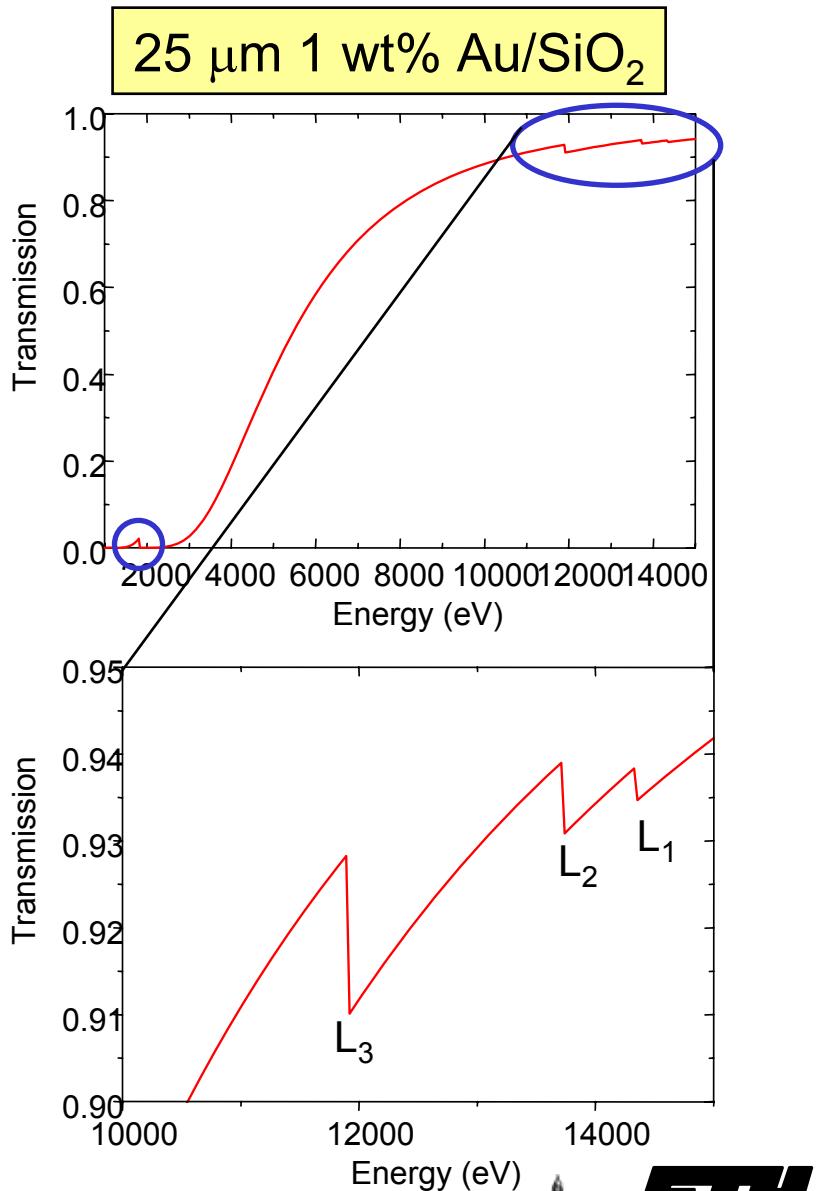
# X-rays



# X-ray absorption through matter

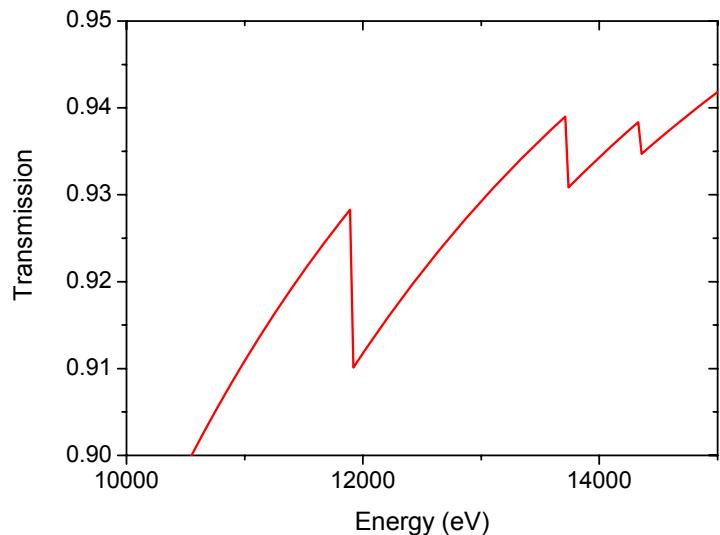


*Lambert Beer's law*  
 $dl = -\mu(E)l dx$   
 $I = I_0 \exp(-\mu(E)x)$

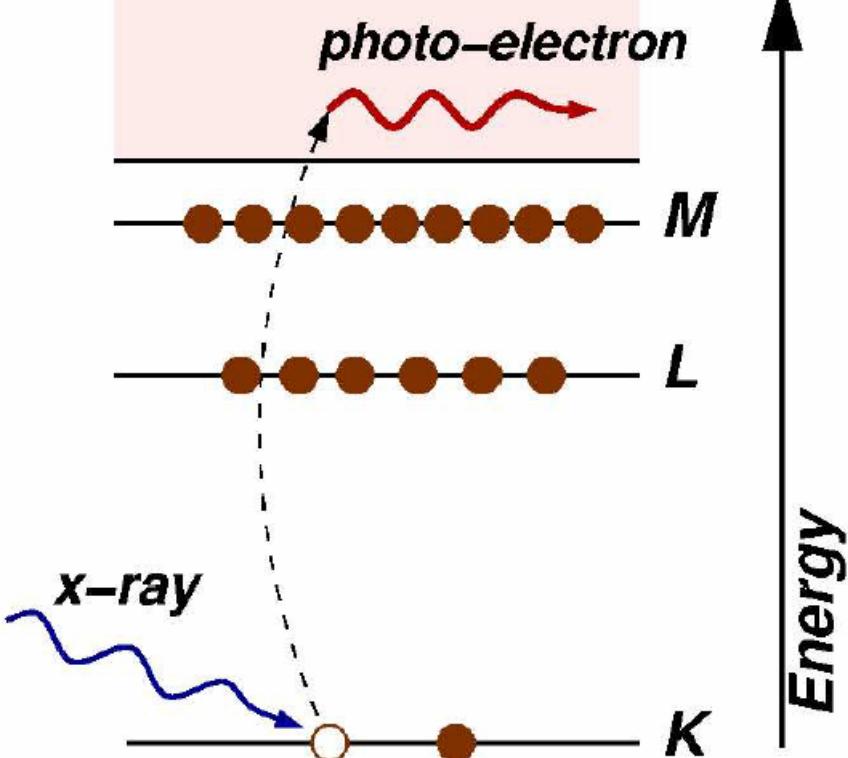


**ETH**

# X-ray absorption through matter



*Continuum*

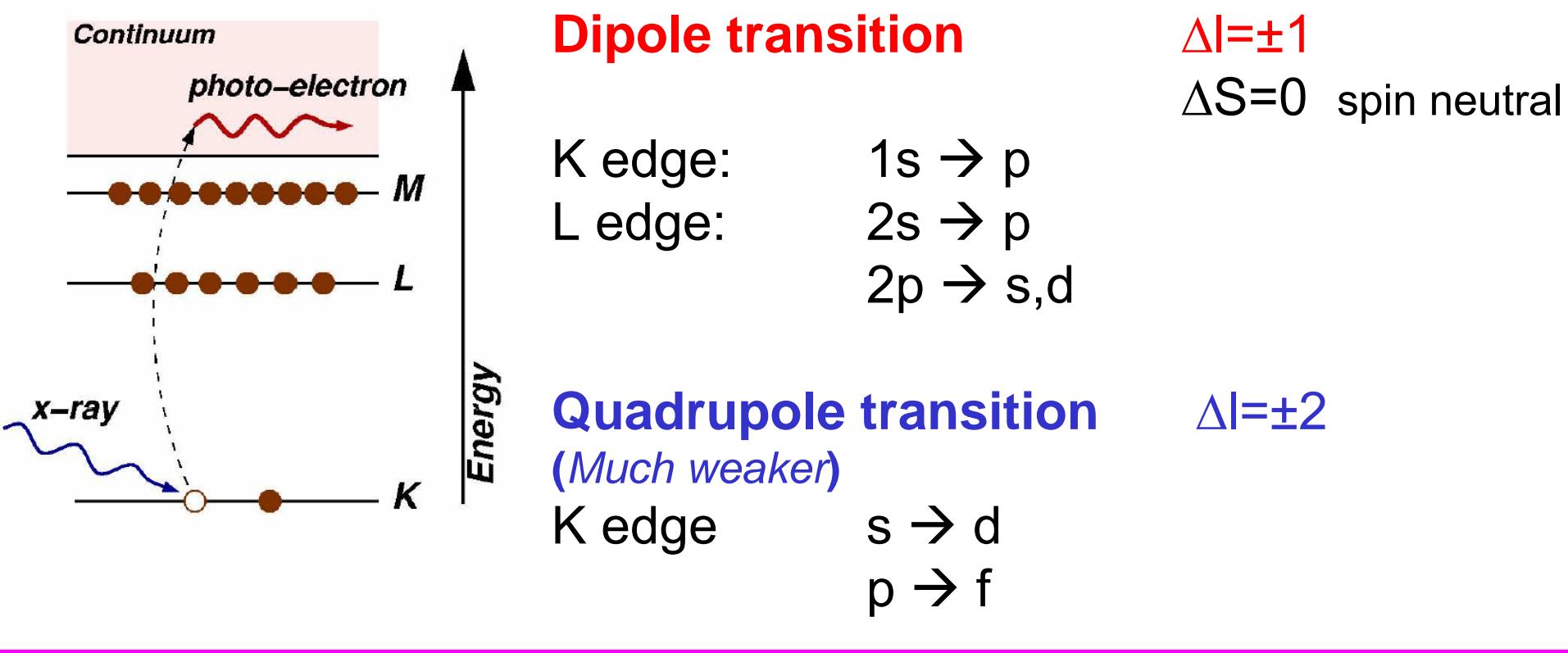


Creation of a photo-electron

$$E_{\text{kin}} = h\nu - E_{\text{Binding}}$$

Element specific





## Transition Probability

Fermi's Golden Rule

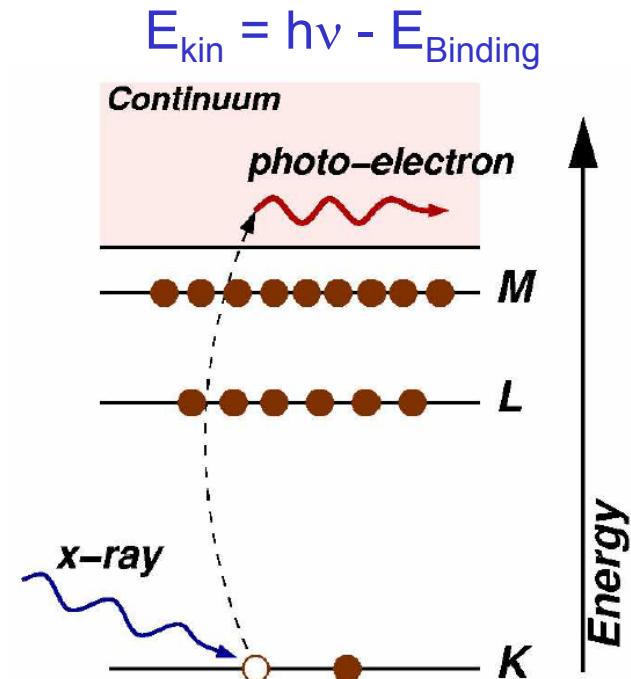
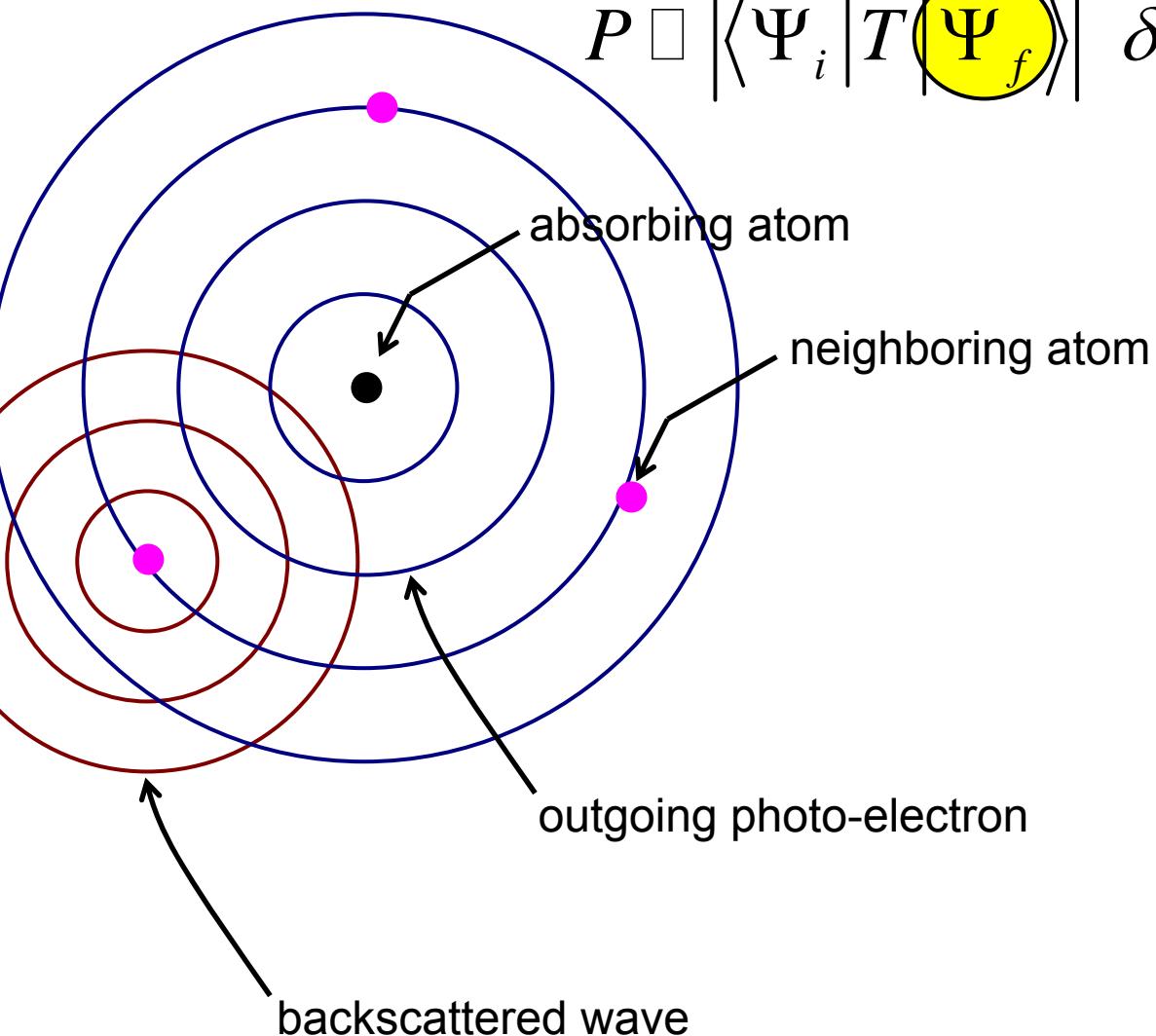
$$P \square \left| \langle \Psi_i | T | \Psi_f \rangle \right|^2 \delta_{E_f - E_i - \hbar\nu}$$

↑  
 Initial state      Final state  
 ↓  
 Transition operator

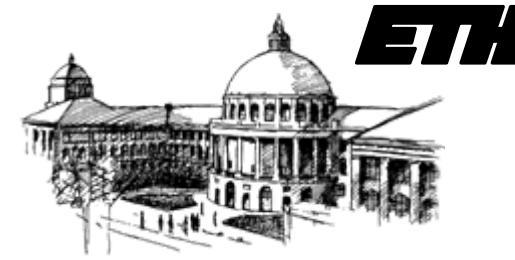


# Transition probability vs Final State

$$P \propto |\langle \Psi_i | T | \Psi_f \rangle|^2 \delta_{E_f - E_i - \hbar\nu}$$

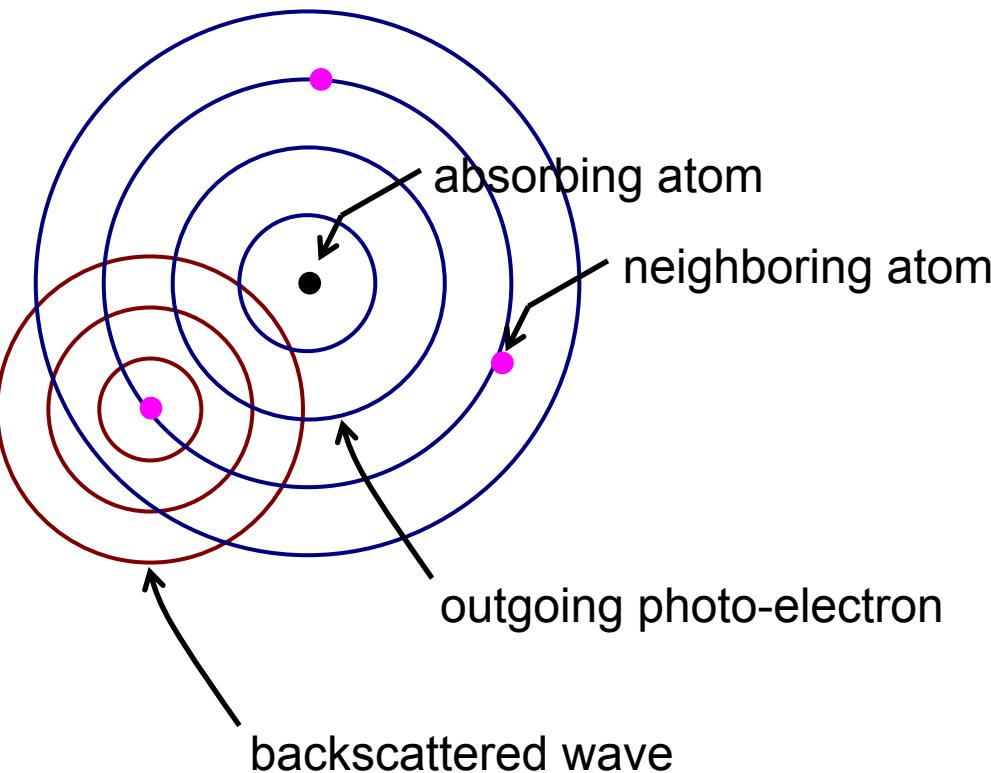


$$\Psi_{\text{final}} = \Psi_{\text{outgoing}} + \Psi_{\text{backscattered}}$$



# Transition probability

$$P \propto \left| \langle \Psi_i | T | \Psi_f \rangle \right|^2 \delta_{E_f - E_i - \hbar\nu}$$

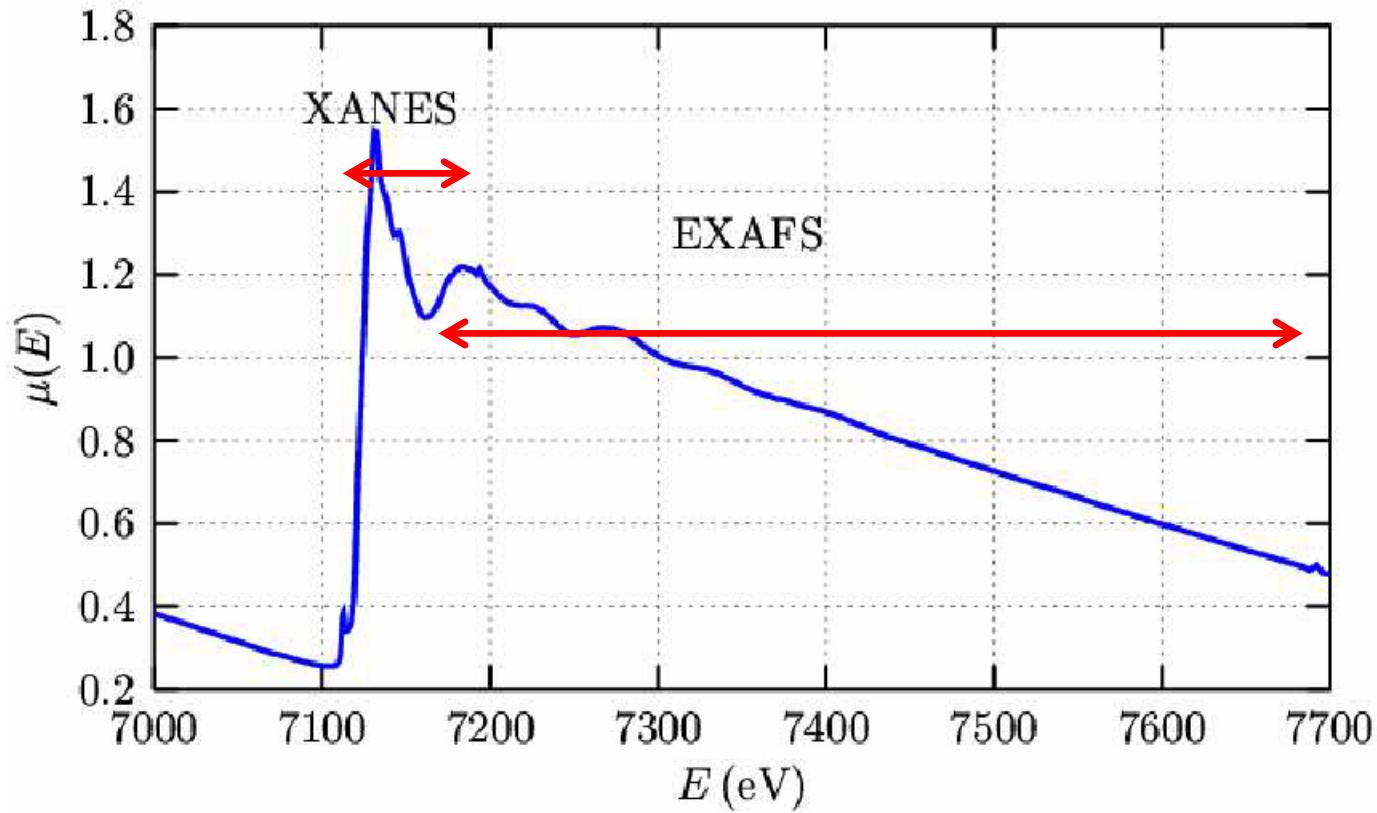


*Scatter pattern is function of*

- # of neighbors, CN
- Distance, R
- Kind of neighbor
- Disorder in R and CN, DWF

$$\Psi_{\text{final}} = \Psi_{\text{outgoing}} + \Psi_{\text{backscattered}}$$

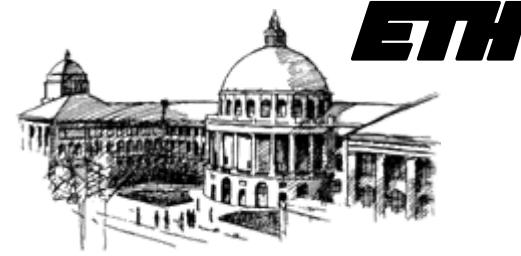




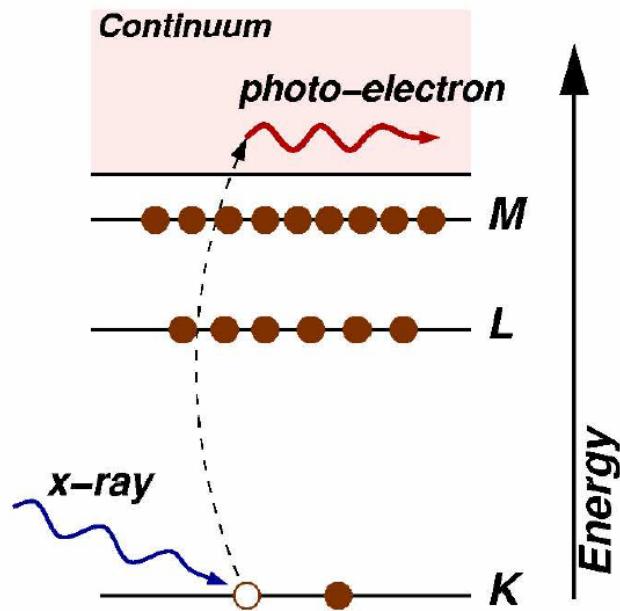
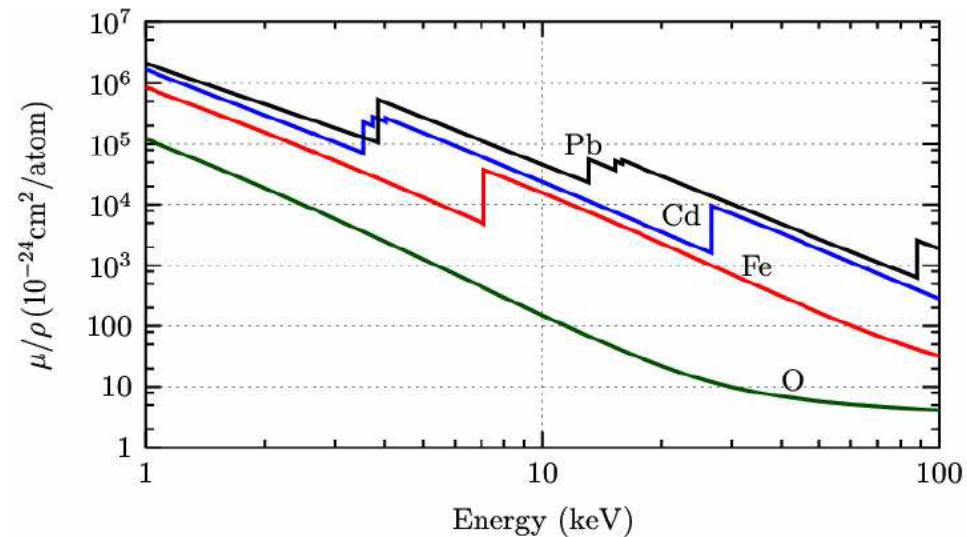
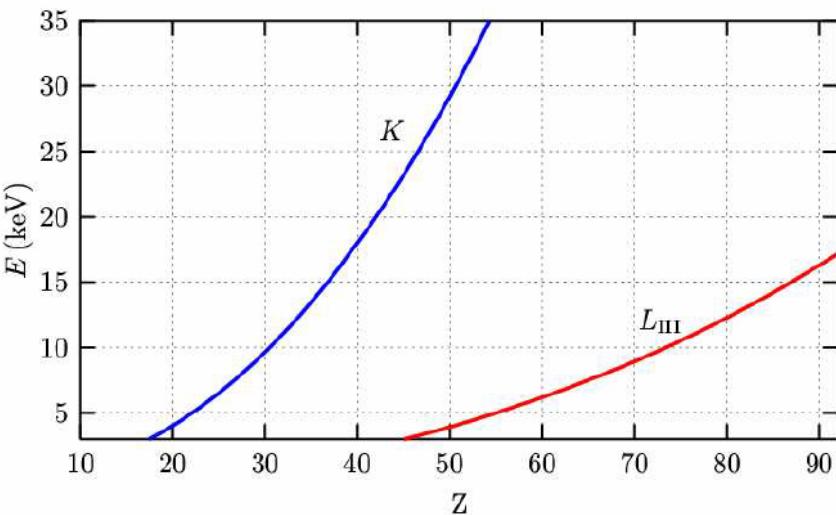
**EXAFS ( $\chi$ )** Extended X-ray Absorption Fine-Structure  
*Single scattering*

**XANES** X-ray Absorption Near-Edge Structure  
*Multiple scattering*

$$\mu = \mu_0 (1 + \chi)$$

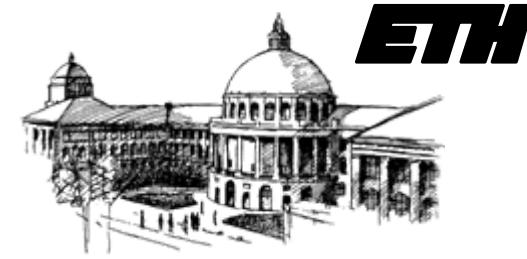


# Edges over the Periodic Table



X-ray data booklet:  
[xdb.lbl.gov](http://xdb.lbl.gov)

Element specific



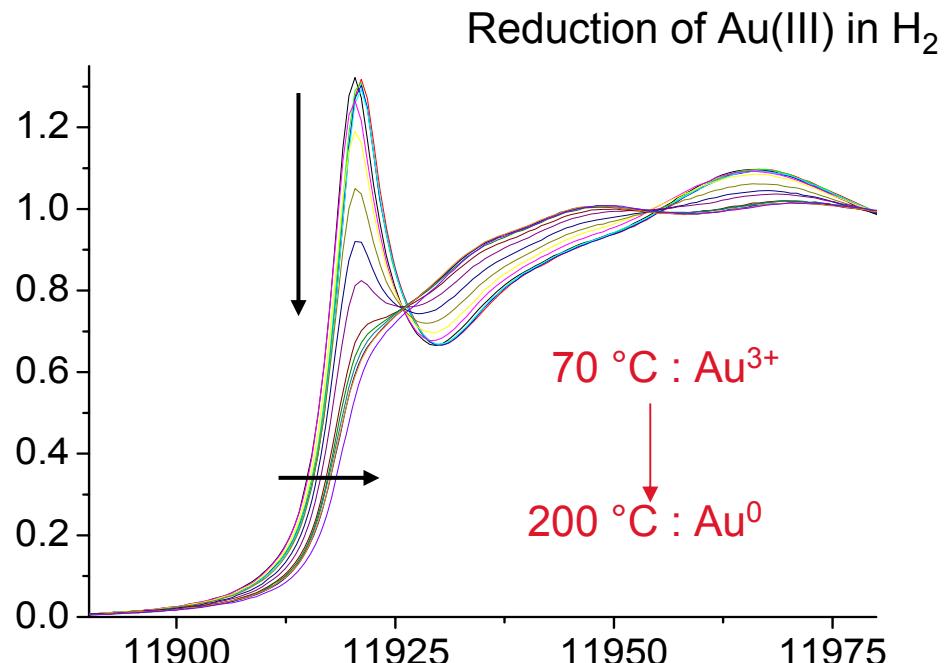
# Information in the spectra?

Local geometry  
element-specific

Oxidation state

Electronic state  
s.a. filling of the d-band

*In-situ data*



# How are the X-rays made?

Synchrotrons provide high flux of X-rays



ESRF, Grenoble



Spring-8 Japan



APS Chicago

*All light sources*

<http://www.lightsources.org/>

*under construction:*

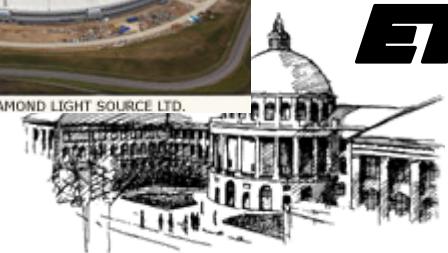


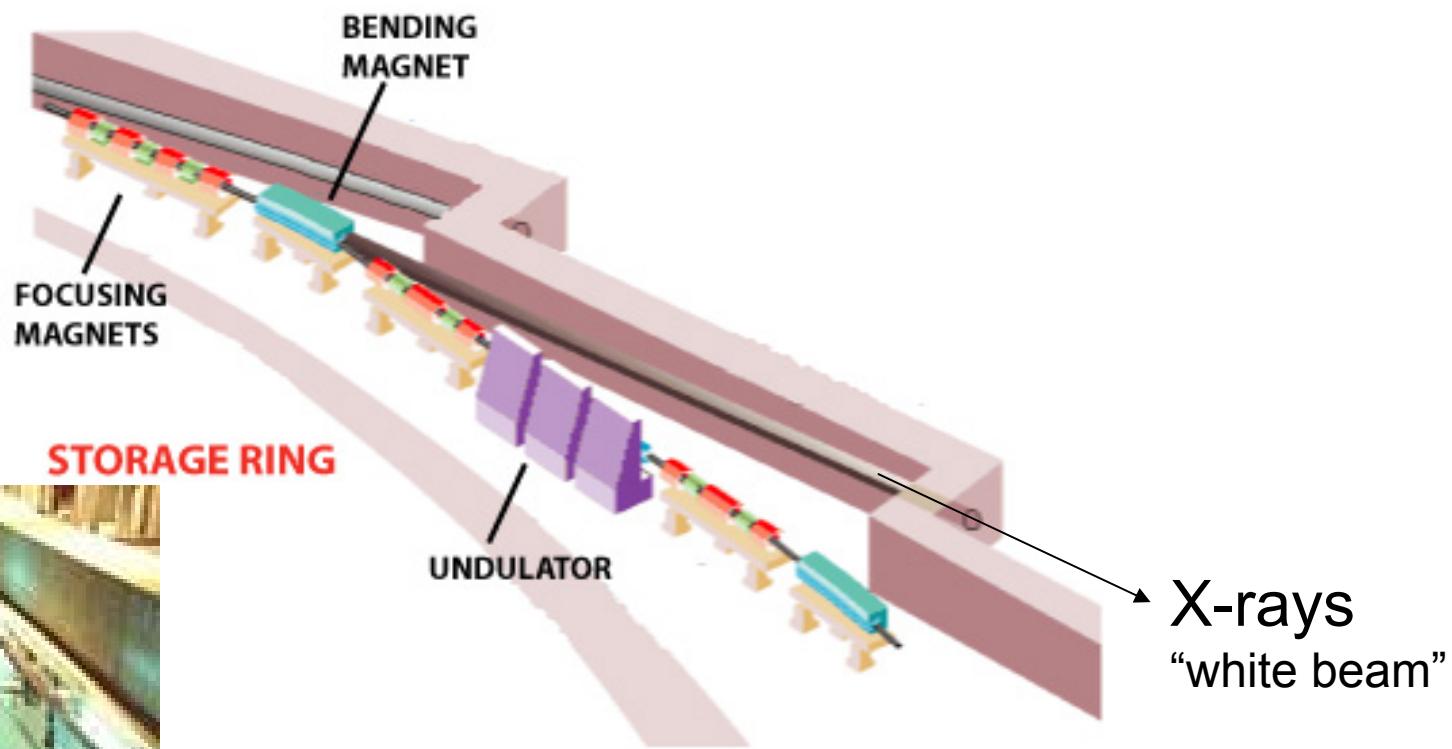
Soleil (Paris)



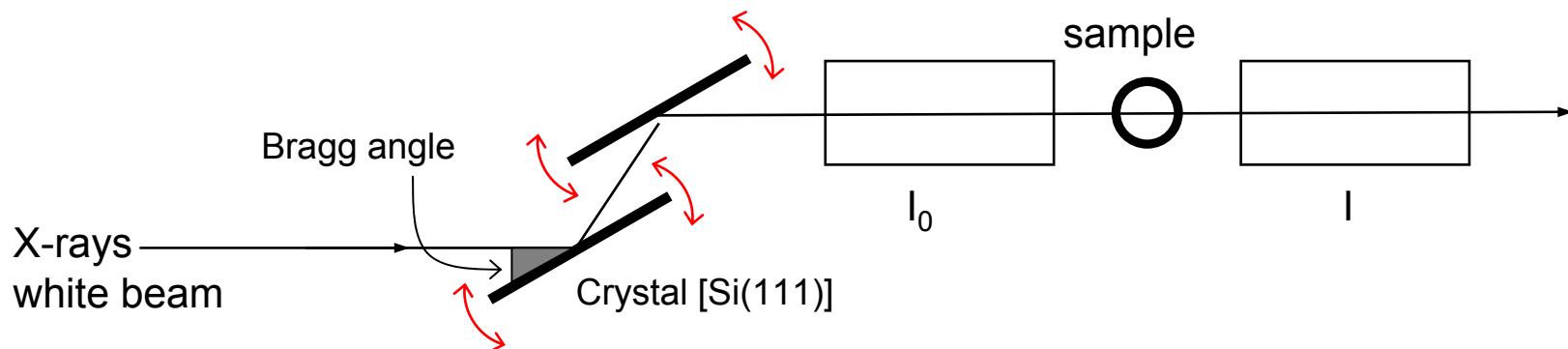
Diamond  
(Oxford)

**ETH**

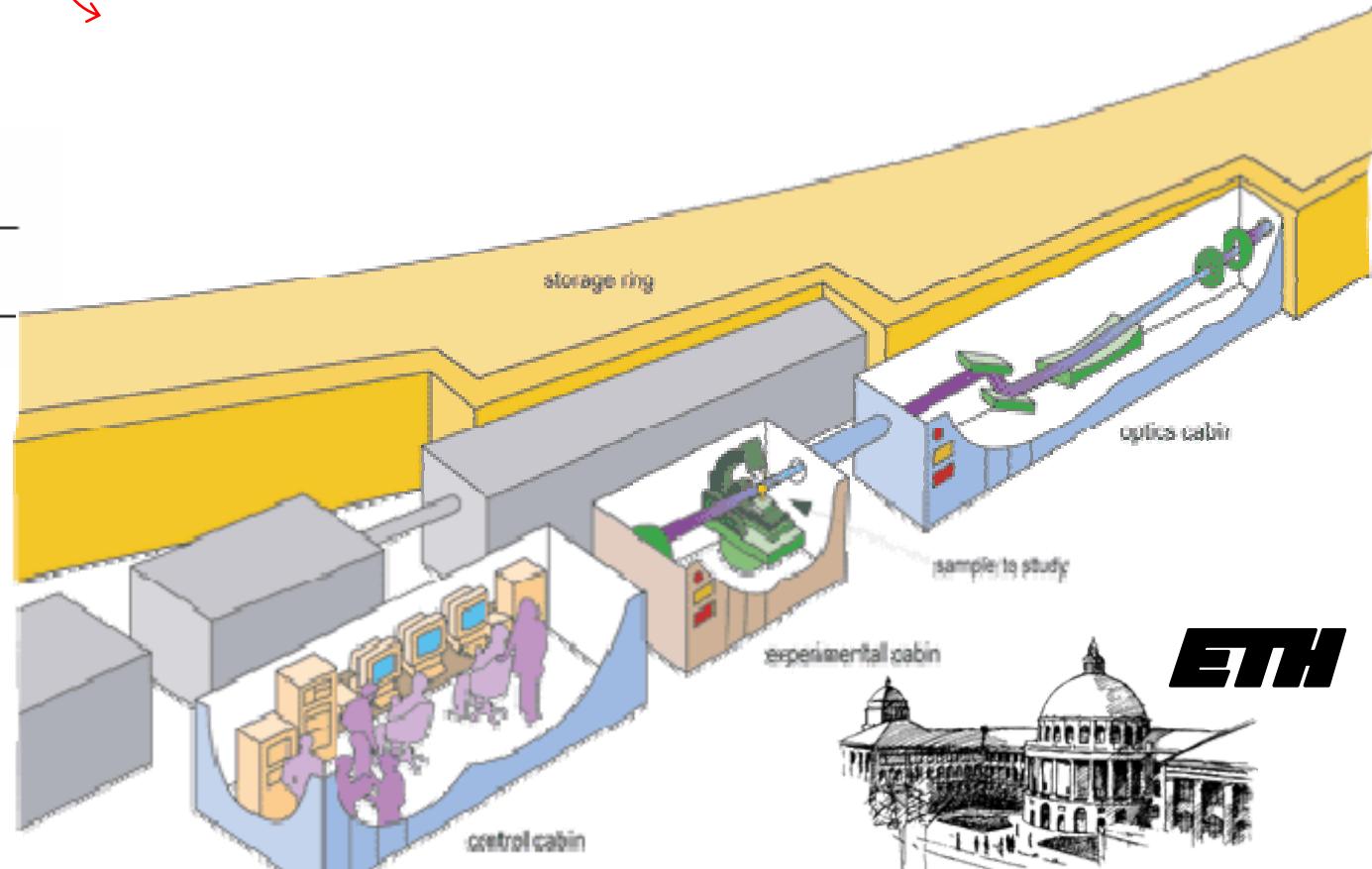
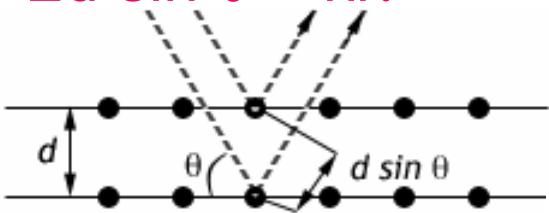




# Tuning the energy Double crystal monochromator

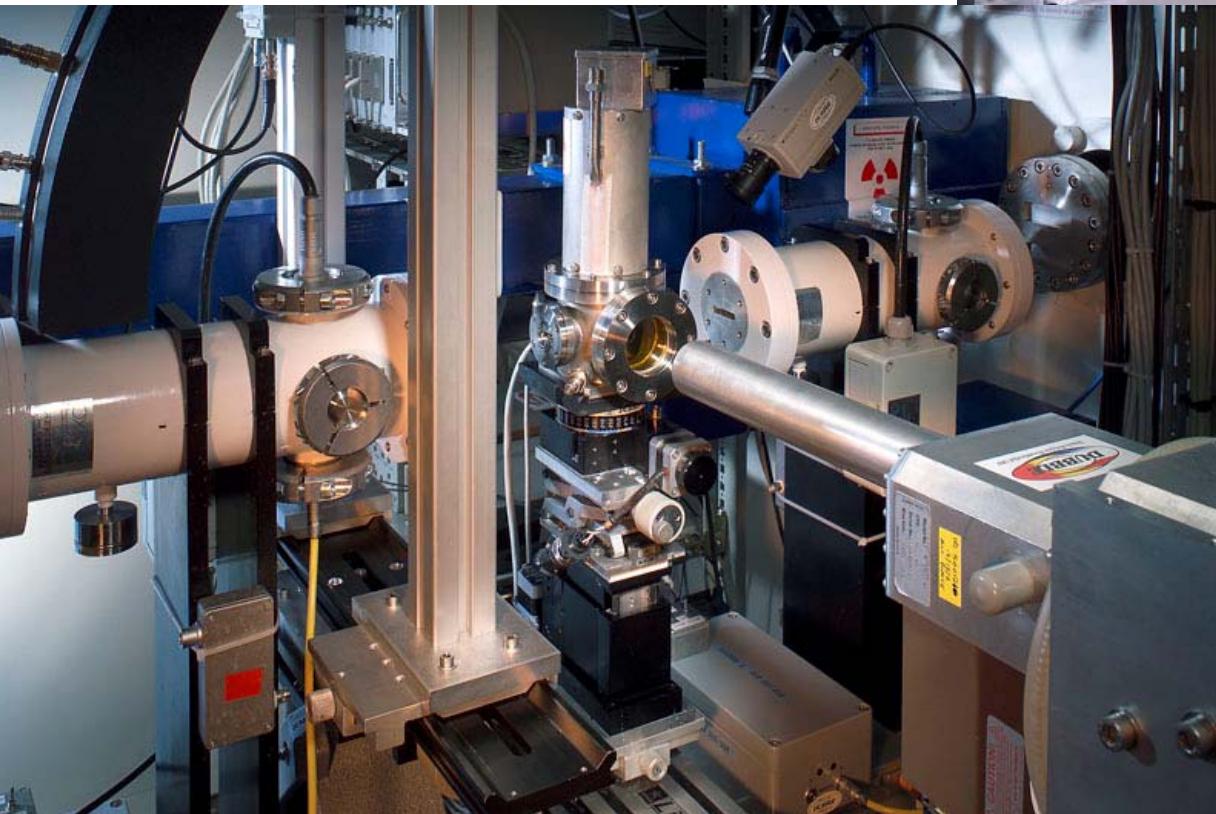
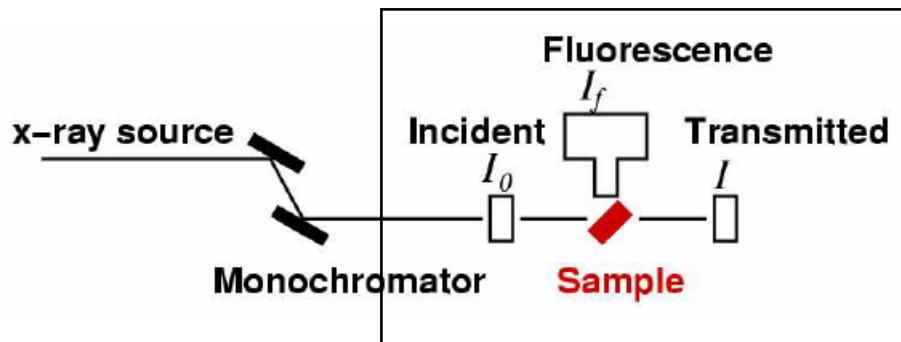


$$2d \sin \theta = n\lambda$$



**ETH**

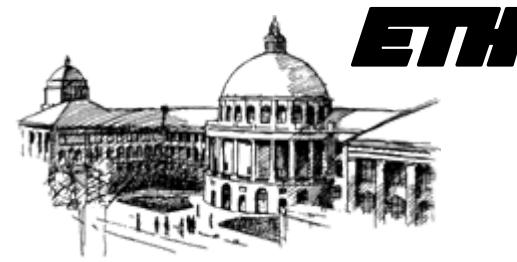
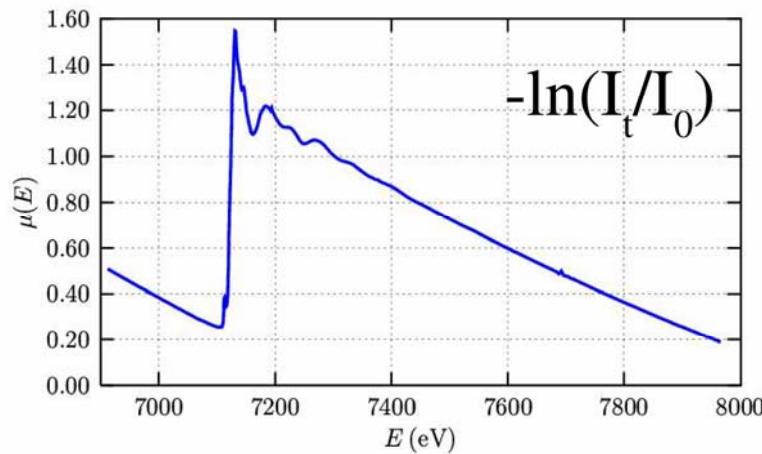
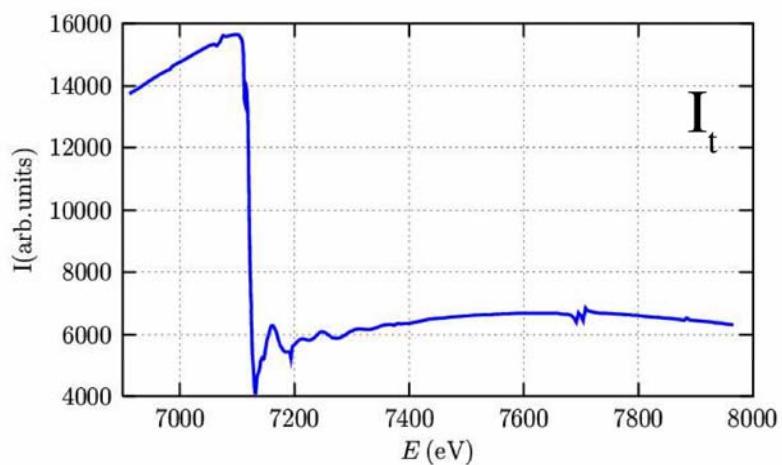
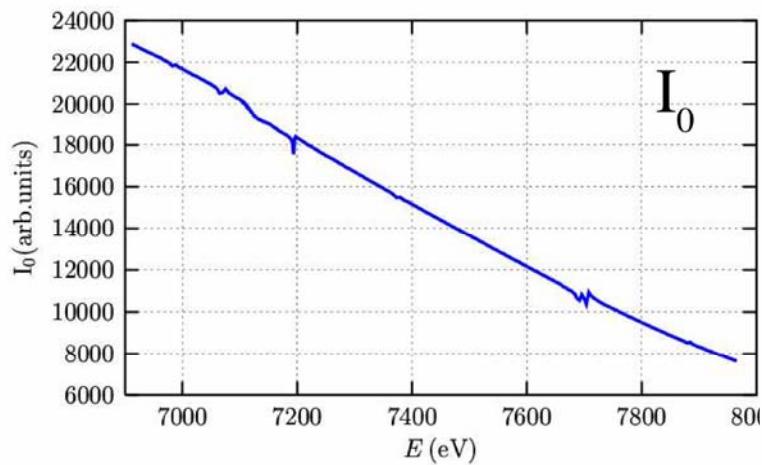
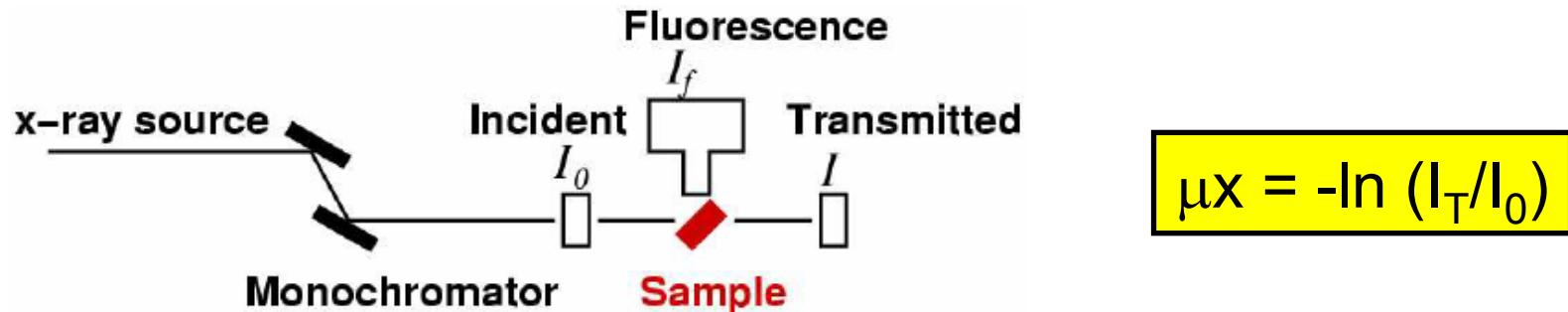
# Experimental Hutch



BM26 (DUBBLE), ESRF Grenoble



# The experiment



**ETH**

# XAS in Catalysis

## *Goal*

Local structure of catalysts under well-defined conditions

precursor state

during / after activation

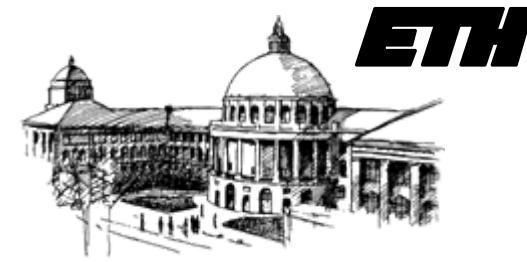
during reaction

deactivation

time-resolution (few msec)

space-resolution (few  $\mu\text{m}$ )

.....



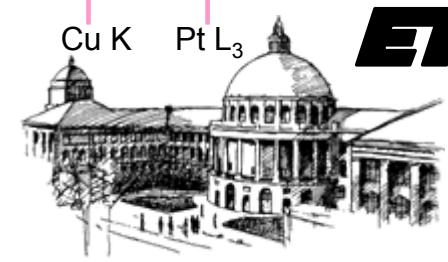
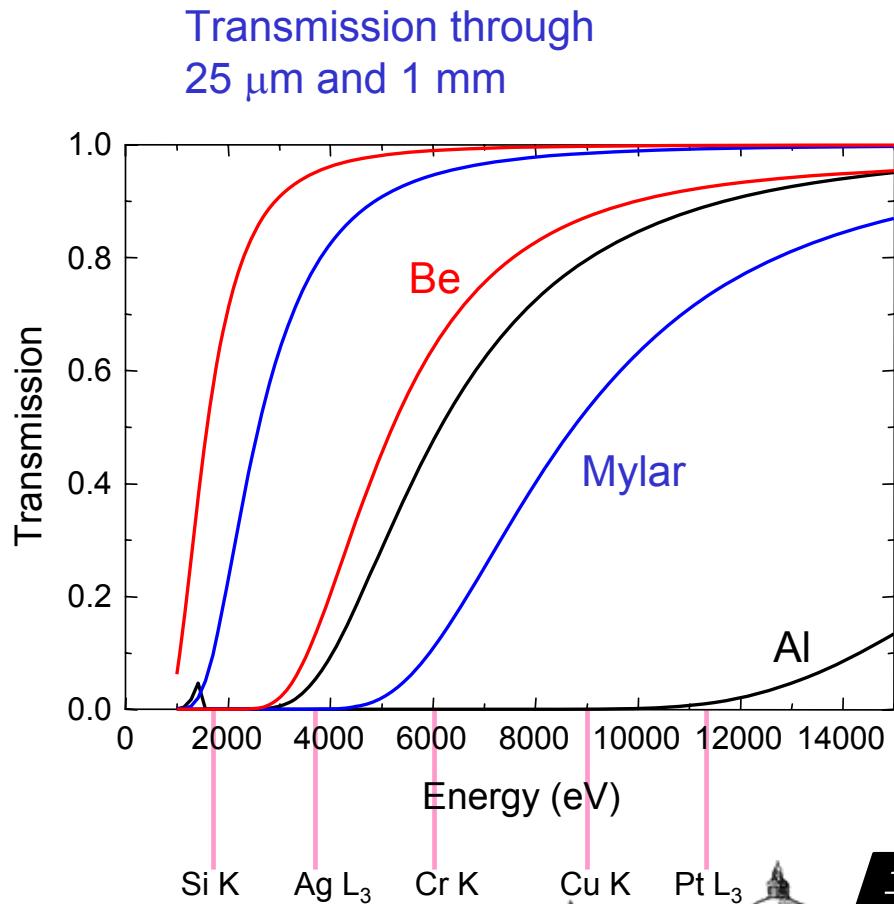
# Sample environment

*Absorption of X-rays is limiting factor*

## Find a good window material

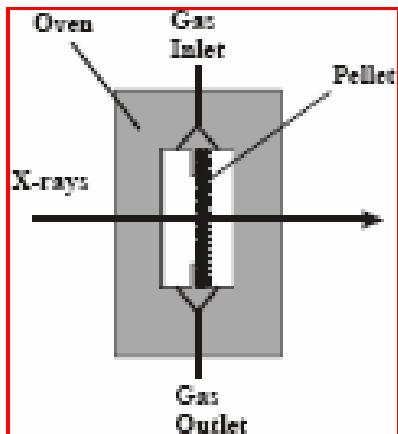
- Size of window
- Thickness
- Inertness
- Temperature resistance
- Pressure
- Safety

*pressure  
temperature  
environment*



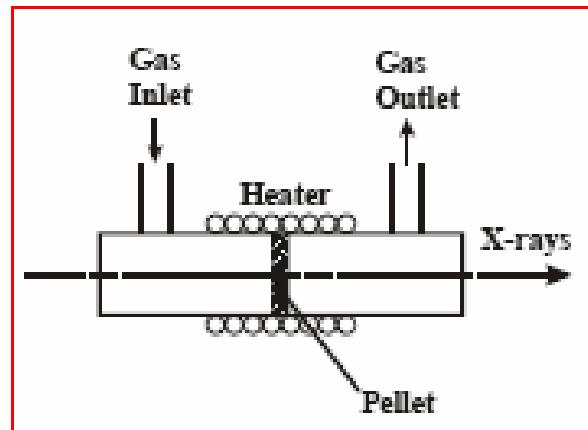
# *In situ* EXAFS cells for gas-solid reactions

**Reaction gas mixture flows around a pellet**



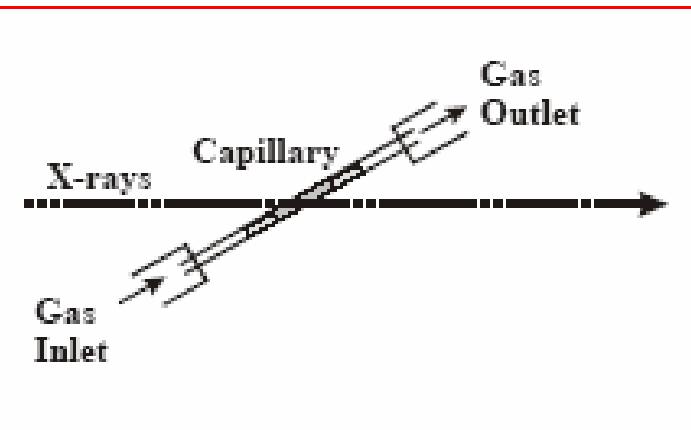
**Large dead volume  
Good for stationary conditions**

**Reaction gas flows through a catalyst pellet**

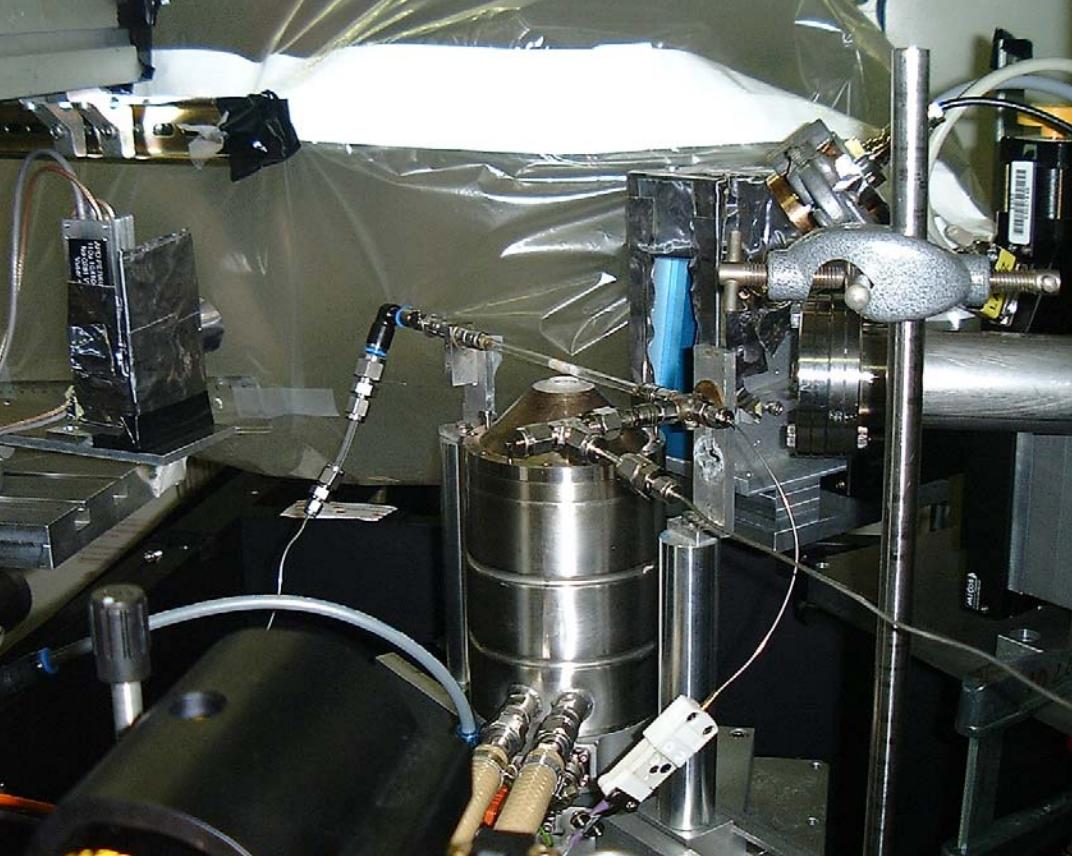


**Critical d/l (smaller effectivity of the catalyst)**

**Small Glass Reactor with very thin windows (0.01mm)**



**Small dead volume  
Optimal d/l  
Good for structural changes  
Structure-activity relations**

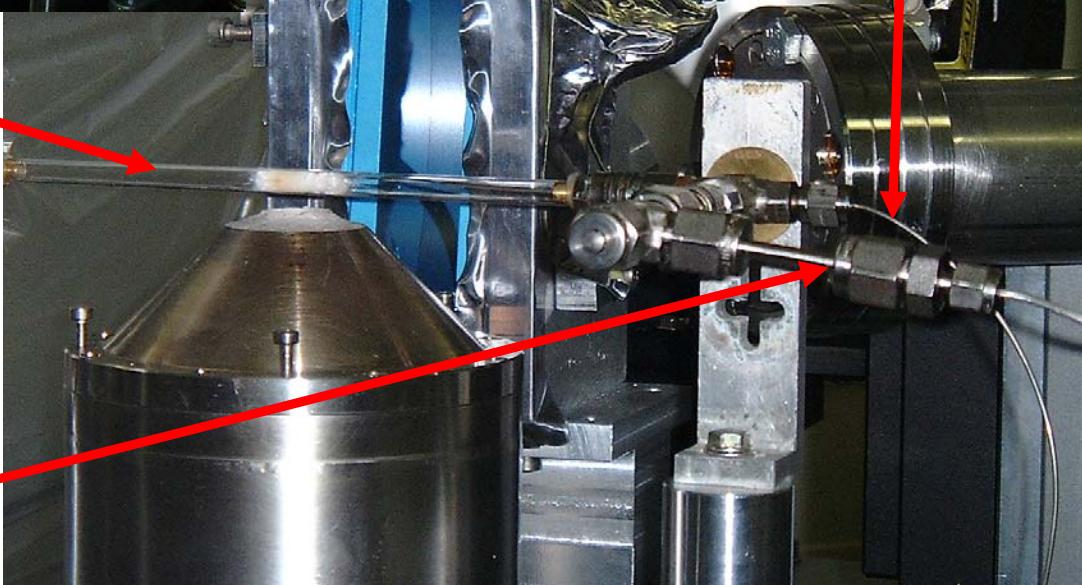


ID26, ESRF

*Angew. Chem. Int. Ed.* 2006, 45, 4651

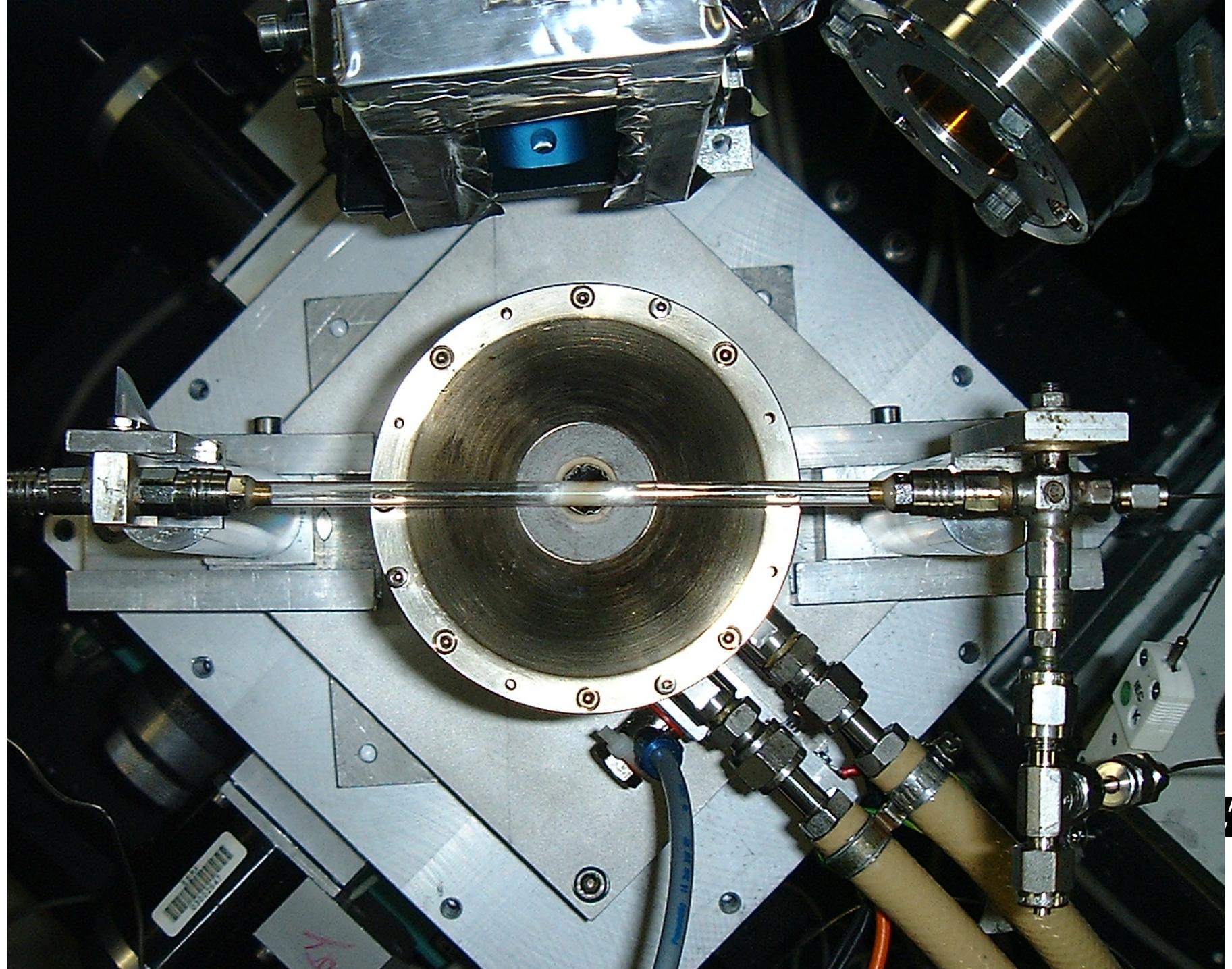
Reactor

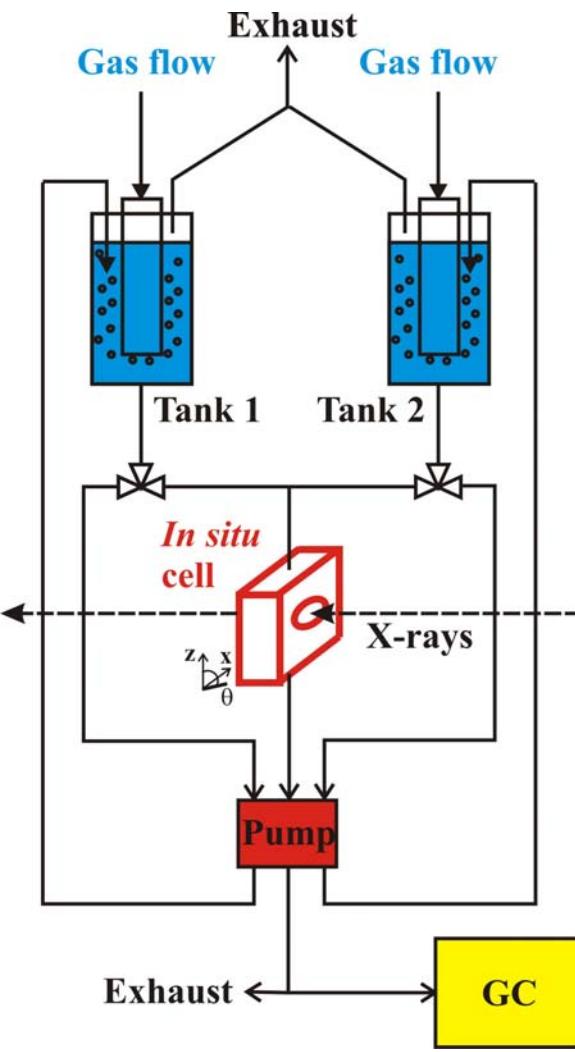
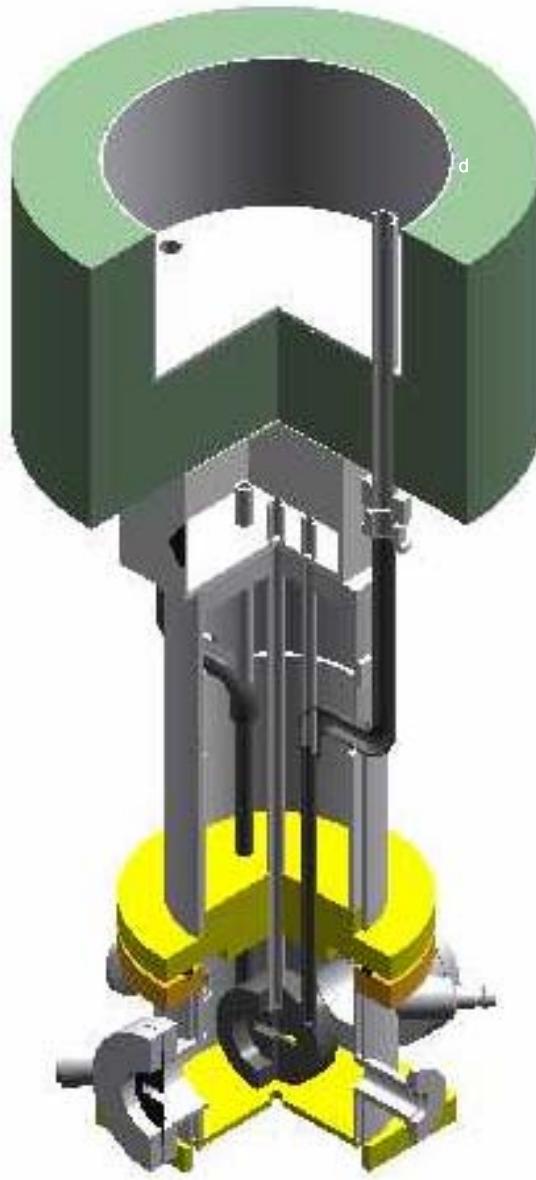
Exit-tube to mass spec



Fluorescence  
detector

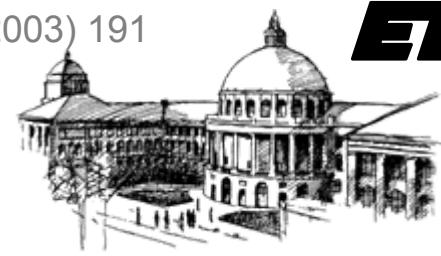
Thermo  
Couple



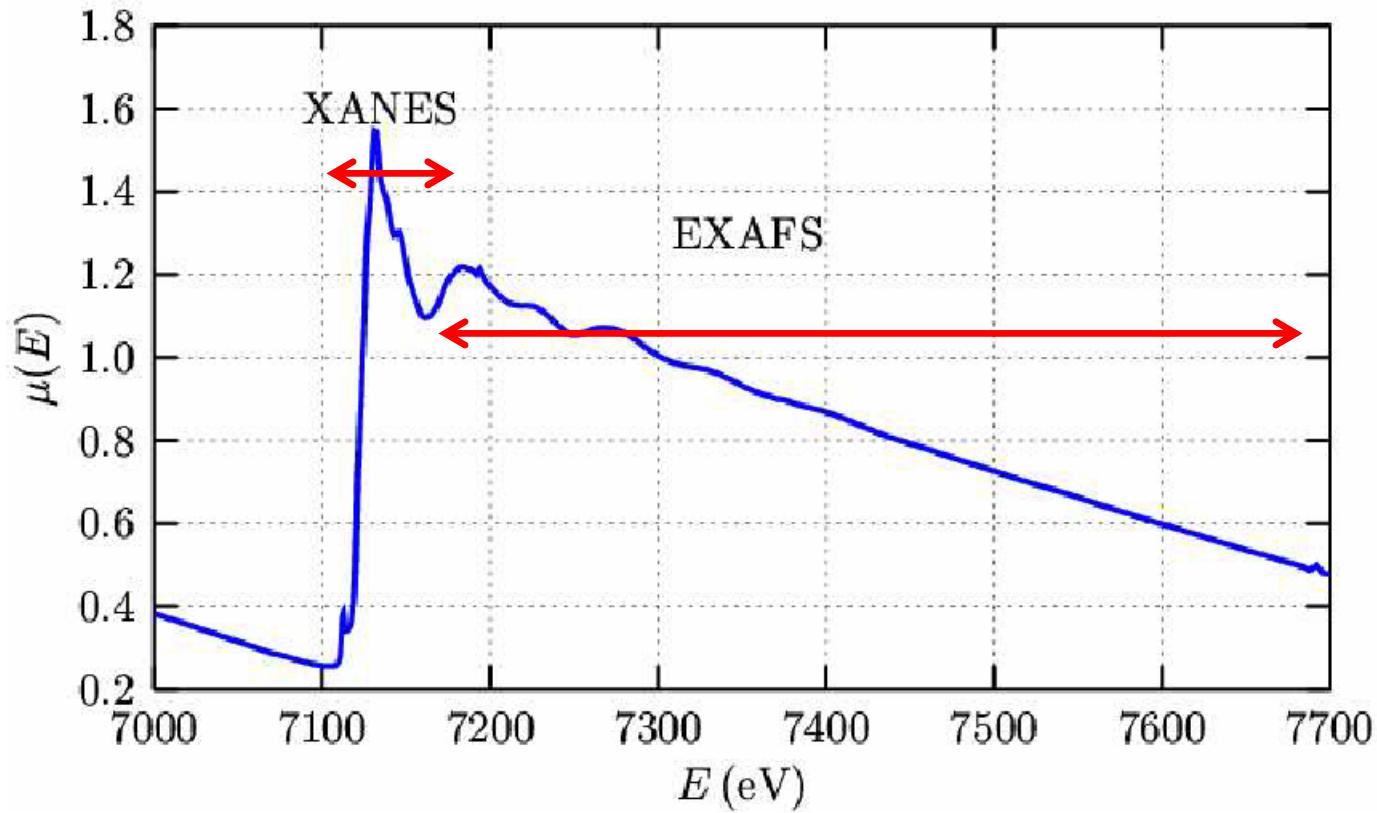


Three-phase system  
Grunwaldt J. Catal. 213 (2003) 191

Koningsberger Rev.Sci. Instr. 60 (1989) 2635



**ETH**



XANES

X-ray Absorption Near-Edge Structure  
*Multiple scattering*

EXAFS

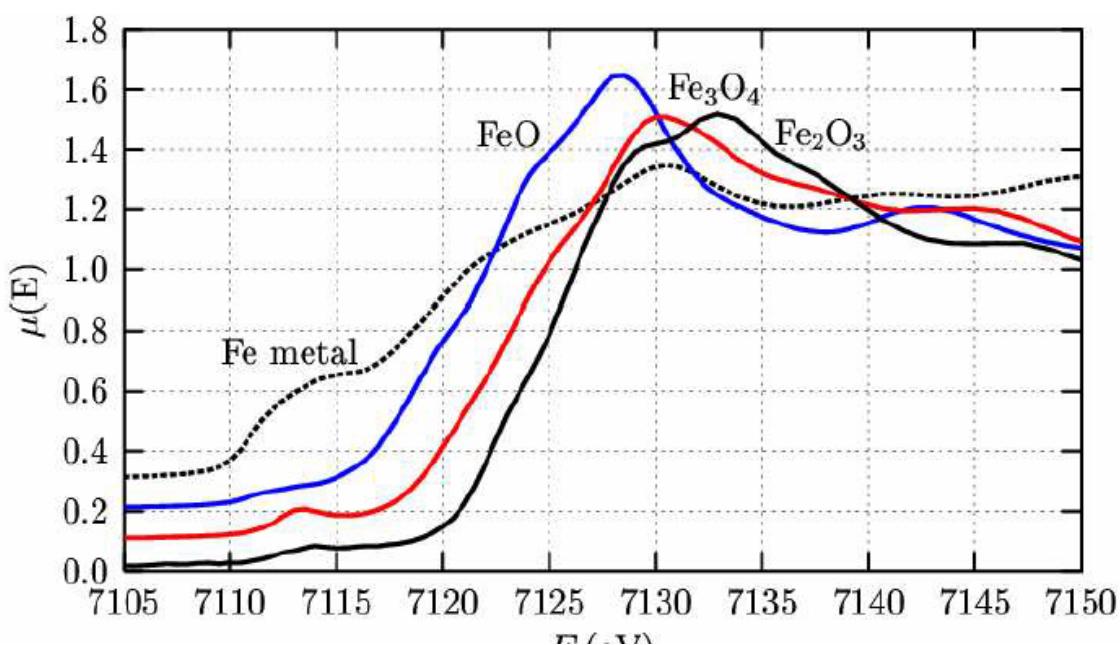
Extended X-ray Absorption Fine-Structure  
*Single scattering*



ETH

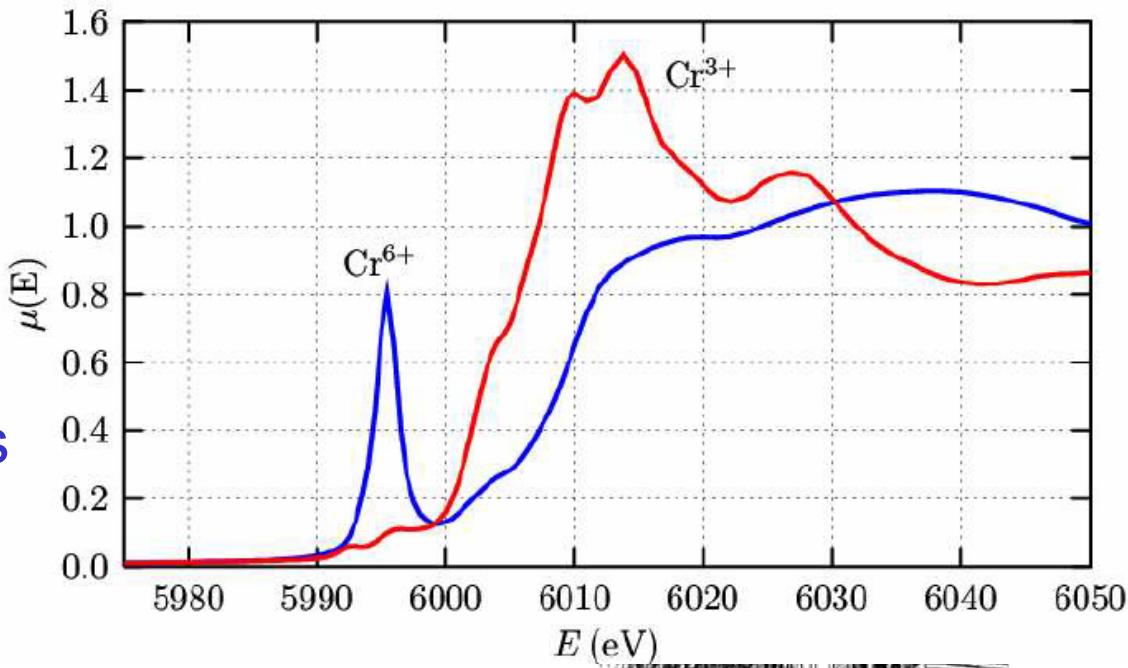
# XANES

Edge position  $\equiv$  oxidation state  
Shape  $\equiv$  geometry

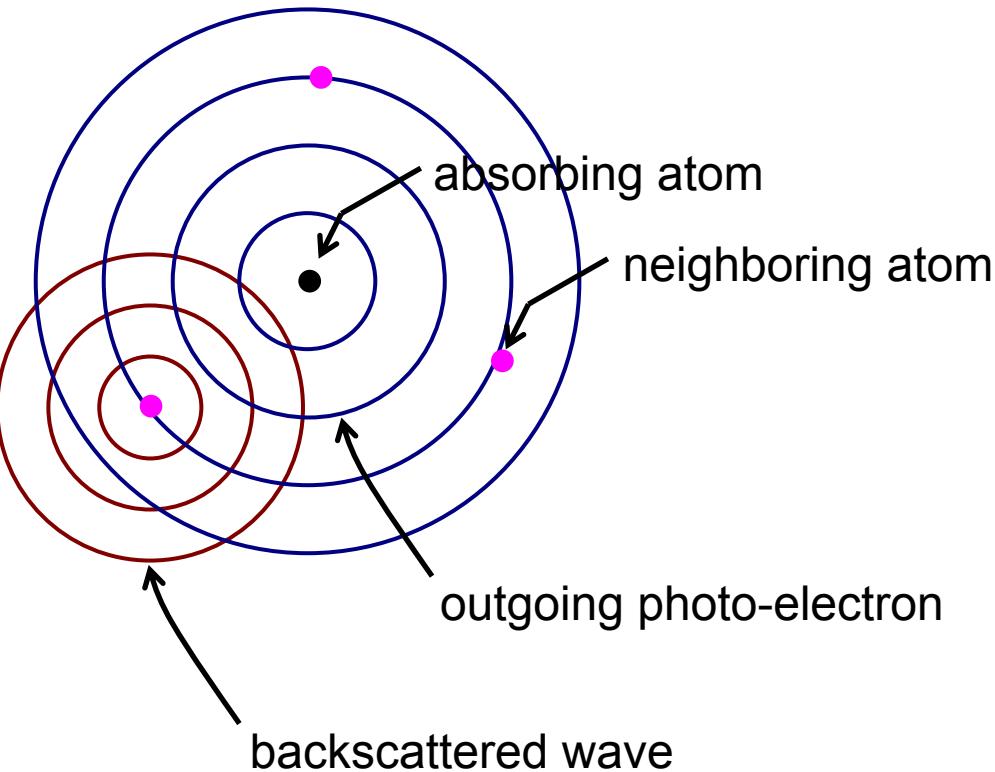


## Strategies

- compare SAMPLE to known compounds
- calculate spectra



# EXAFS

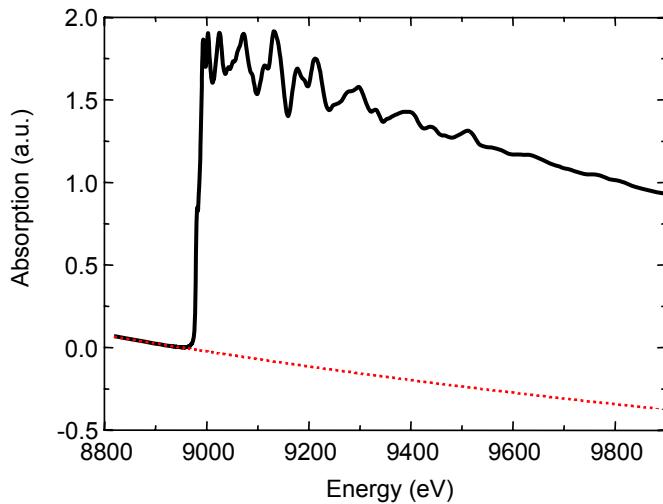


*Scatter pattern is function of*

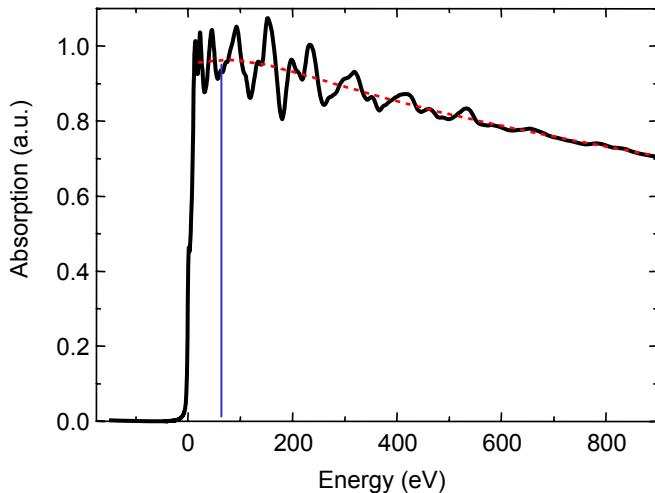
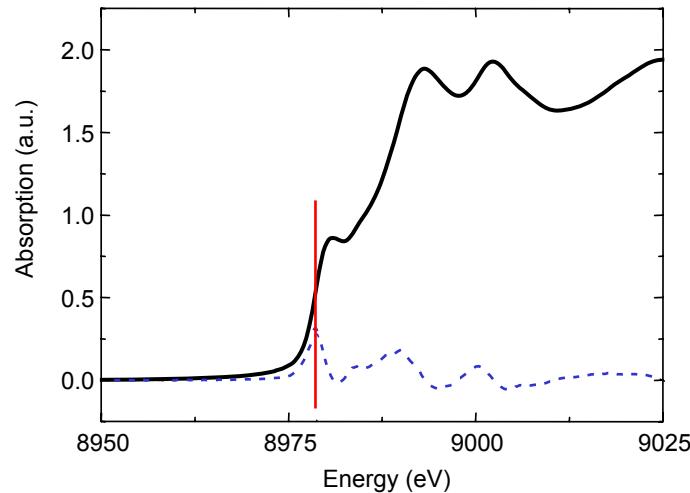
- # of neighbors, **CN**
- Distance, **R**
- Kind of neighbor
- Disorder in R and CN, **DWF**

# EXAFS data analysis

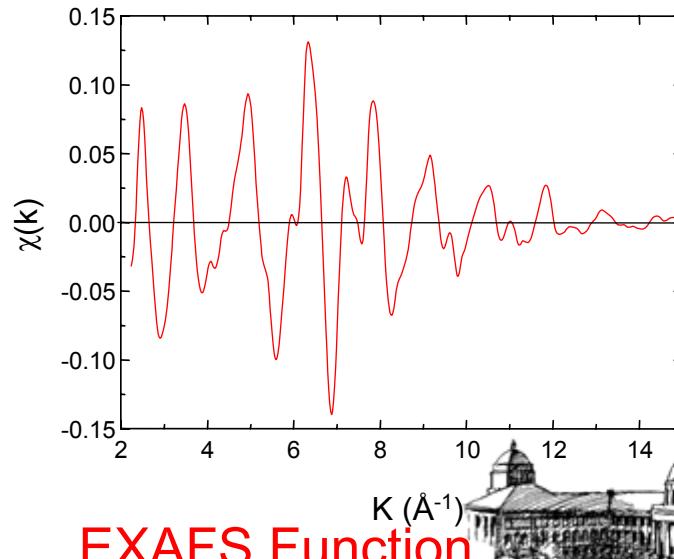
Pre-edge subtraction



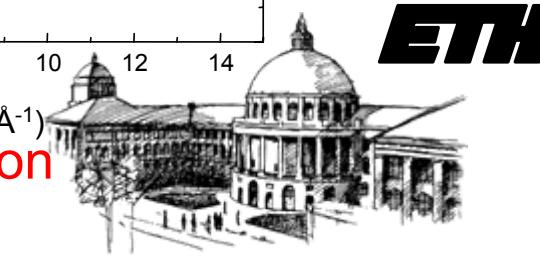
Edge energy determination

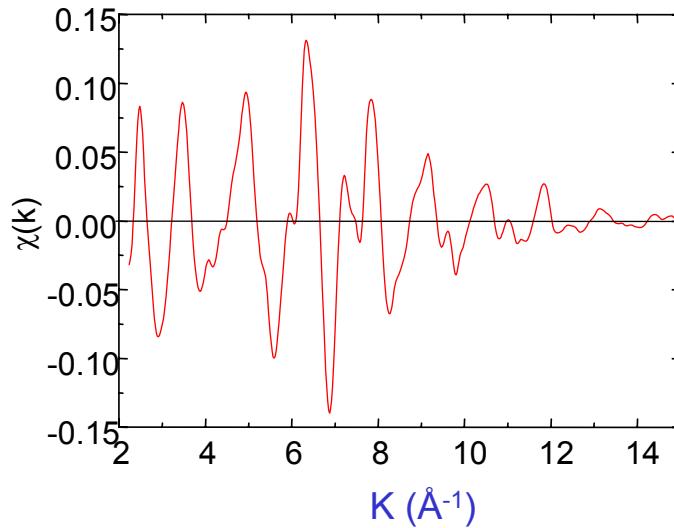
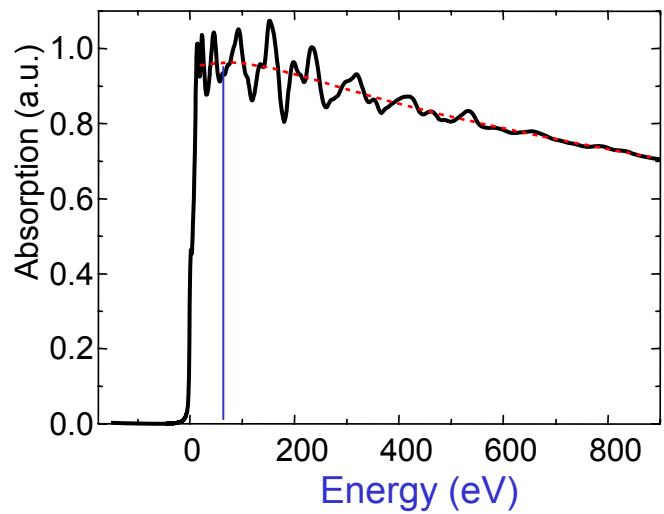


Background and Normalization



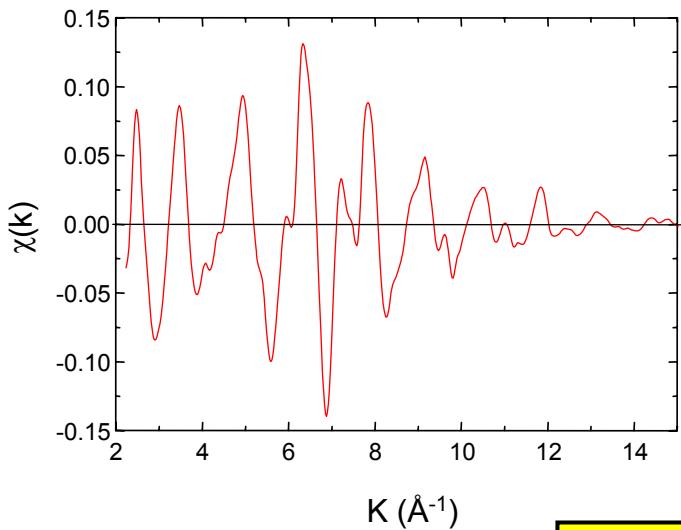
EXAFS Function



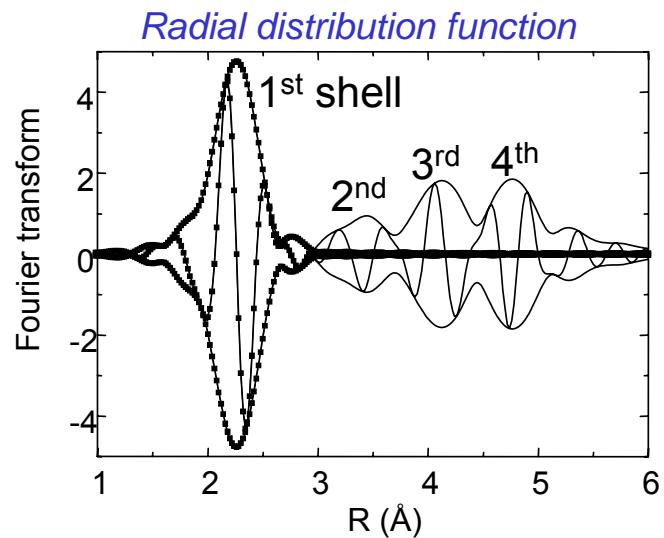


$$k = \left[ \left( \frac{8\pi^2 m}{h^2} \right) (h\nu - E_0) \right]^{1/2}$$





Fourier transformation



**EXAFS formula**

$$\chi(k) = \sum A(k) \sin(2kR + \phi)$$

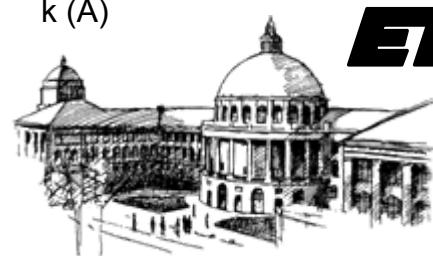
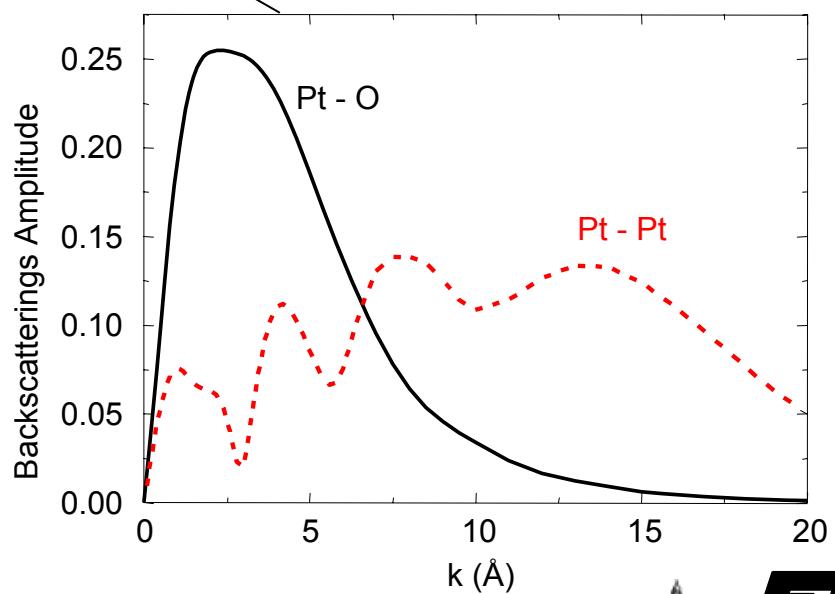
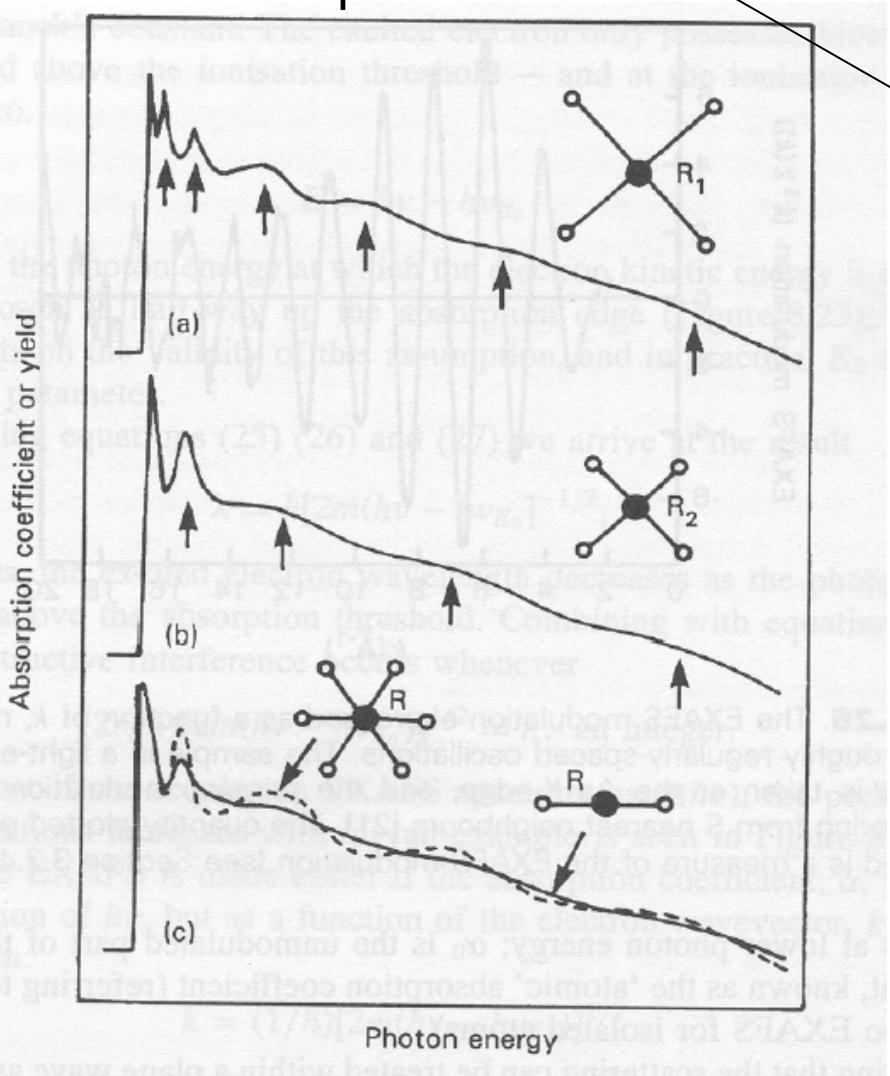
$$\chi(k) = \sum_i N_i F_i(k) \frac{S_0^2}{kR_i^2} \exp\left(\frac{-2R_i}{\lambda}\right) \exp\left(-2\sigma_i^2 k^2\right) \sin\left(2kR_i + \varphi_j(k)\right)$$

Scatter power
Damping
Disorder



$$\chi(k) = \sum_i N_i F_i(k) \frac{S_0^2}{kR_i^2} \exp\left(\frac{-2R_i}{\lambda}\right) \exp(-2\sigma_i^2 k^2) \sin(2kR_i + \varphi_j(k))$$

Scatter power      Damping      Disorder

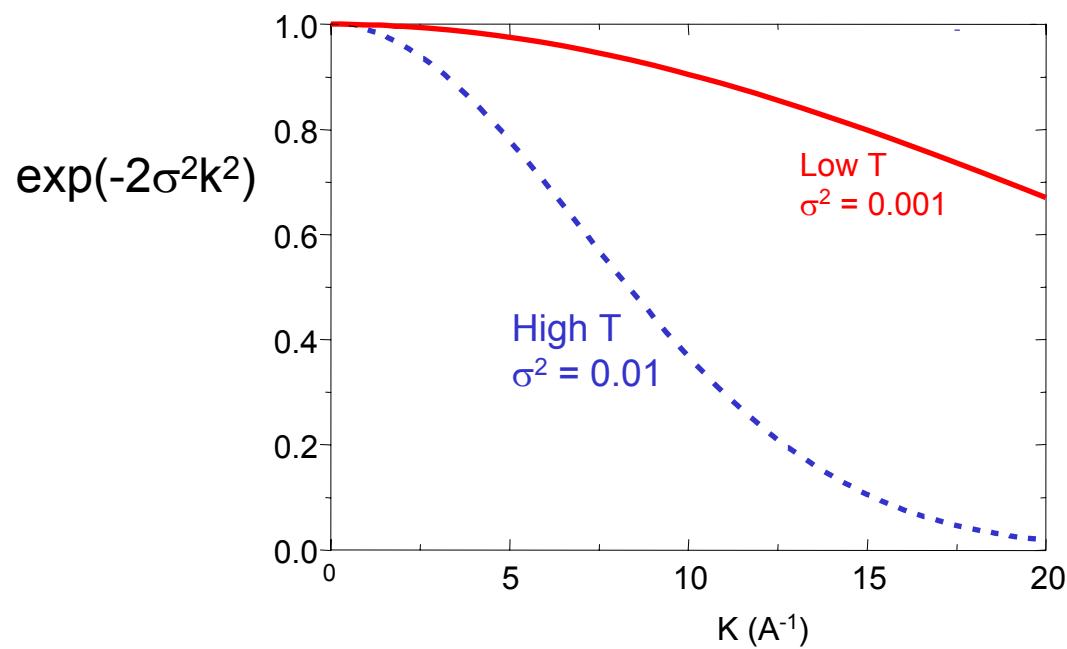


# Temperature effect on EXAFS / XANES

$$\chi(k) = \sum_i N_i F_i(k) \frac{S_0^2}{kR_i^2} \exp\left(\frac{-2R_i}{\lambda}\right) \exp(-2\sigma_i^2 k^2) \sin(2kR_i + \varphi_j(k))$$

Scatter power      Damping      Disorder

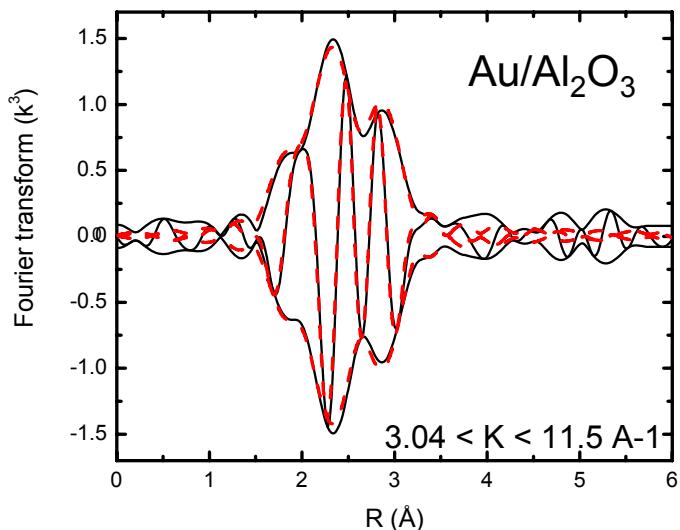
*Temperature effect*



# Getting structural information from EXAFS

$$\chi(k) = \sum_i N_j F_i(k) \frac{S_0^2}{k R_i^2} \exp\left(\frac{-2R_i}{\lambda}\right) \exp\left(-2\sigma_i^2 k^2\right) \sin(2kR_i + \varphi_j(k))$$

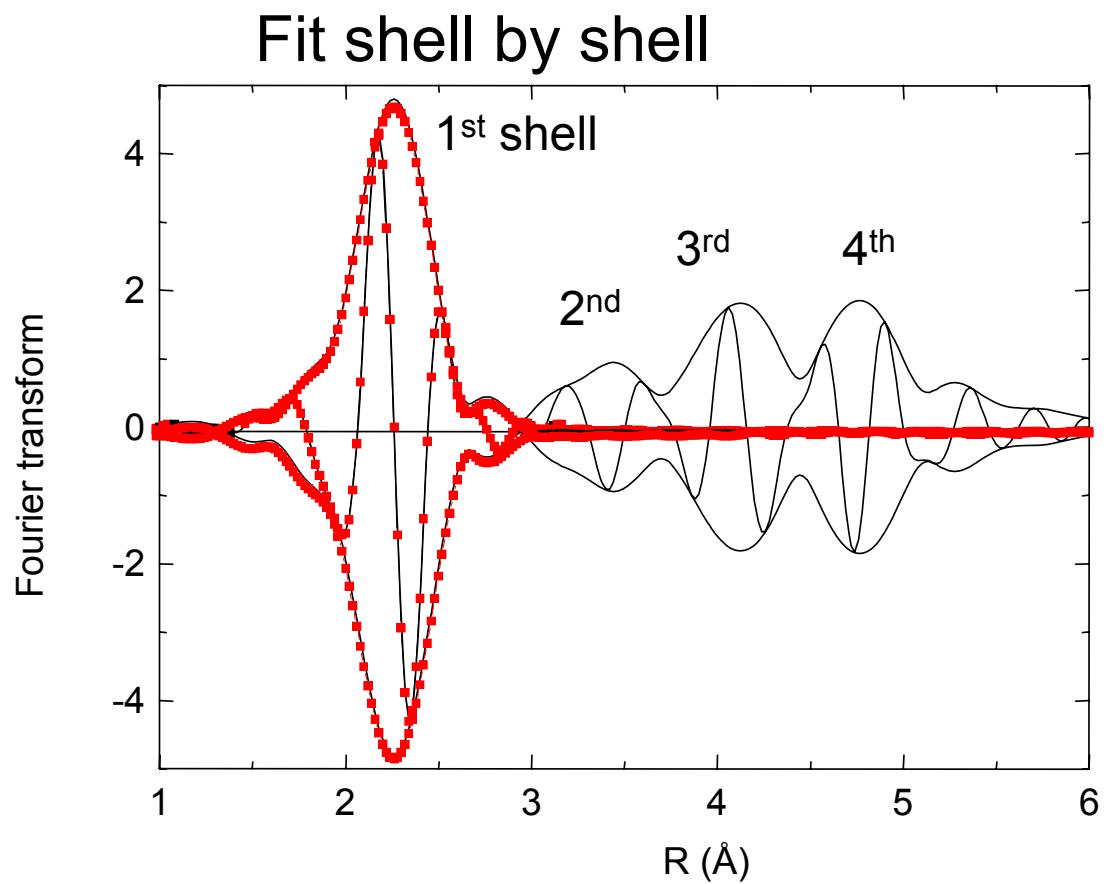
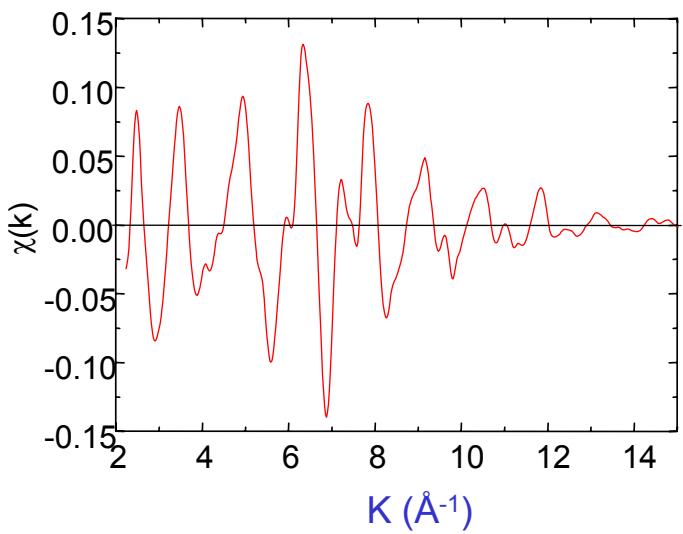
$F_j$ ,  $\varphi_j$ , and  $S_0^2$  from reference compound or theory



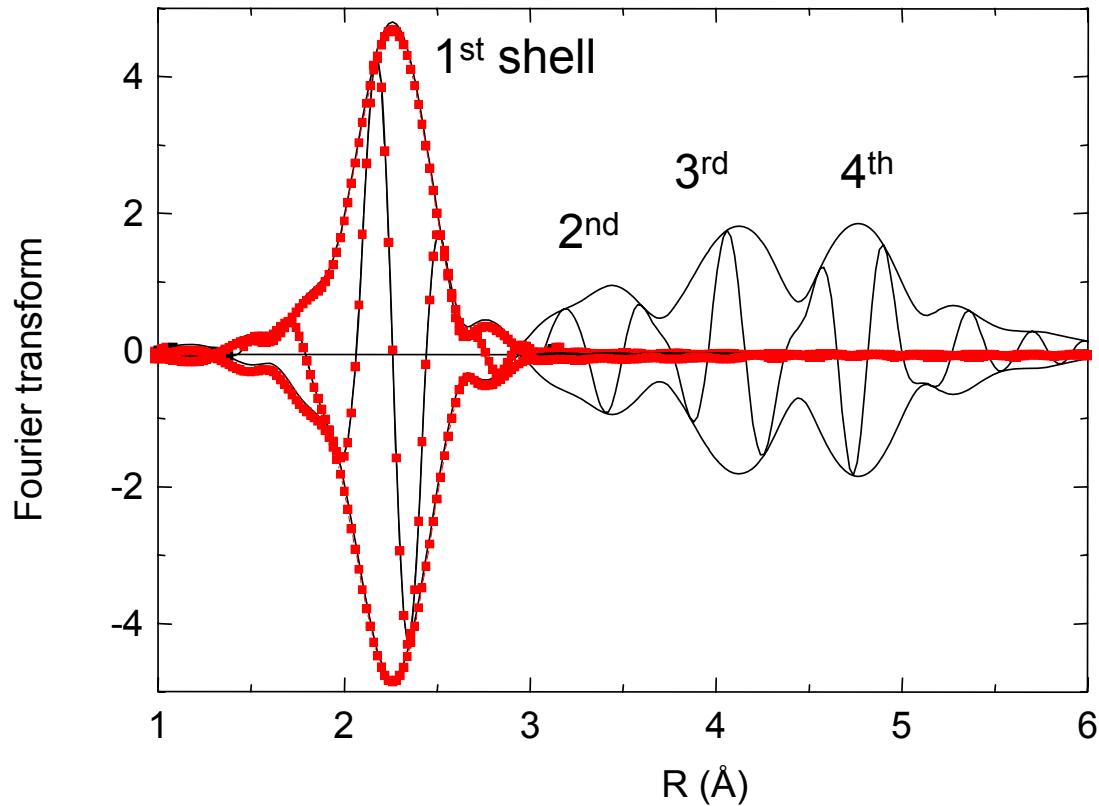
Coordination number	<b>6.8</b>
Au-Au distance	<b>2.76 Å</b>
ΔDWF	<b>0.0058</b>
C3	<b>9 E-6</b>
C4	<b>3E-6</b>

Added parameter:  $\Delta E_0$





# Accuracy?



Absolute

R      0.04 Å  
N      20 %  
DWF    0.002

Relative

R       $\leq 0.015$  Å  
N       $\leq 10$  %



# Summary

Adsorption of X-rays through matter

Local structure

Probing empty DOS

Measurement conditions (> 1500 K; >200 bar)

Amorphous, liquid, or crystalline samples

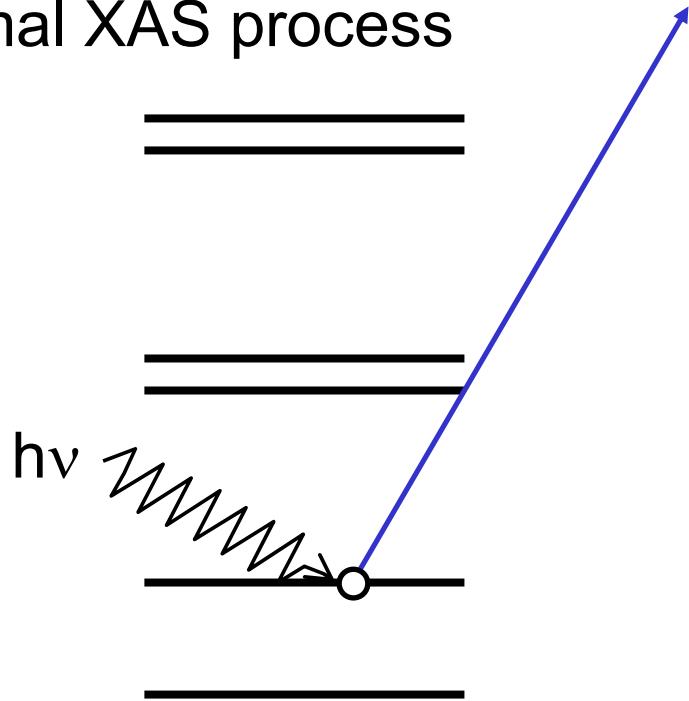
Time resolution (~msec)

Less than a monolayer on flat support

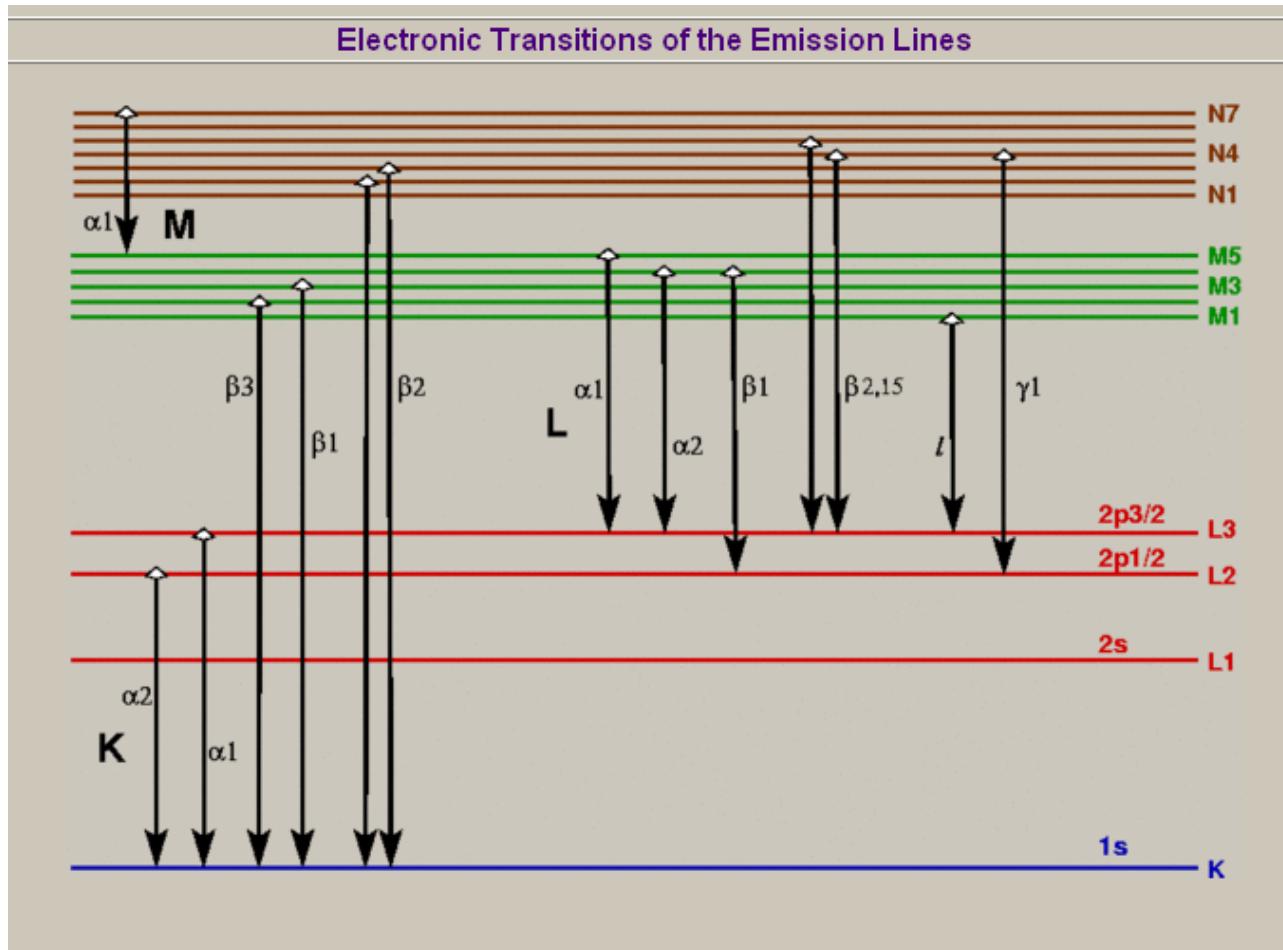


# High energy resolution fluorescence detected XAS

Normal XAS process



# Emission Spectroscopy



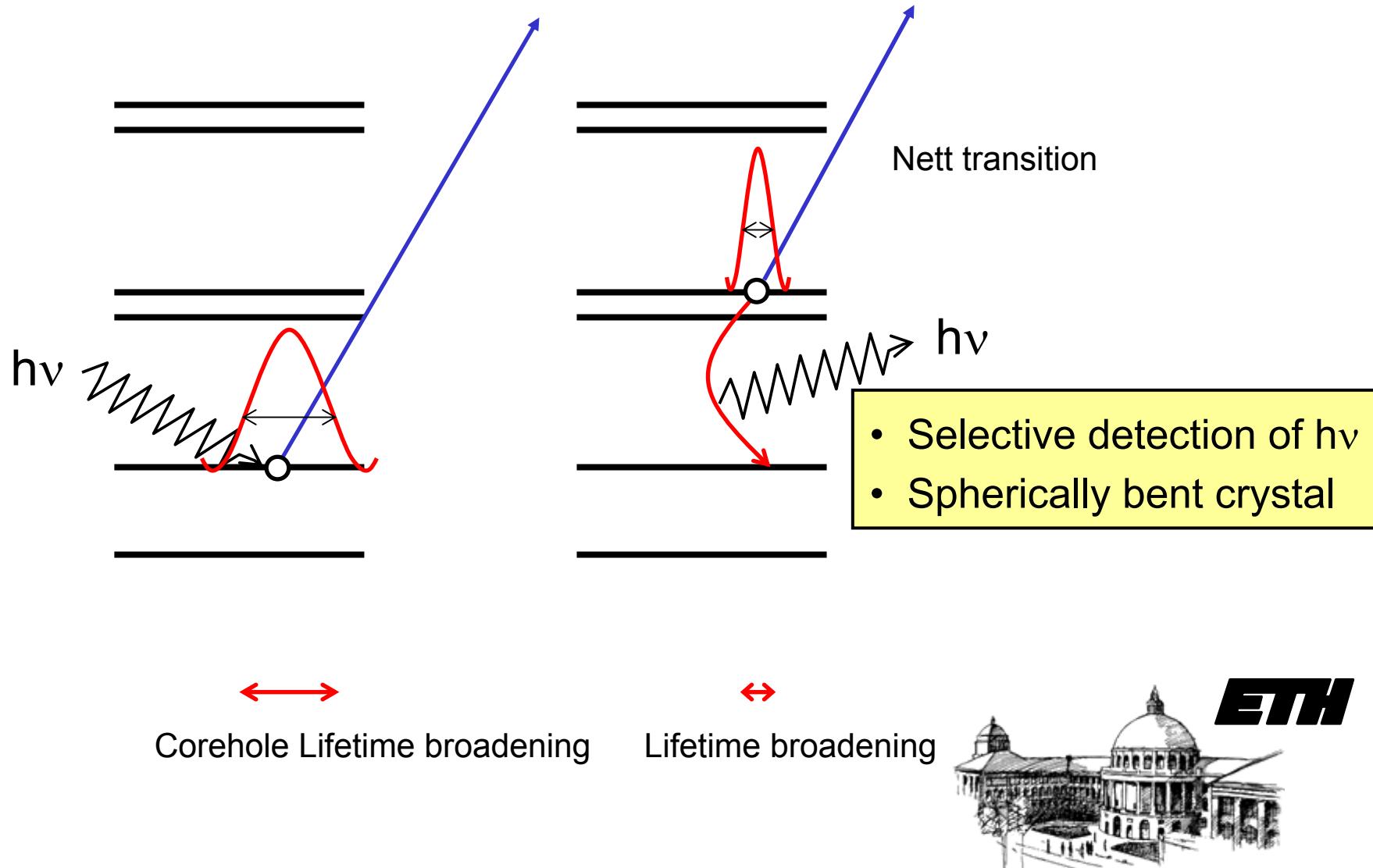
e.g. Pt (L3 edge):

$$\text{La1 (L3-M5)} = 9442$$

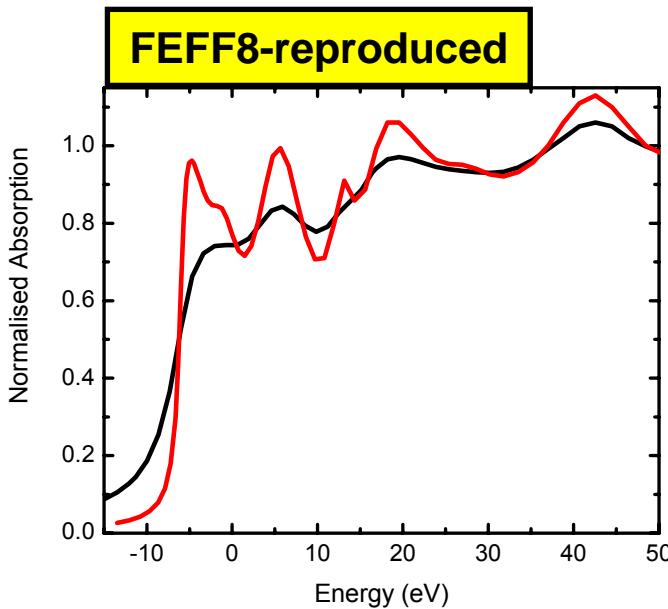
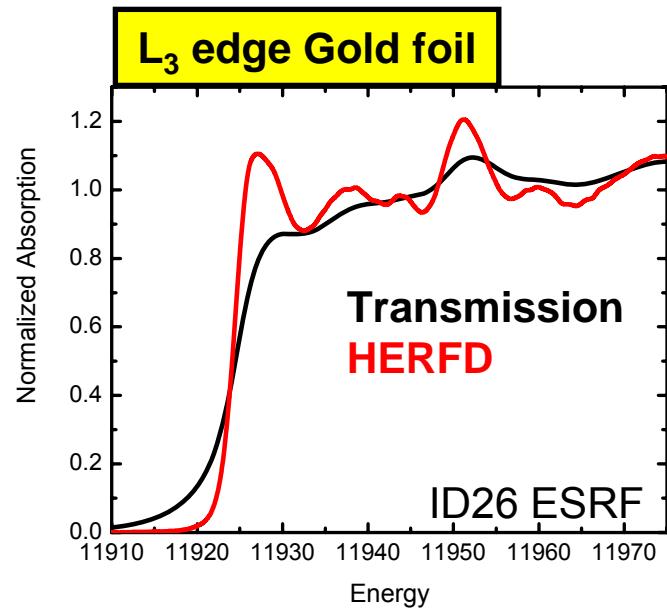
Some transitions more likely to occur than others



# High energy resolution fluorescence detected XAS



# High energy resolution fluorescence detected XAS



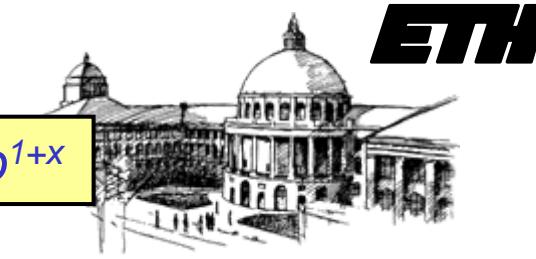
## Good

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

## Not so good

- Low yield of good photons
- No time-resolution

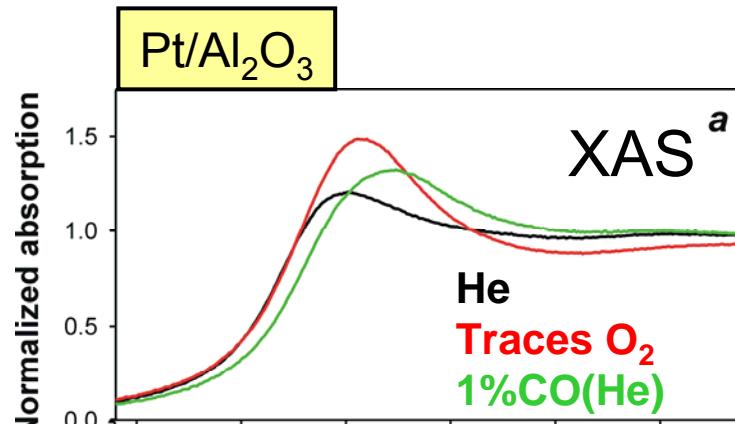
*Gold whiteline: spd-rehybridization results in  $5d^{10-x}6sp^{1+x}$*



## Adsorption of CO on Pt/Al<sub>2</sub>O<sub>3</sub>

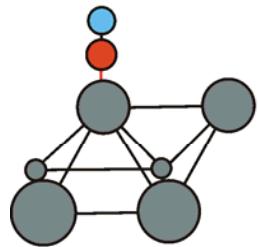


# High energy resolution fluorescence detected XAS

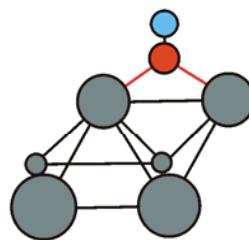


# FEFF8 simulation

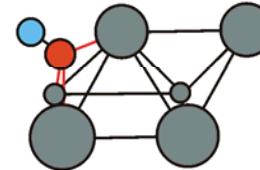
Pt<sub>6</sub>CO atop



Pt<sub>6</sub>CO bridged

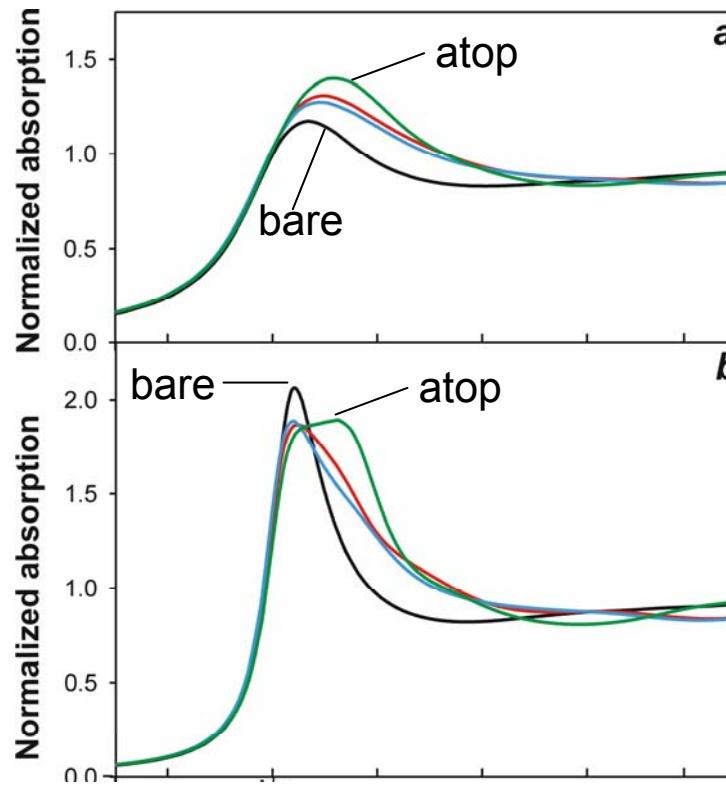
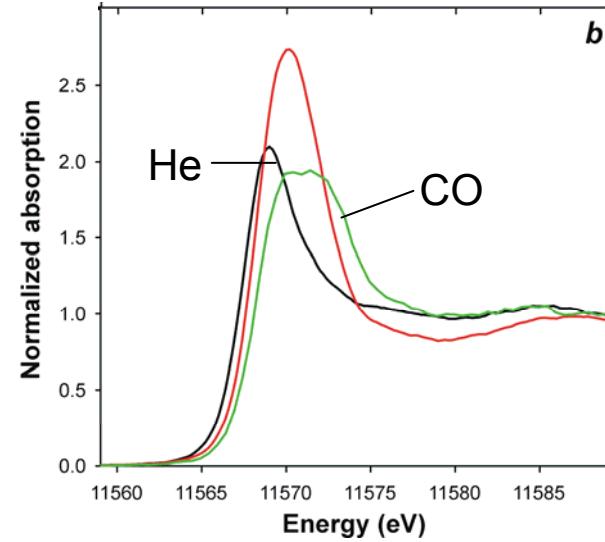


Pt<sub>6</sub>CO face bridging



Pt  
C  
O

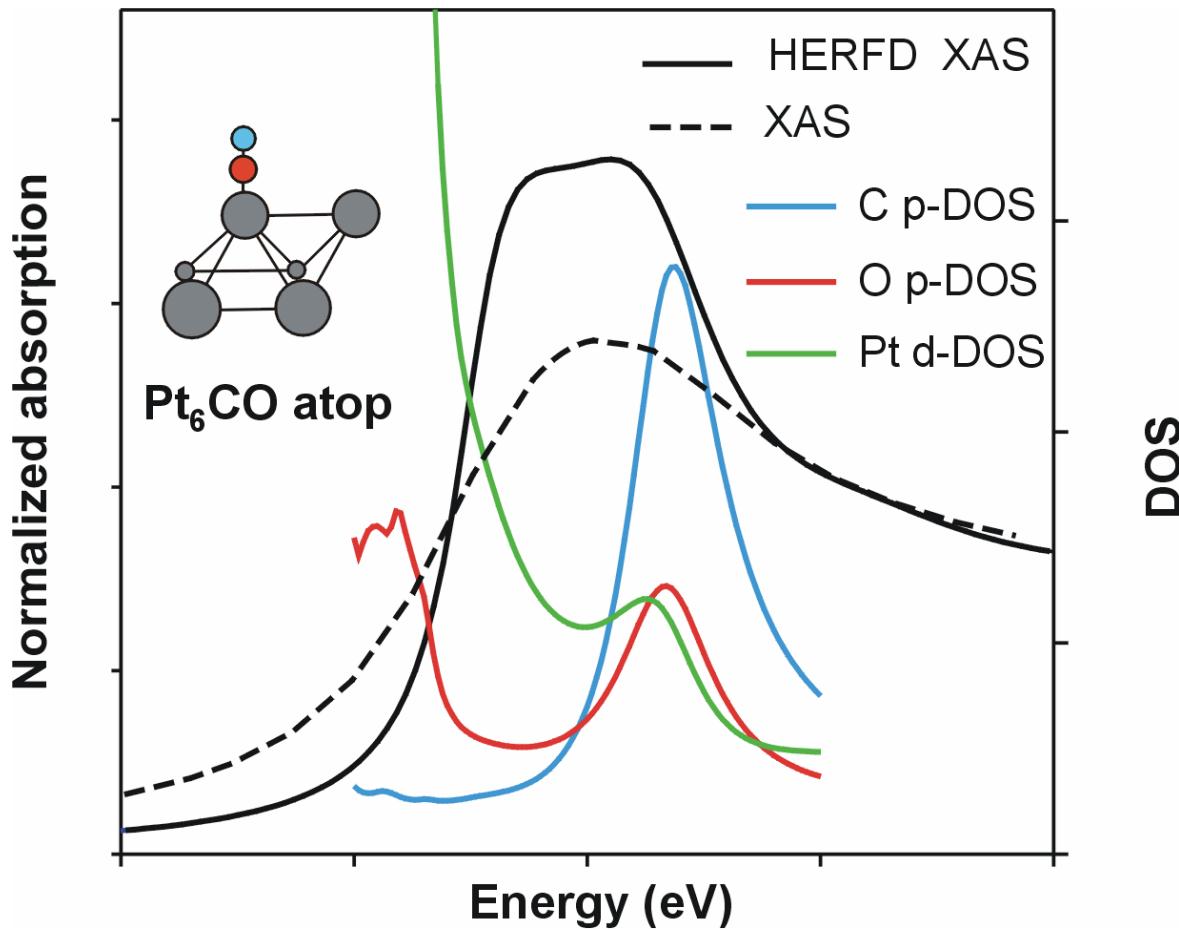
Experimental



XAS

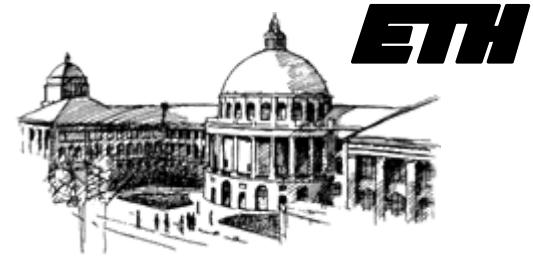
HERFD





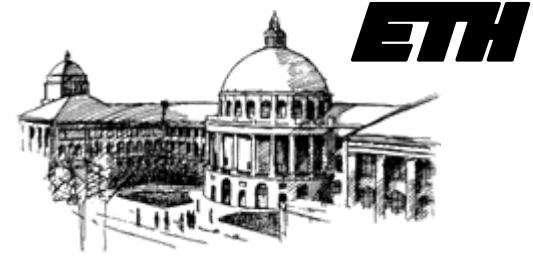
*Structure of adsorption sites can be determined  
FEFF8 reproduces experiment and provides LDOS*



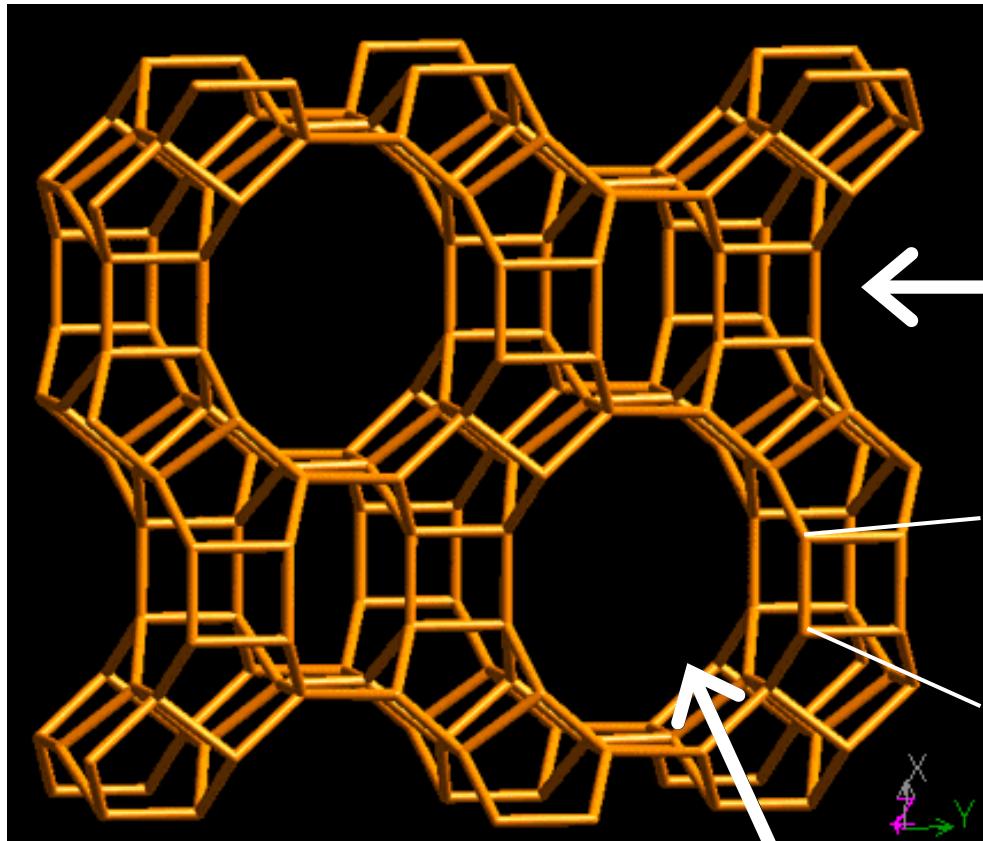


# Structure of Aluminum in Zeolites in extreme conditions

## Development of in-situ XAFS for low Z elements



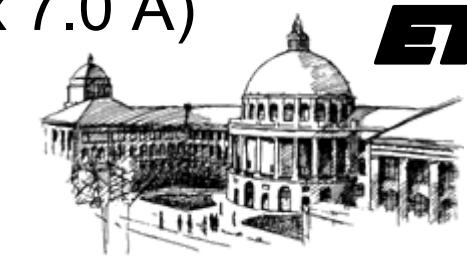
# Zeolites

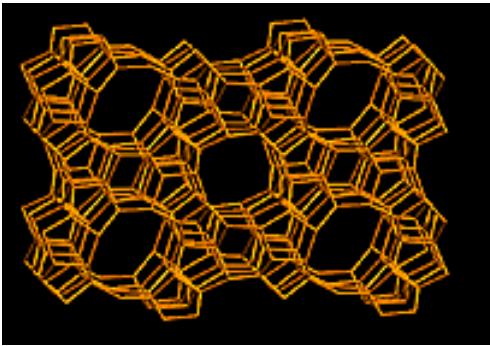


Mordenite

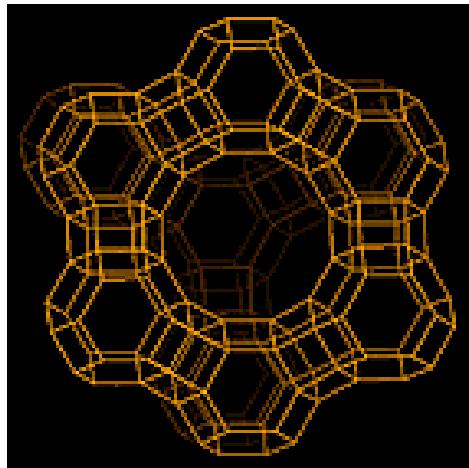
NB kinetic diameter of hexane is ~5 Å

12 MR (6.5 x 7.0 Å)



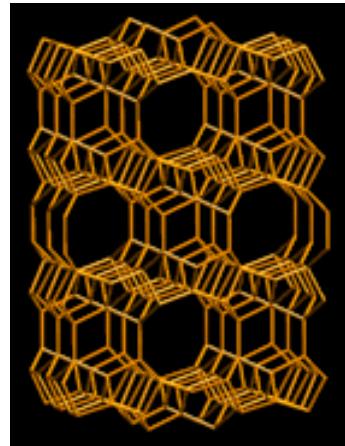


ZSM-5

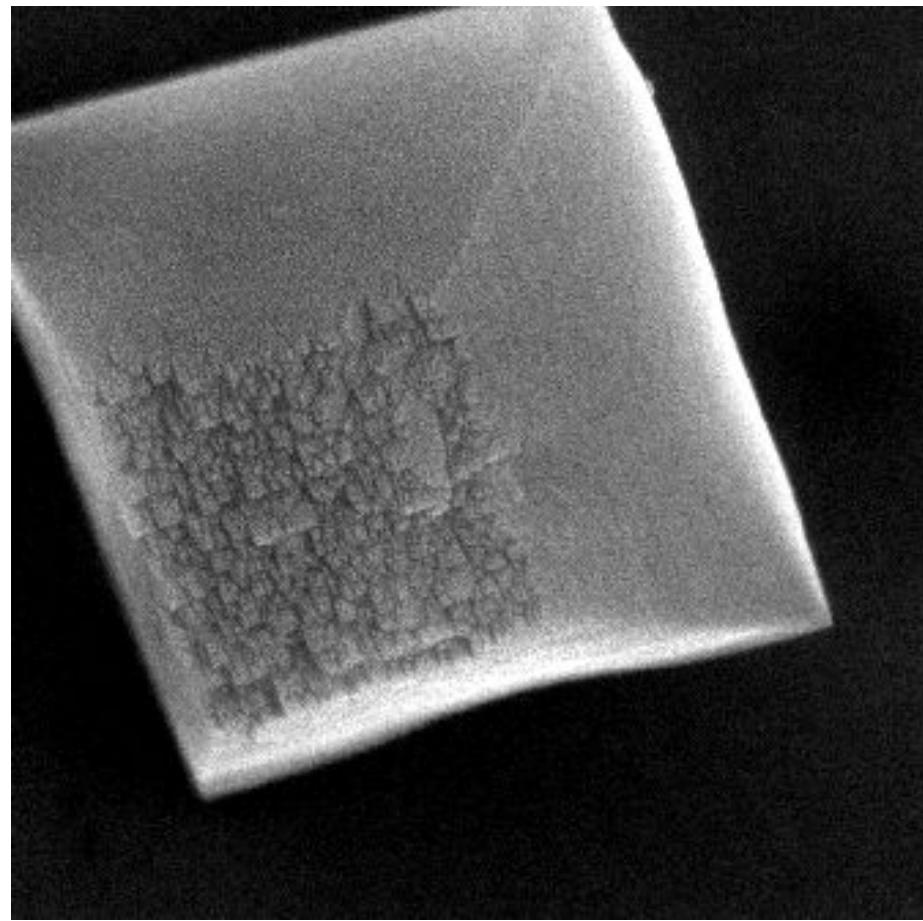


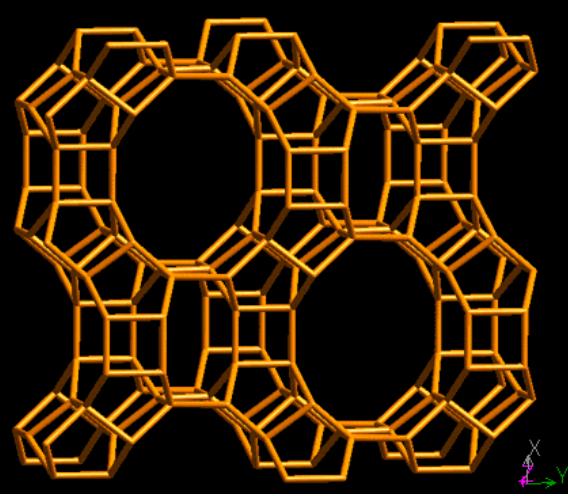
Y-zeolite

Beta



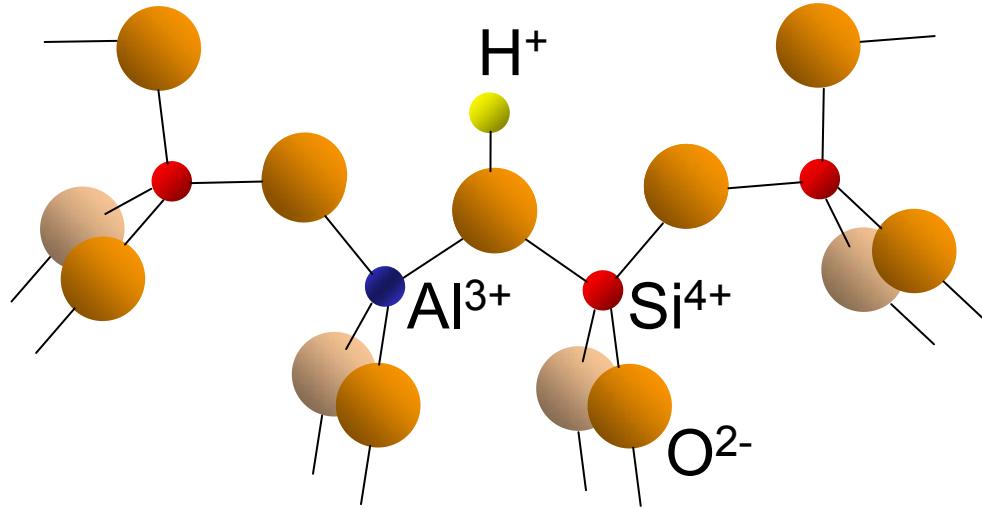
SEM of Beta





# Acid sites in zeolites

Brønsted:



Lewis:

*Octahedral or three coordinate??*  
Essentially unknown

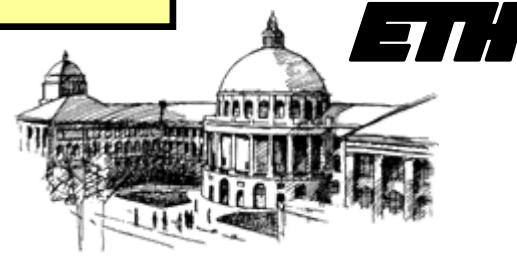


# Zeolite Activation by Steaming

- Pore-topology (mesopores)
- Loss of Brønsted acid sites
- Lewis acid sites
- Dealumination of framework
- Extra-framework aluminum

*Structure – performance relations*

*Detailed structure?*



# Structure - Activity Relationship

**Q:** What is structure of a zeolite  
under reaction / treatment conditions?

*In-situ* spectroscopy:  
observe changes as function of varying conditions

*Time resolution*

Aluminum coordination as function of conditions

*Al K-edge X-ray Absorption Spectroscopy*



# In-situ Al K-edge XAFS on zeolitic samples

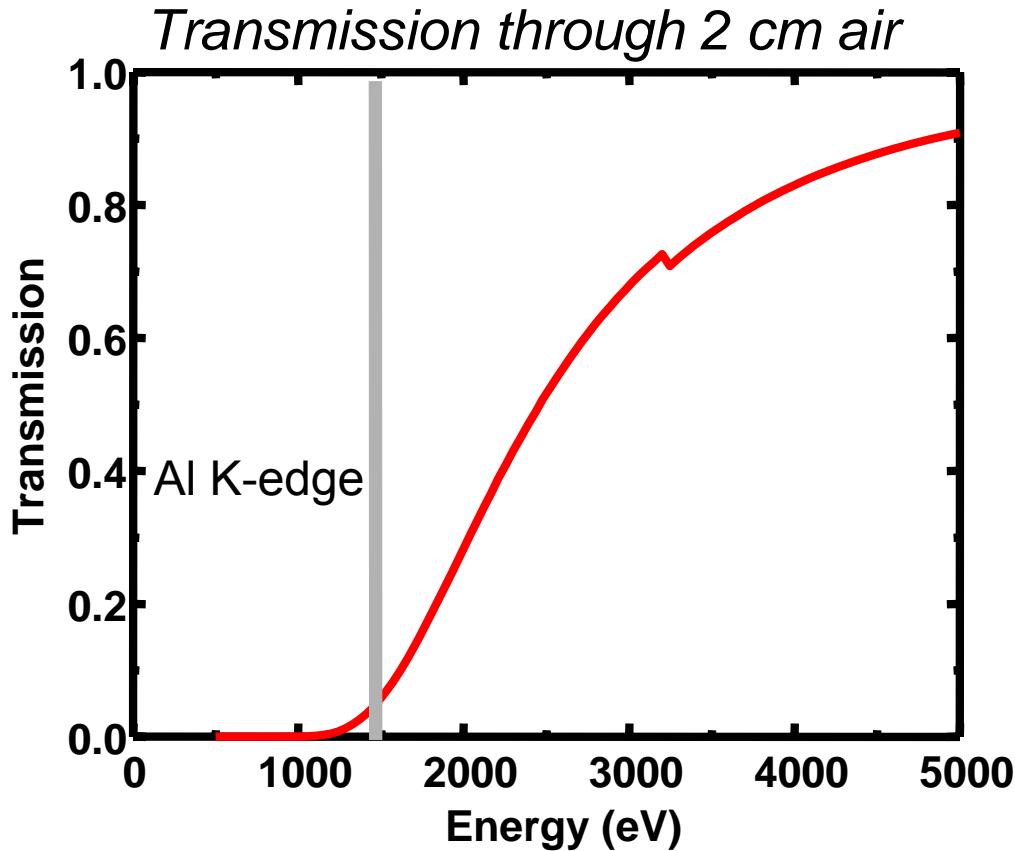
1995

- ◆ No experimental *in-situ* cell
- ◆ Limited structural information from near-edge spectra
- ◆ No theoretical basis of spectra



# In-situ Al K-edge XAFS

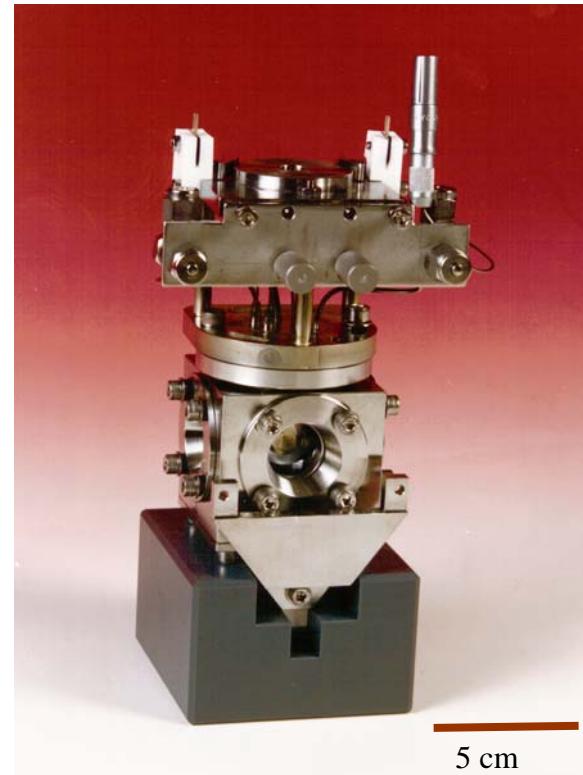
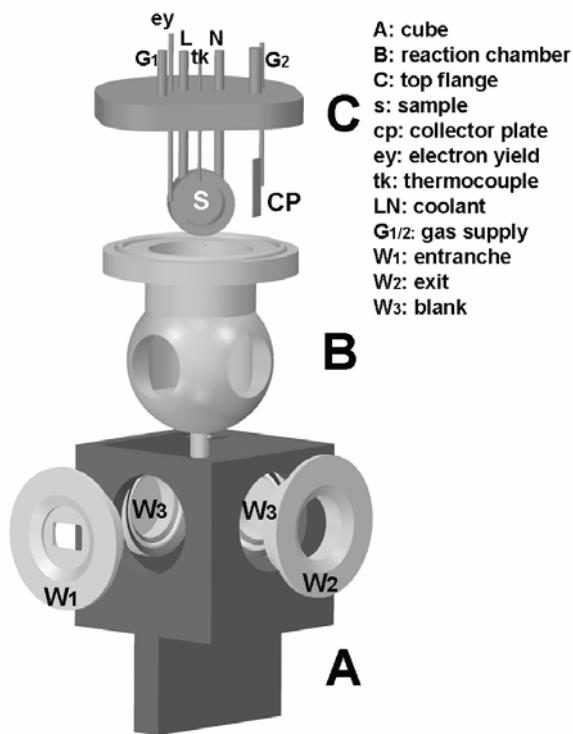
*Strong absorption of X-rays*



- Special instrumentation
- Interpretation of spectra

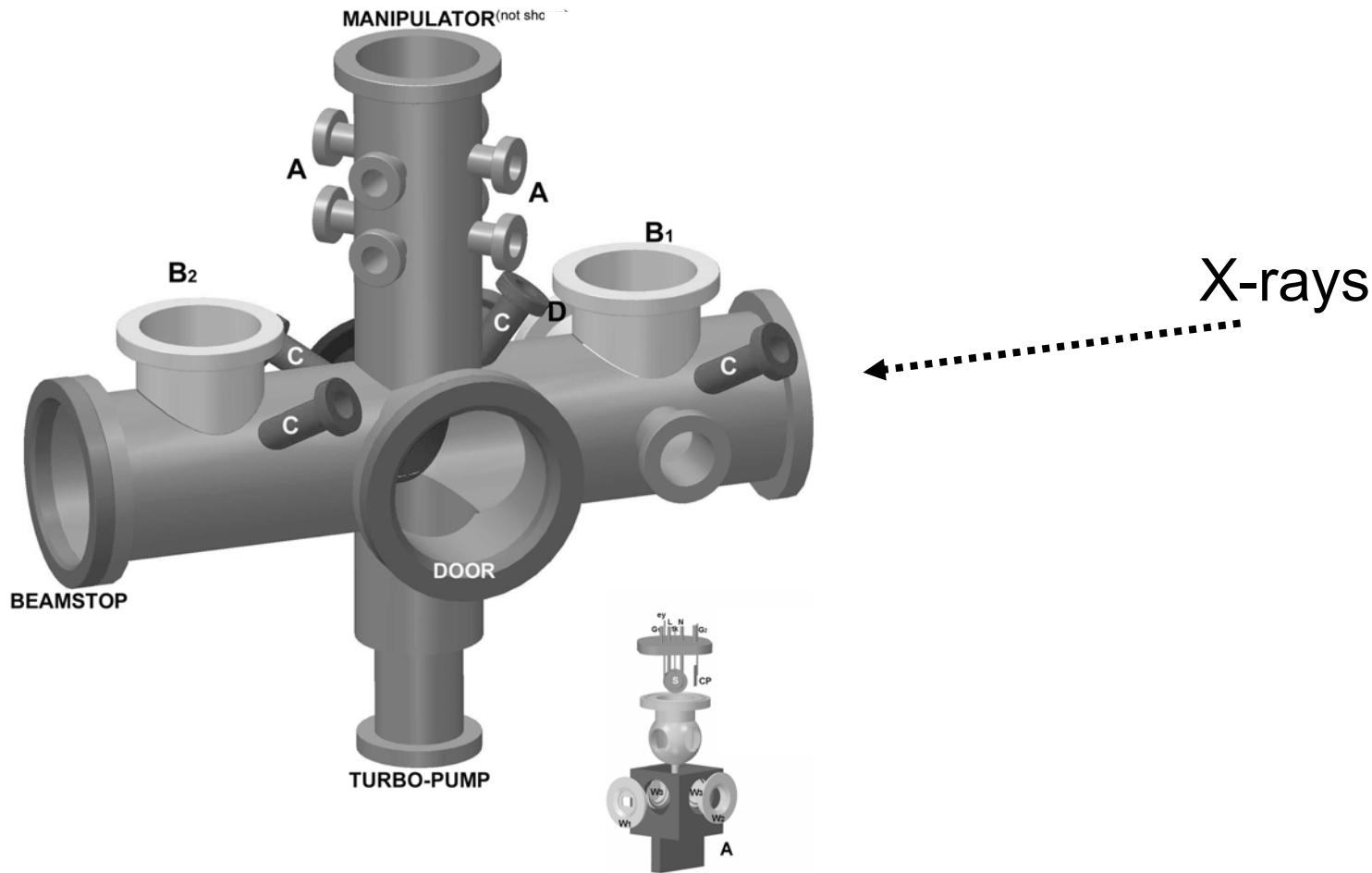


# Developed Instrumentation

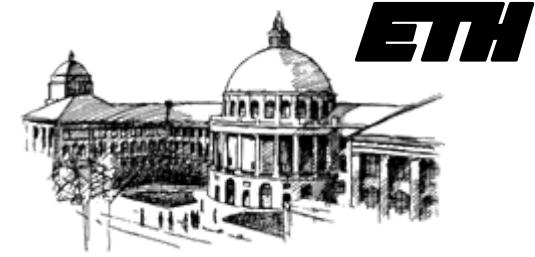


- ♠ Fluorescence and electron yield detection
- ♠ Polymer coated Be windows

# Developed Instrumentation



Installed at Station 3.4 SRS Daresbury  
SRS has a cell



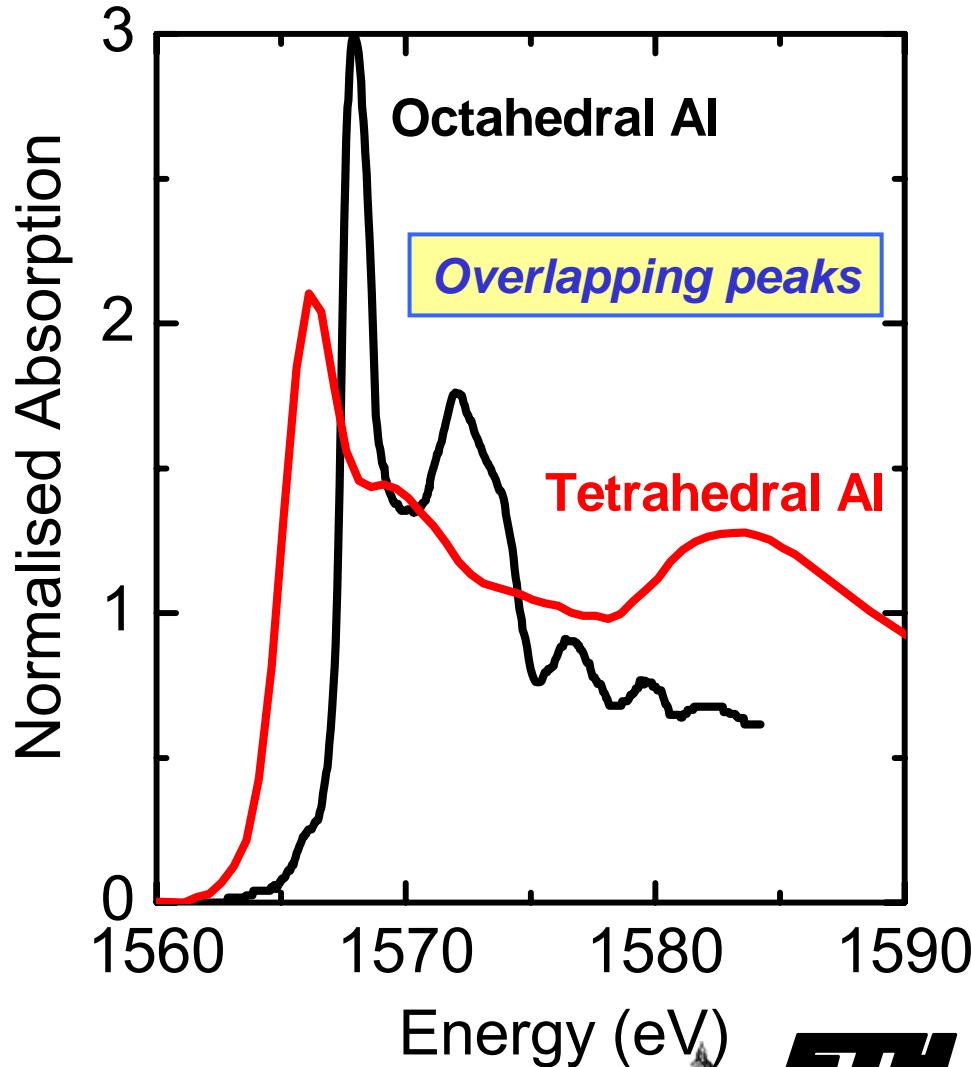
# Al K-edge XAFS

## Characteristics:

- Quantitative
- Conditions:
  - $100 < T < 1000\text{K}$
  - $10^{-6} < P < 10^3 \text{ mbar}$
- 5-10 min per spectrum
- Solid -gas / -liquid systems
- Si/Al ratios  $> 50$  ( $< 1\text{wt\% Al}$ )

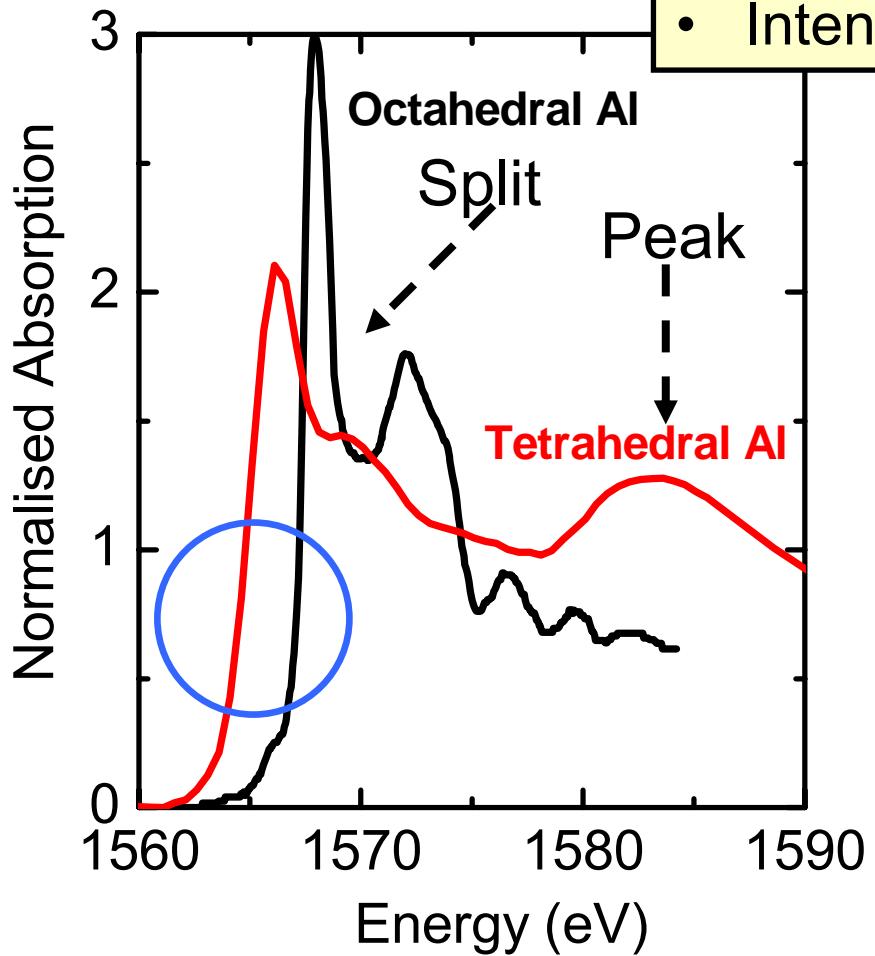
## Coordinations:

- Edge position
- Shape
- Intensity



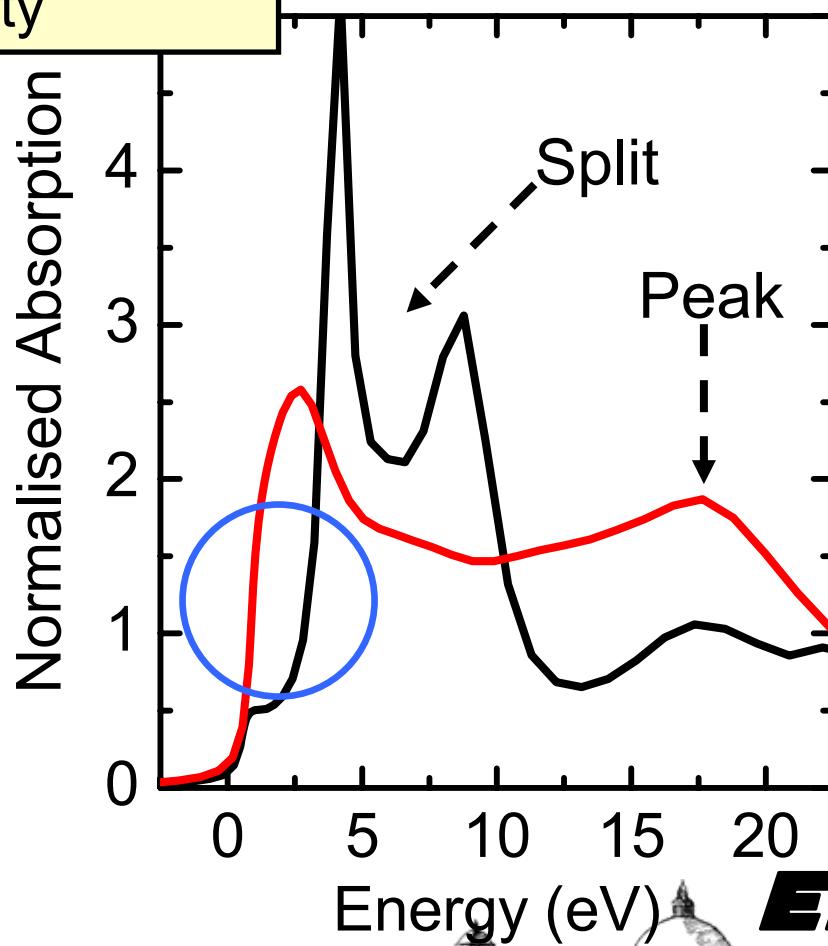
# Al coordinations from XAS spectra

Experimental:



- Edge position
- Shape
- Intensity

FEFF8 Simulation:



# Samples

*Crystalline zeolites in H-form, in-situ calcination of NH<sub>4</sub> zeolite*

H-Beta

H-Mordenite

H-Y

*Activated zeolites through steam dealumination*

H-USY

*Amorphous silica-alumina (14% Al<sub>2</sub>O<sub>3</sub>)*

# Measurements Conditions

Low T: in presence and absence of low P<sub>p</sub> water

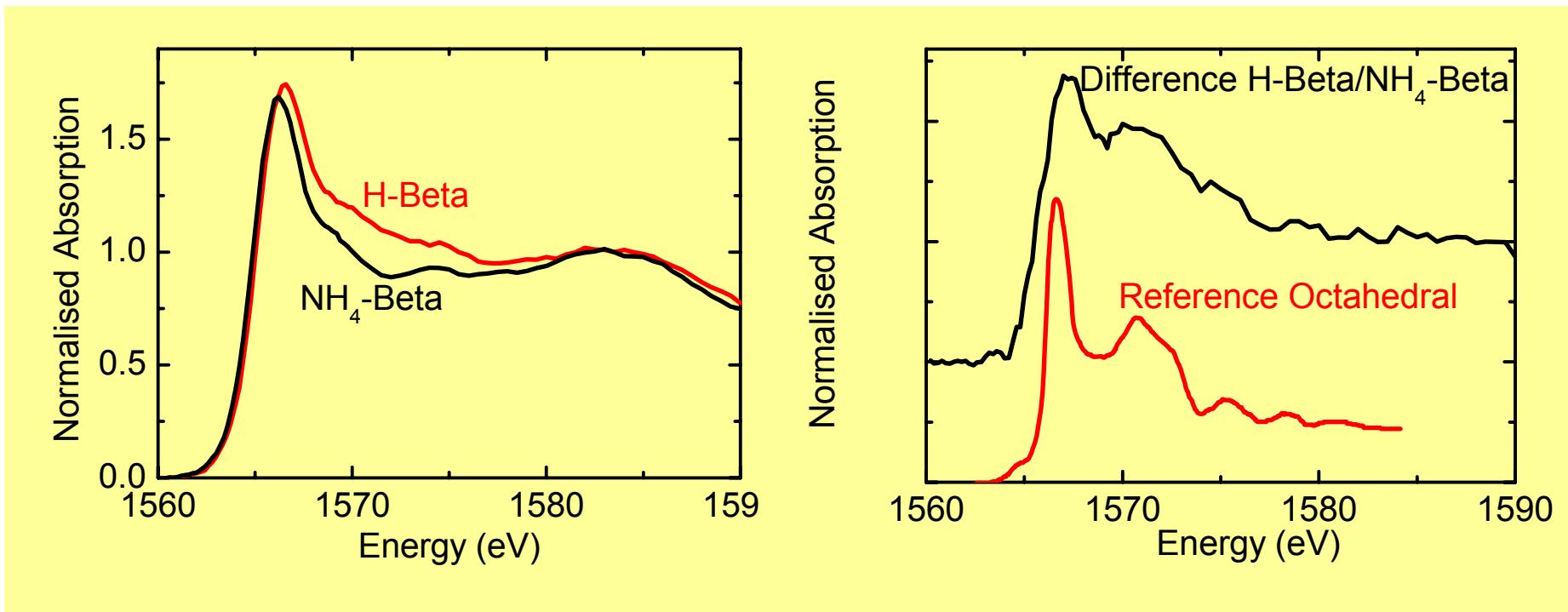
High T: in vacuum



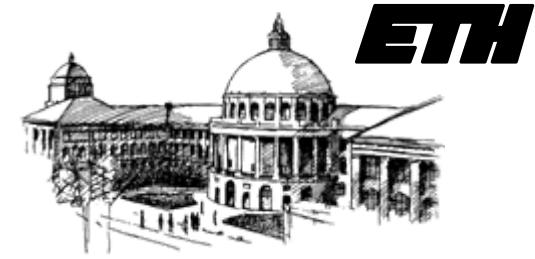
# Al XAFS at low temperature

*Measurement conditions:*

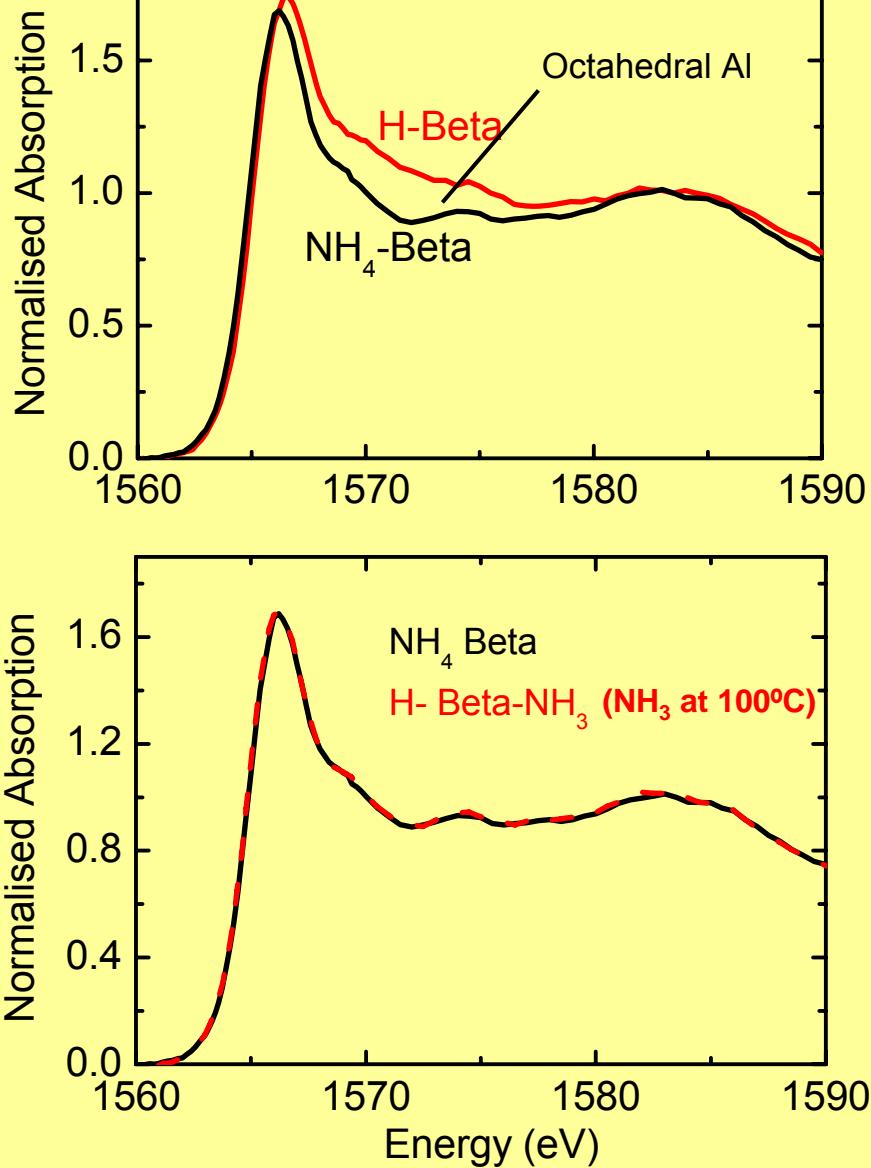
- Samples in a wet environment: flowing He / H<sub>2</sub>O
- Room temperature



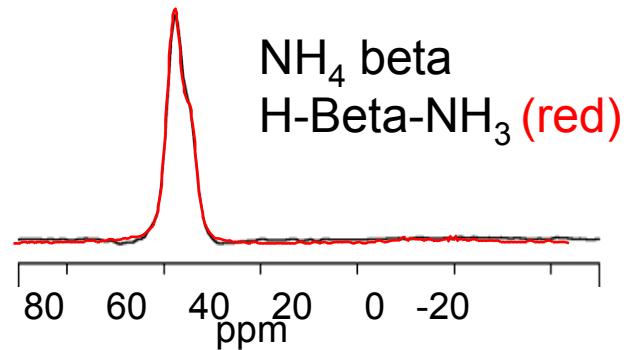
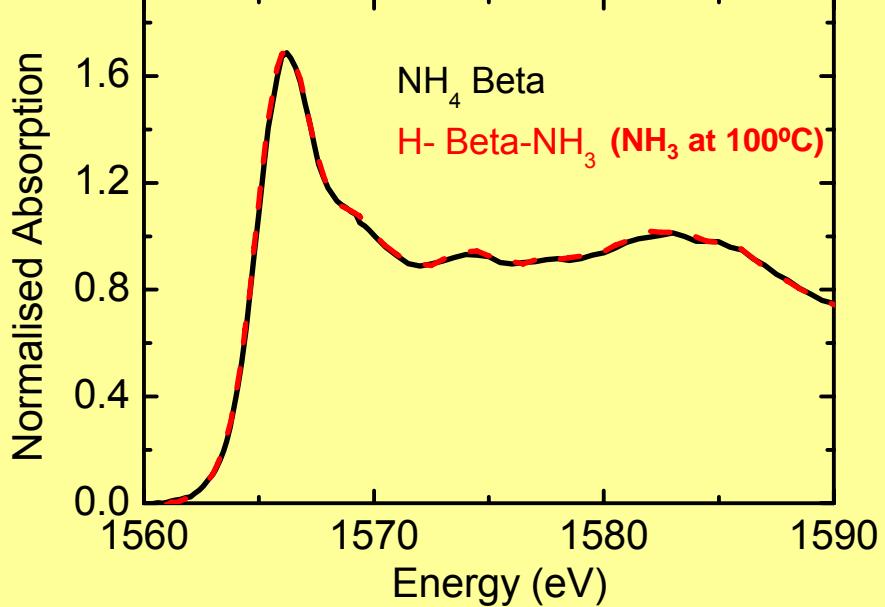
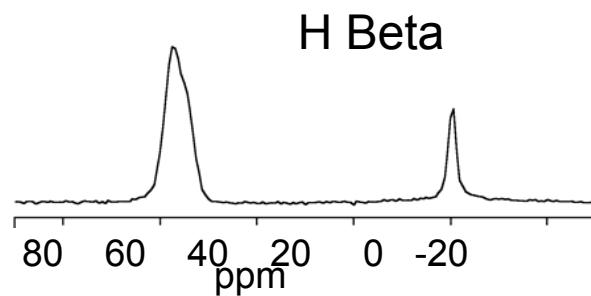
*Octahedral Al in H-Beta*



# Al XAS vs $^{27}\text{Al}$ MAS NMR

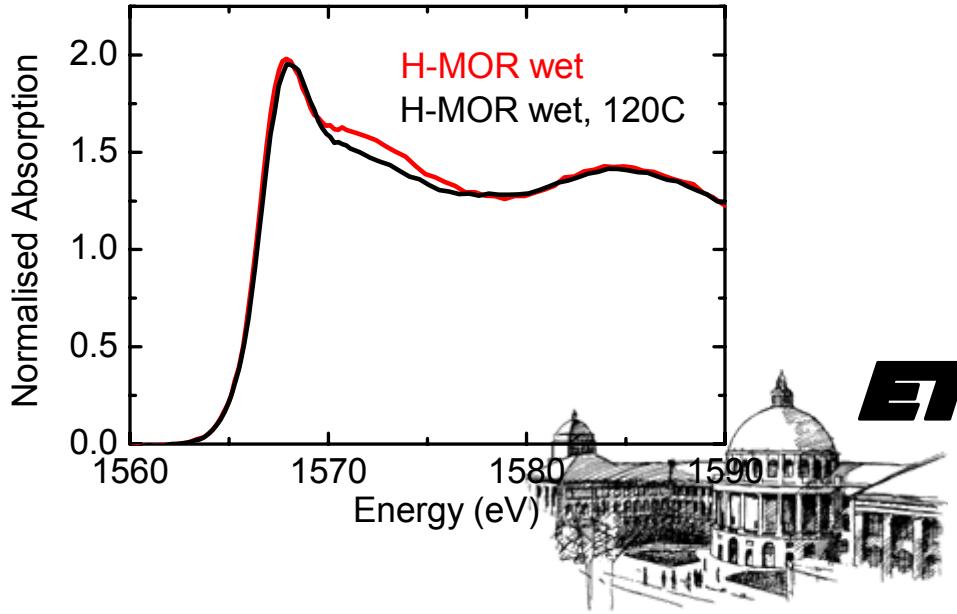
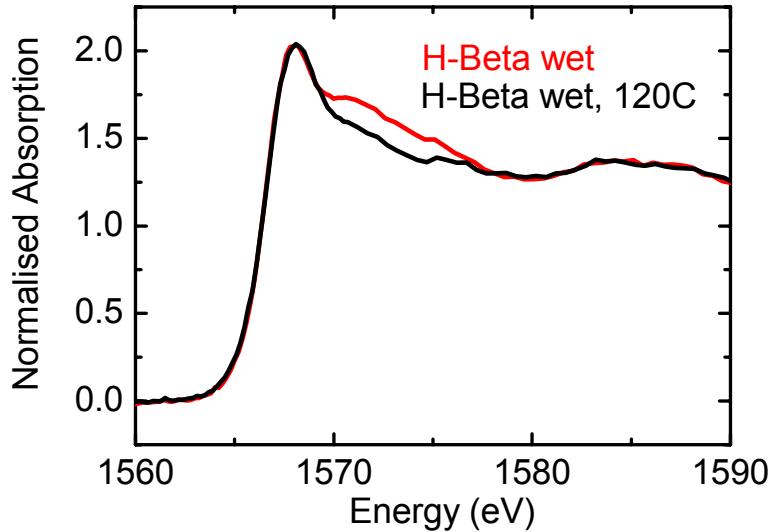
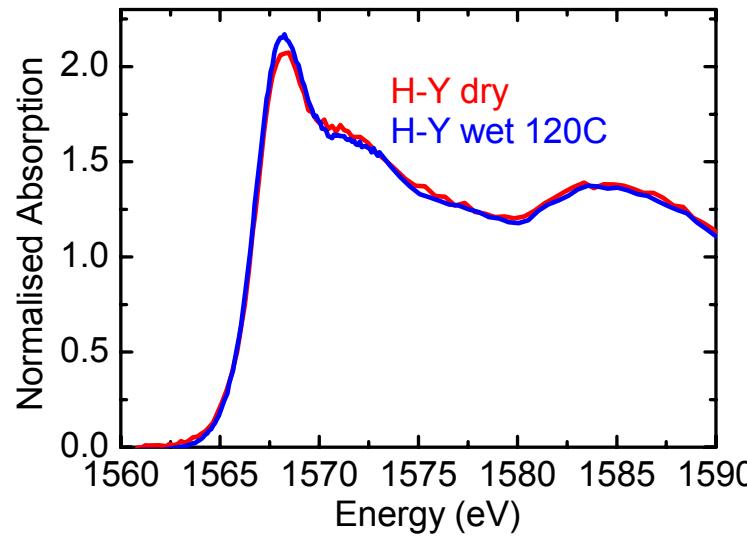
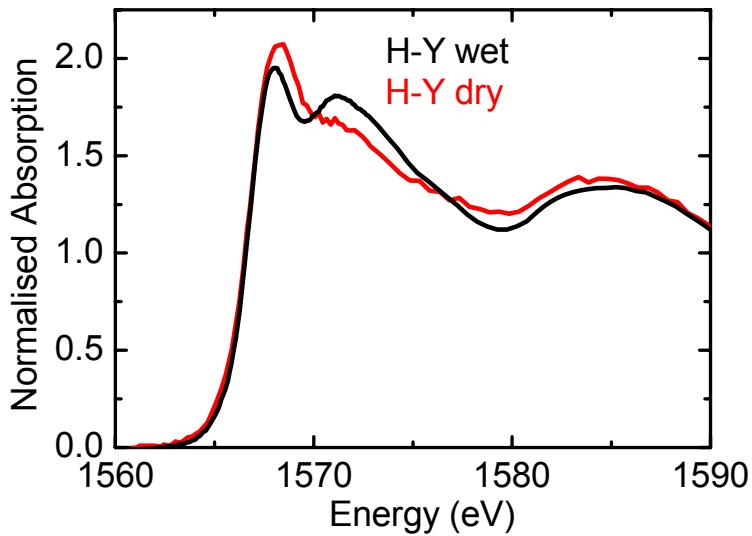


$^{27}\text{Al}$  MAS NMR

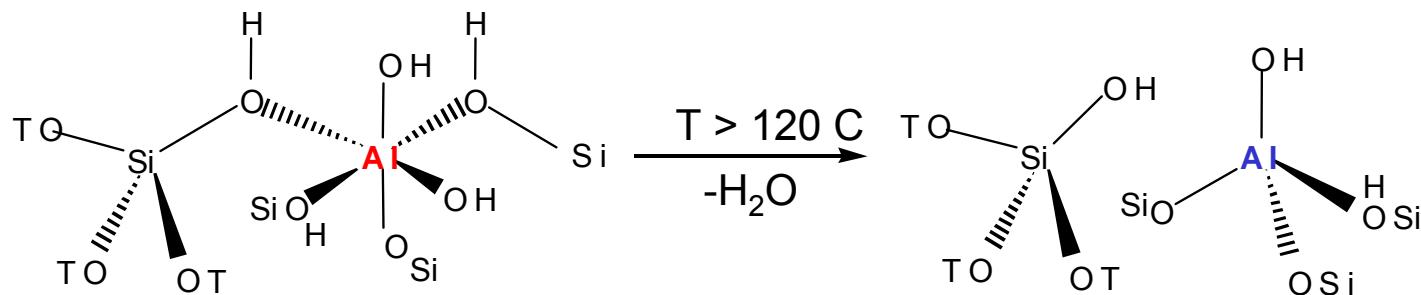


# Al XAFS at low temperature

NH<sub>4</sub>-Zeolite  $\xrightarrow{450^\circ\text{C}}$  H-Zeolite [dry and wet]  $\xrightarrow{120^\circ\text{C}}$  H-Zeolite



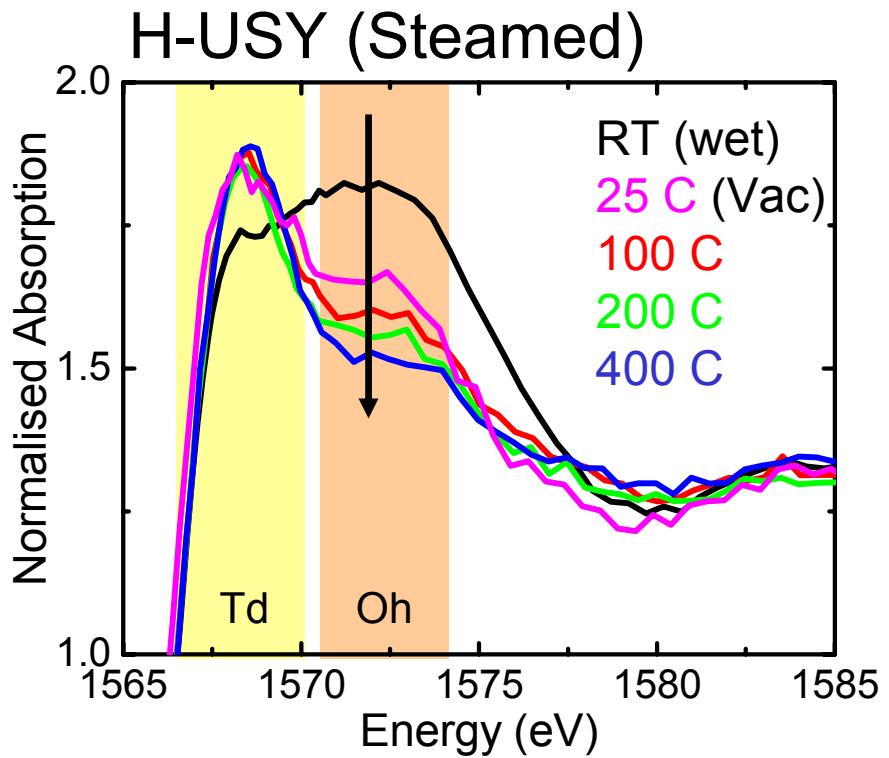
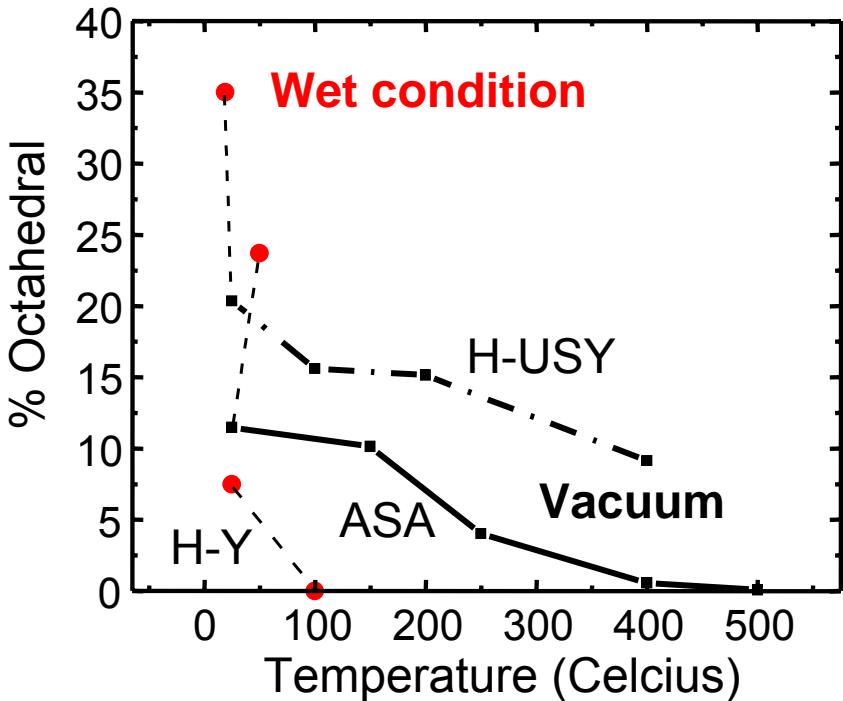
# Resumé



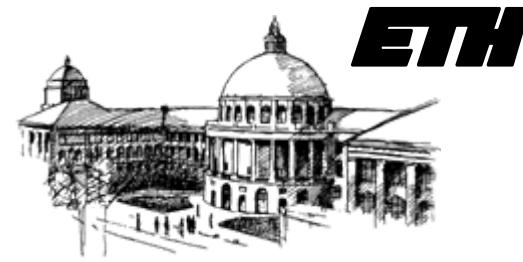
- Acidic zeolites have octahedral Al only when H<sub>2</sub>O is present
- Octahedral forms at room temperature  
*Wouters J. Am. Chem. Soc. 120 (1998) 11419*
- Octahedral aluminium not stable at T > 120 C
- Beta, Mordenite and zeolite Y show same behavior



# Zeolite Steam-activation: Octahedral Al



*Coordination changes with condition*



# Local Structure of the Zeolitic Catalytically Active Site During Reaction

## In situ EXAFS

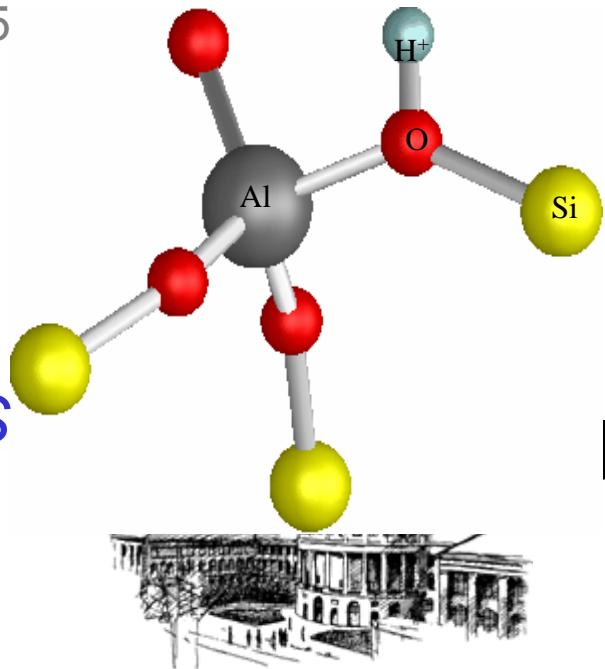
What do we know?

- BAS is bridging hydroxyl group
- Theory: distorted tetrahedral

Haw JACS 124 (2002) 10868

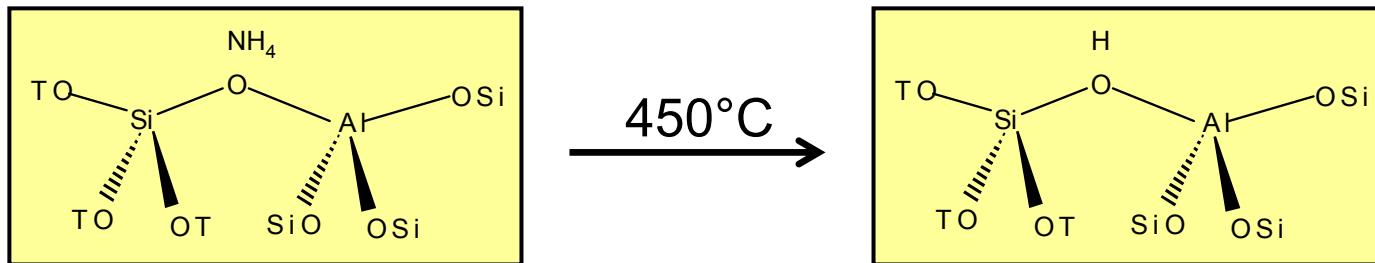
- NMR in dehydrated conditions gives extreme broad peaks

Kentgens JACS 123 (2001) 2925



*In situ generation of BAS*

*Oligomerization of olefins over the BAS*

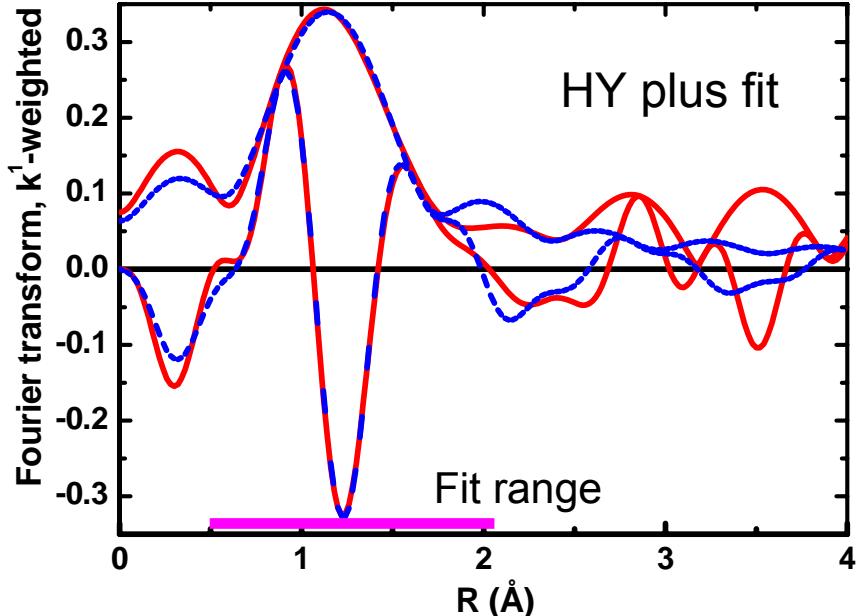


↓  
5% ethylene in He

AI EXAFS at various temperatures

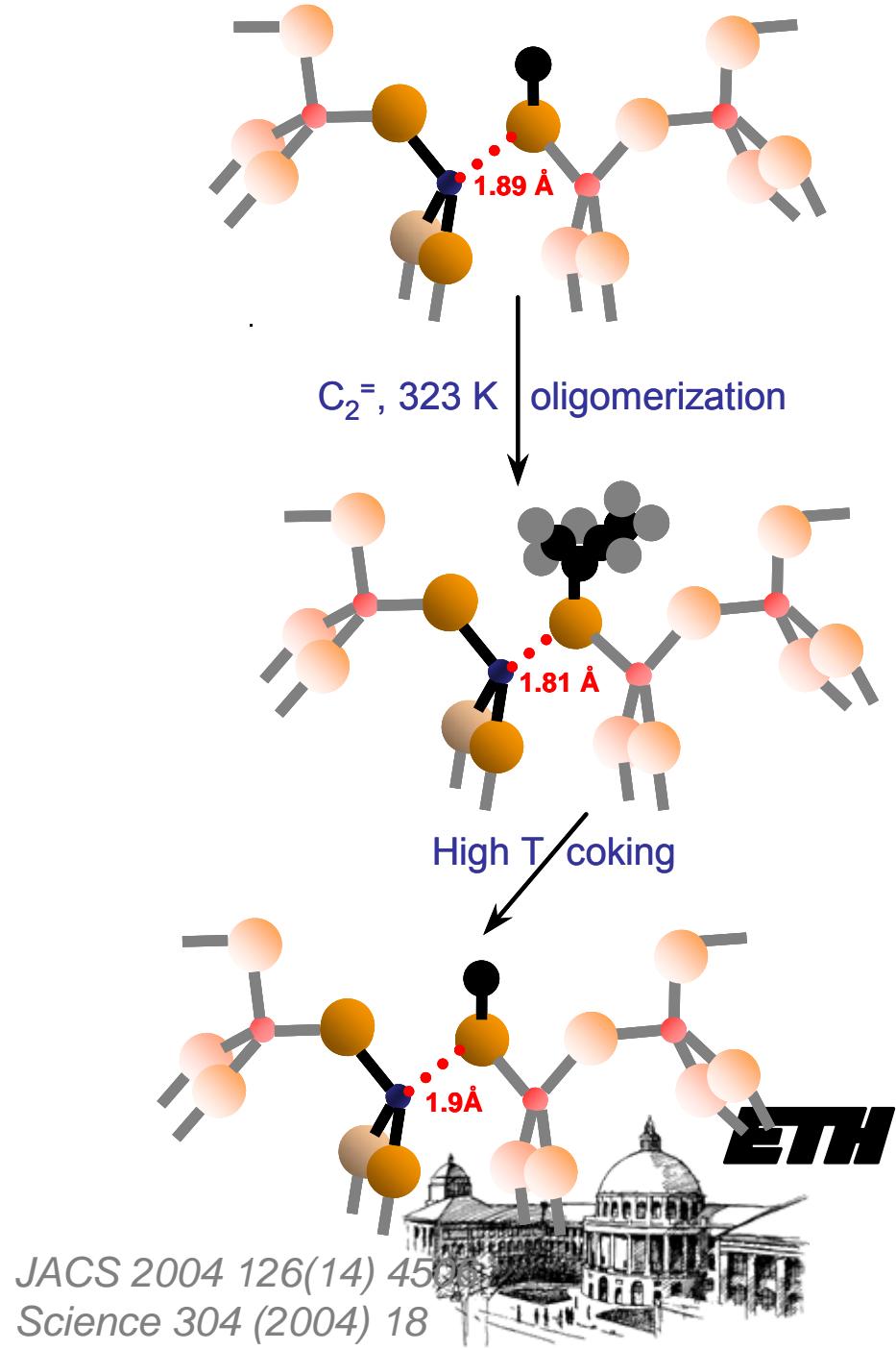
At T>RT C<sub>2</sub>= oligomerization

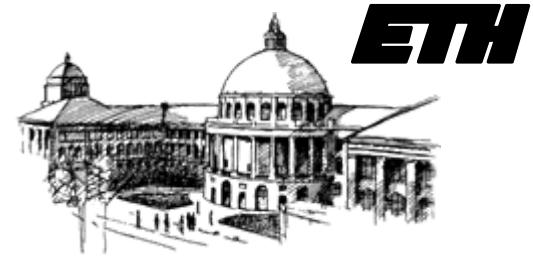




	CN	$R$ ( $\text{\AA}$ )
NH <sub>4</sub> -Y (RT)	4.4	1.68
H-Y (RT)	3.1	1.66
	1.1	1.89
H-Y C <sub>2</sub> = (323 K)	3.4	1.64
	1.1	1.81
H-Y C <sub>2</sub> = (625 K)	2.9	1.65
	1.1	1.91

van Bokhoven





# Catalysis by Gold

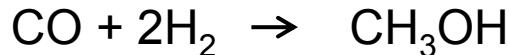
Partial / complete oxidation of hydrocarbons

methane, alkenes, methanol

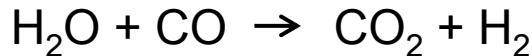
Hydrogenation / dehydrogenation reactions

alkenes, alkynes, alkadienes, (un)saturated ketones

Methanol synthesis



WGS



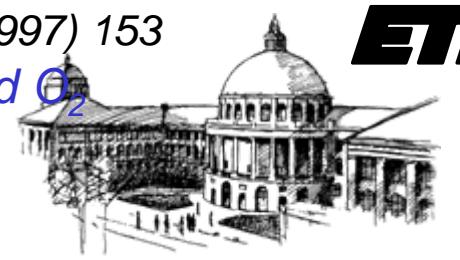
Nitric Oxide reduction (with CO, olefins, or H<sub>2</sub>)

CO oxidation

1925: Active in CO oxidation

*highly active in presence of H<sub>2</sub>: Haruta Catal. Today 36 (1997) 153*

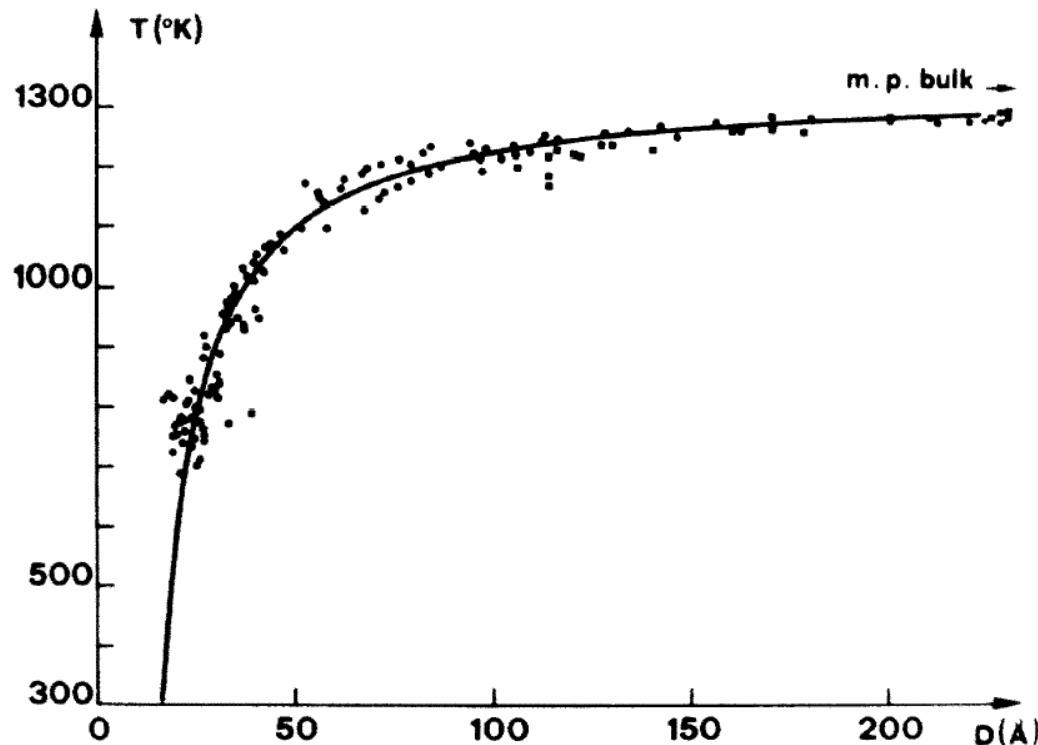
Selective CO removal, air purification, high-purity N<sub>2</sub> and O<sub>2</sub>



# Catalysis by Gold

## Physical properties

- bulk metallic gold is thermodynamically stable
- melting point and metallicity of the particle is function of particle size



Buffat Phys. Rev. A 13 (1976) 2287

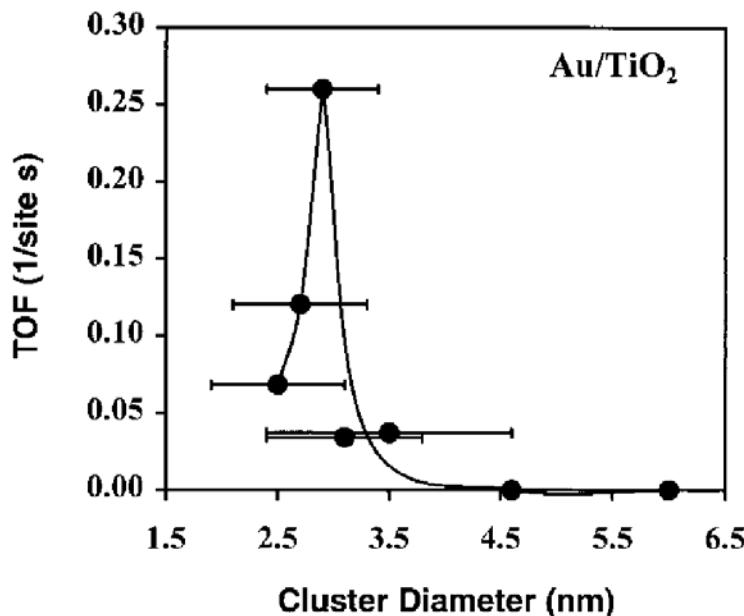


# Catalysis by Gold

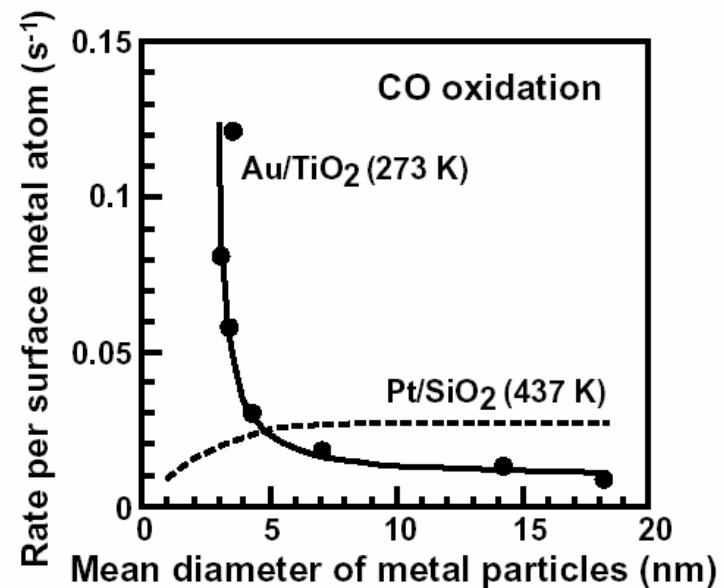
## Physical properties

- bulk metallic gold is thermodynamically stable
- melting point and metallicity of the particle is function of particle size

## CO oxidation: particle-size effect



Goodman *Science* 281 (1998) 1648



Haruta *Cattech* 3 (2002) 102



# Catalysis by Gold

Physical properties:

- bulk metallic gold is thermodynamically stable
- melting point and metallicity of the particle is function of particle size

CO oxidation: particle-size effect

Large support effects:

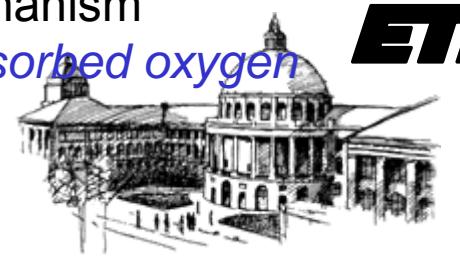
$\text{SiO}_2$ : hardly active

$\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ : moderately active

$(\text{TiO}_2)$   $\text{Fe}_2\text{O}_3$ ,  $\text{CeO}_2$ , *other reducible supports*: very active & less dependent on particle sizes; No clear relation to reducibility of support

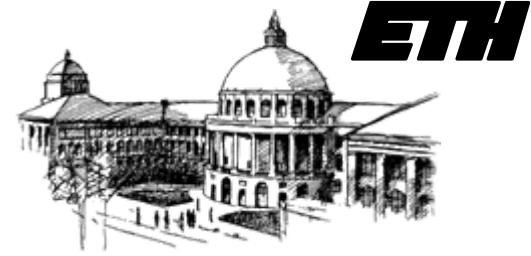
Active species in gold oxidation catalysis?

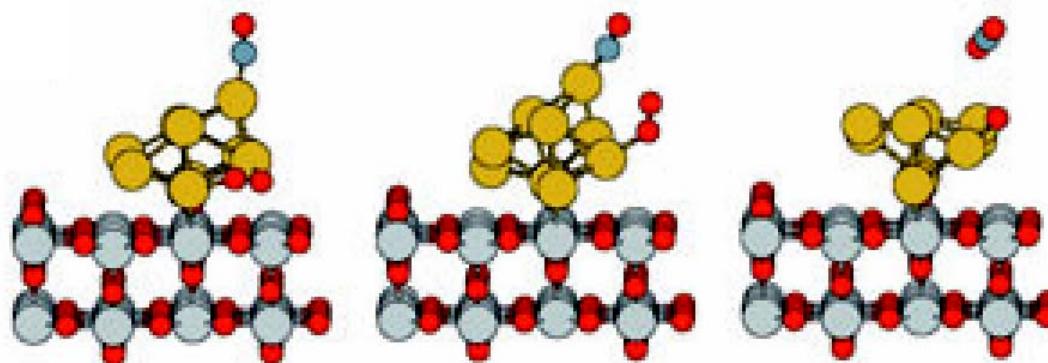
- Carbonate-mechanism excluded
- Small particles become active as soon as they are non-metallic (Goodman)
- Oxidic gold (I or III) is active species (Gates)
- Theory supports both gold-only and support-aided mechanism
- Support supplies oxygen *via molecularly (activated) adsorbed oxygen*  
*via Mars van Krevelen*



*How is oxygen activated on the catalyst?*

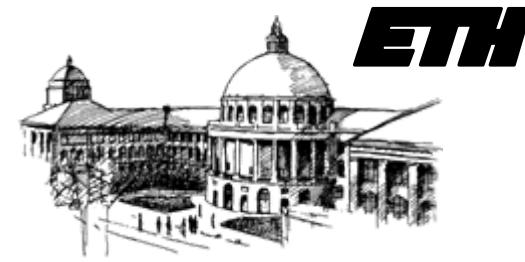
*How can the most inert metal be so active?*



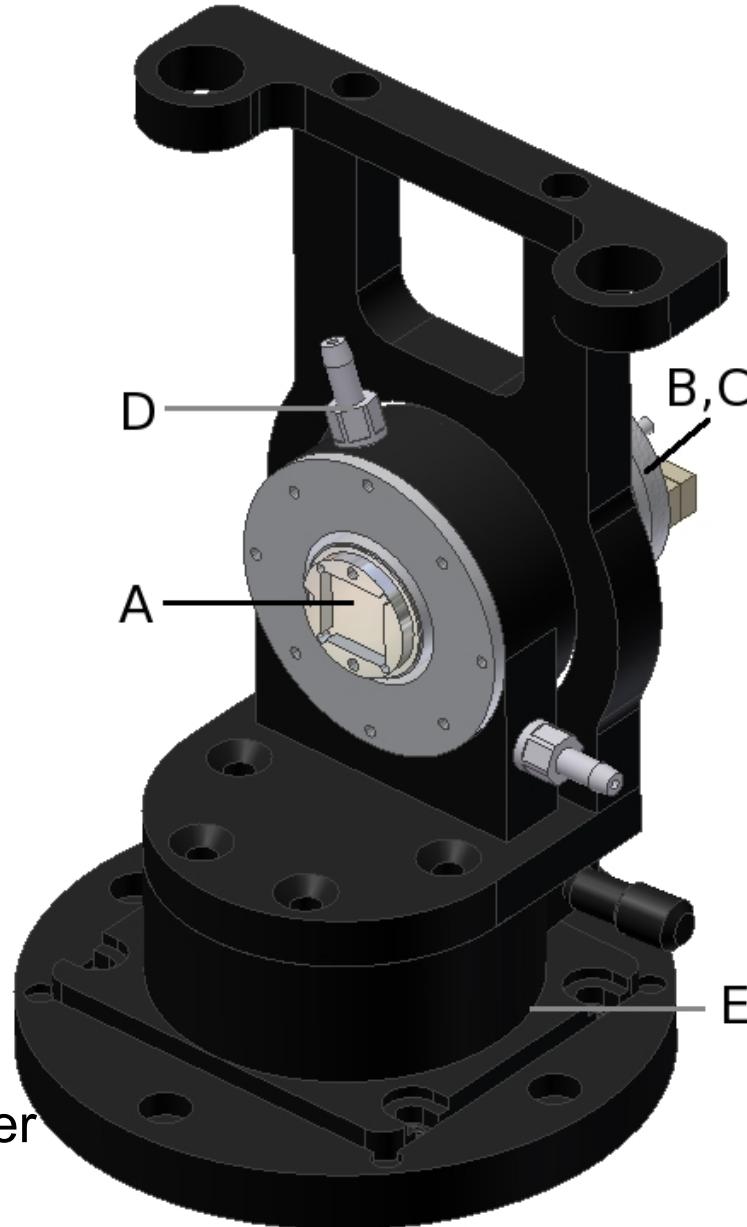
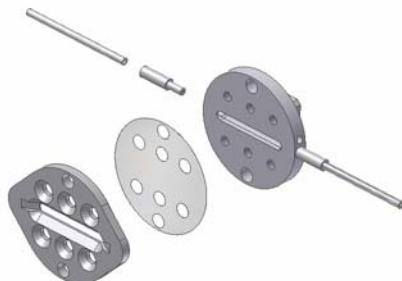


Nørskov et al. *Angew. Chem.* **44** (2005) 1824

Small gold particles adsorb oxygen  
(and react)



# EXAFS Cell



- $\text{LN} < T > 600 \text{ } ^\circ\text{C}$
- $10^{-6} < P > 3 \text{ bars}$
- Catalysts measured as sieve fraction / pellet
- Combined with mass-spectrometer
- (Near) plug-flow characteristics

# Structure of gold catalysts

## Sample Preparation

- Deposition precipitation  $\text{HAuCl}_4$  adjusted pH
- Washing with a base to remove chlorine

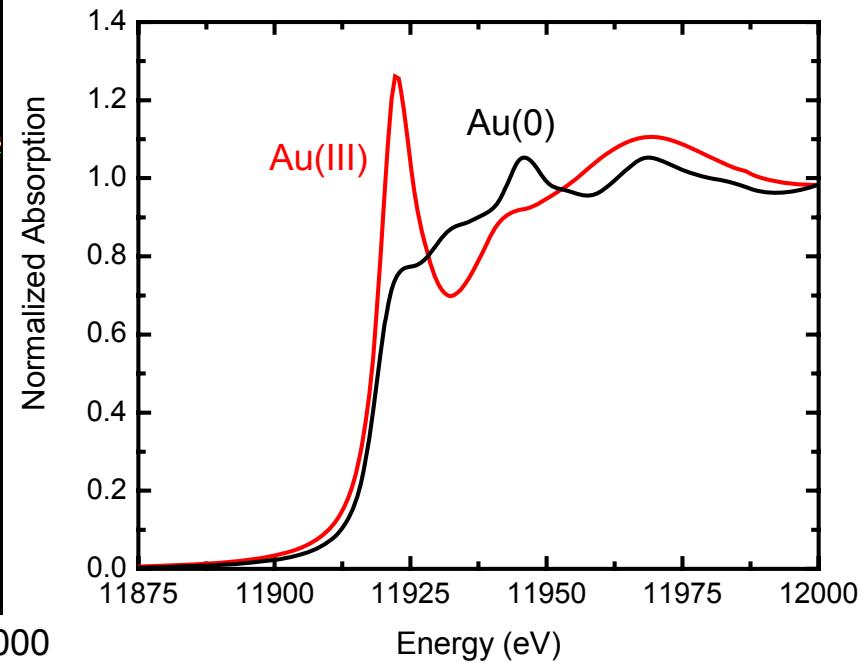
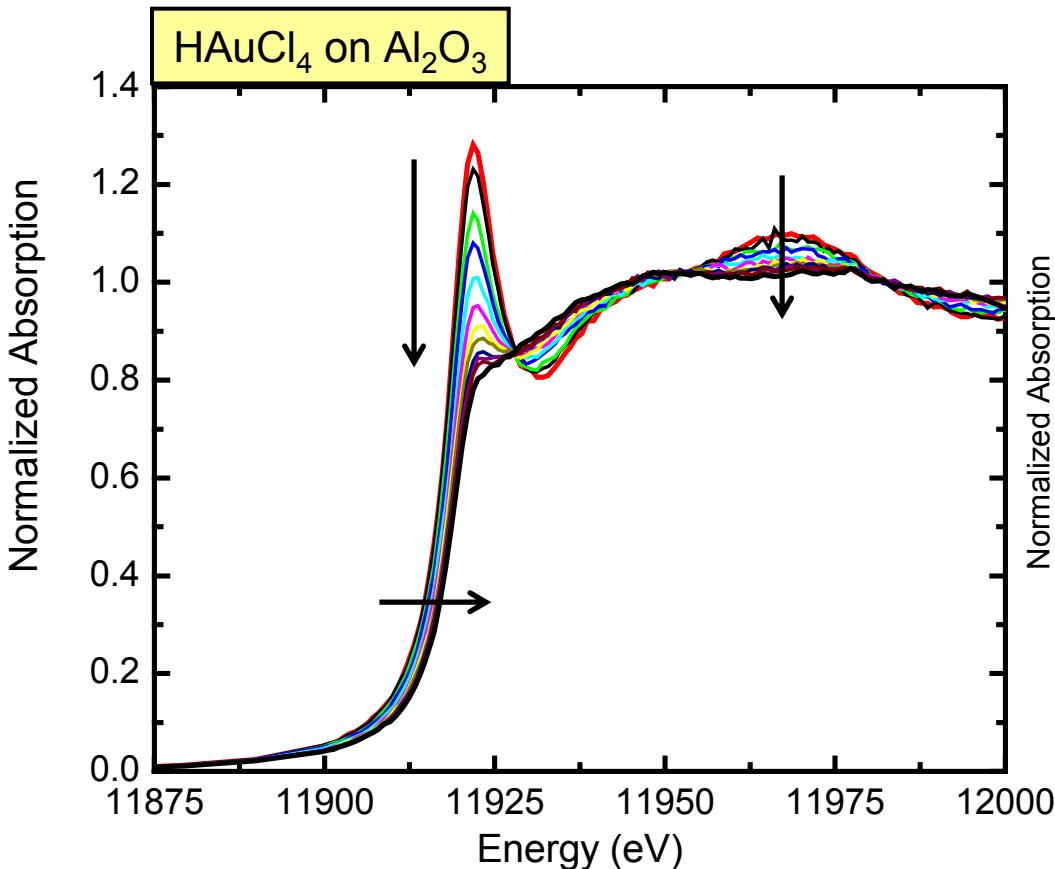
## *Supports*

$\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{CeO}_2$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{Nb}_2\text{O}_5$

Full EXAFS & XANES analyses



# Temperature-Programmed Reduction

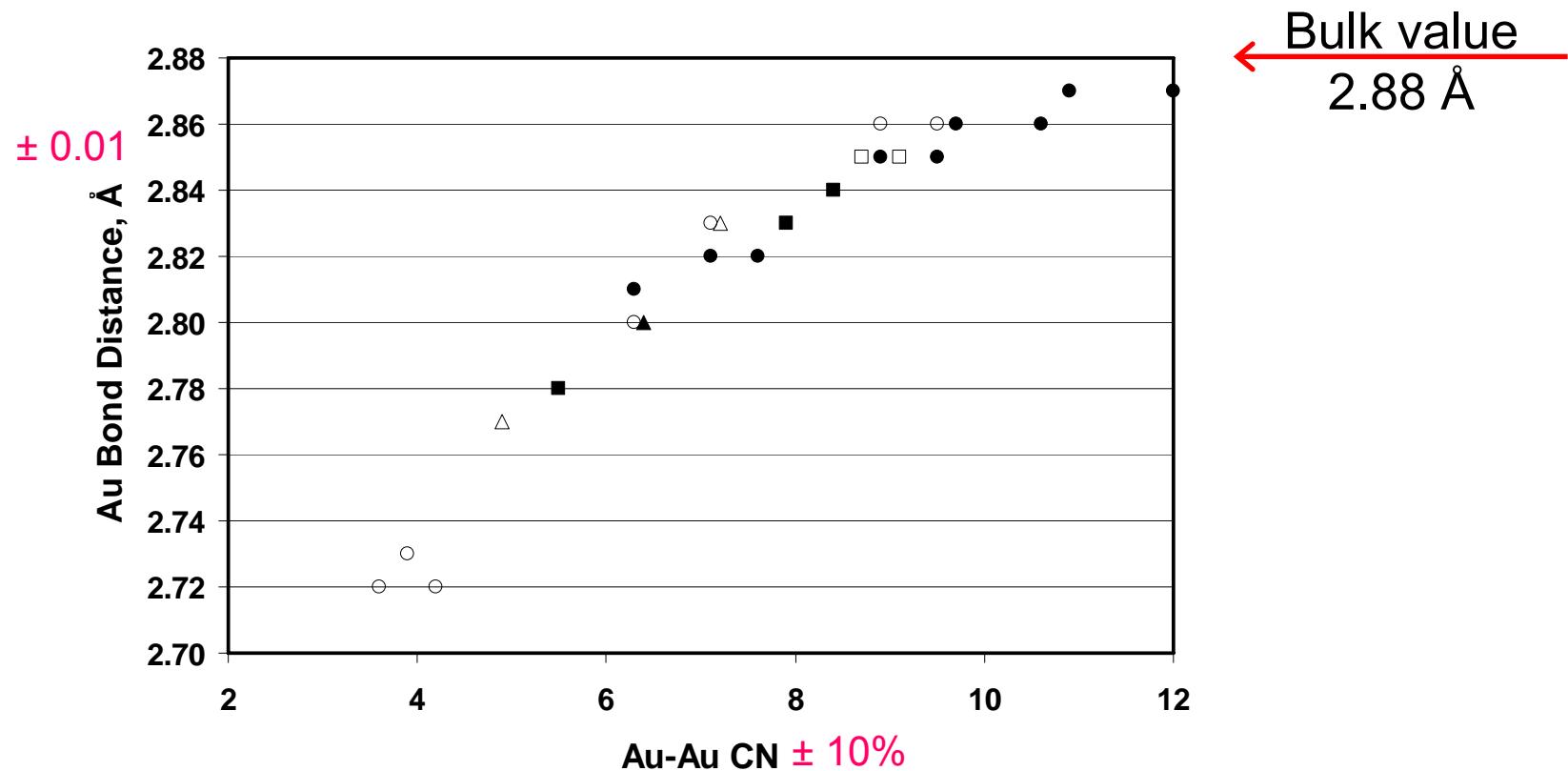


*Direct reduction from  $\text{Au(III)}$  to  $\text{Au}(0)$  (on all supports)*

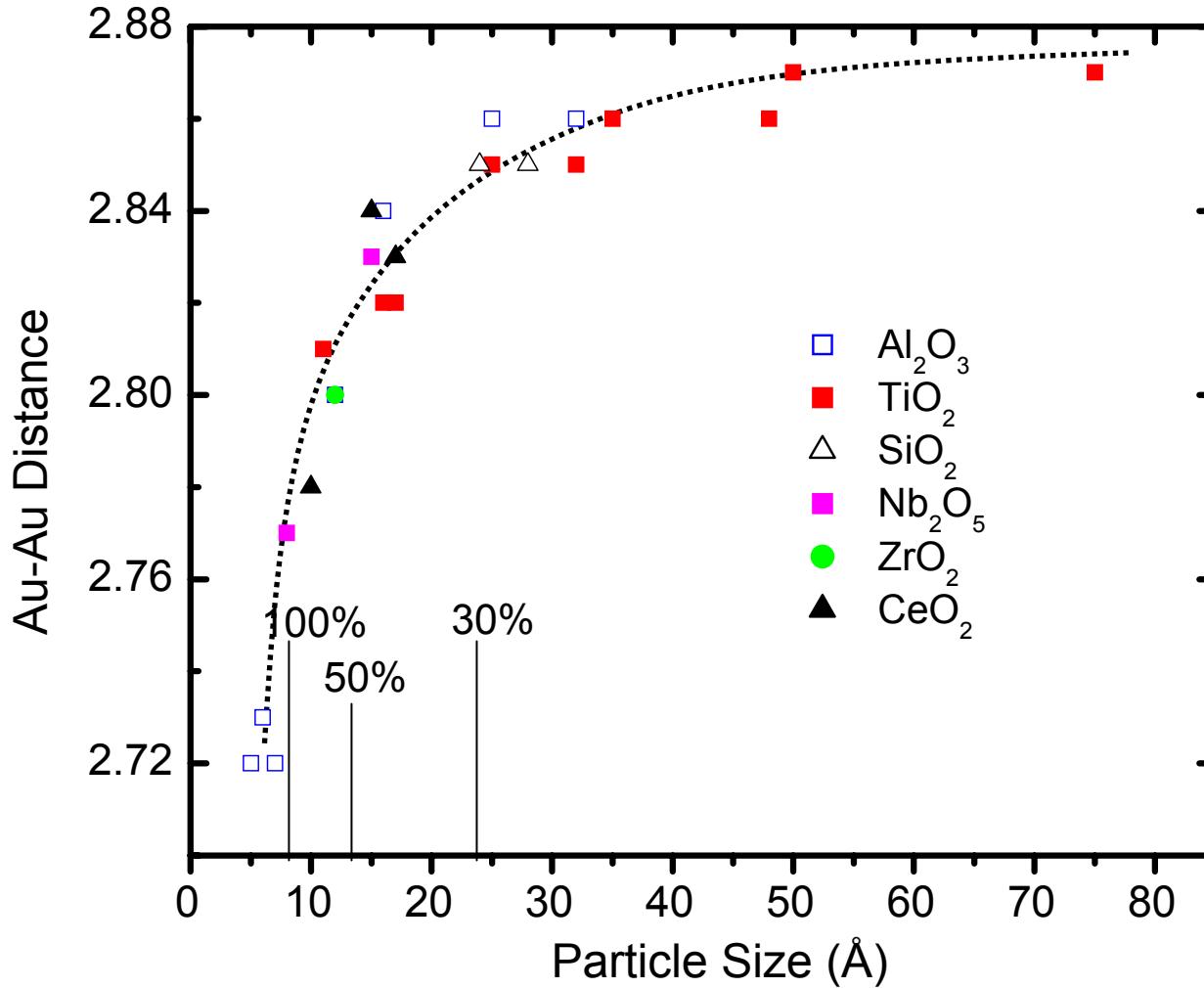
*Reduction temperature is strong function of support*



# EXAFS Fitting Results of Reduced Catalysts



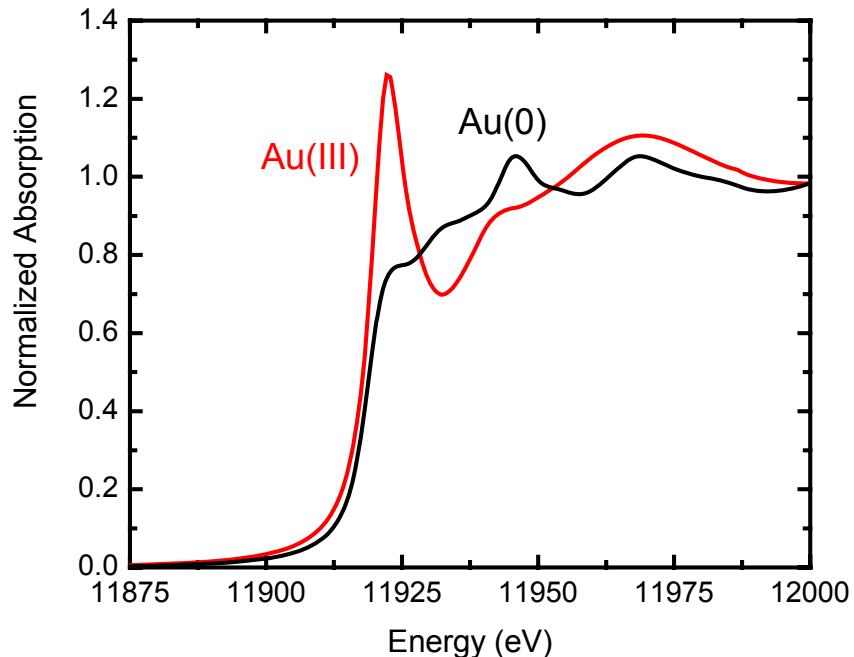
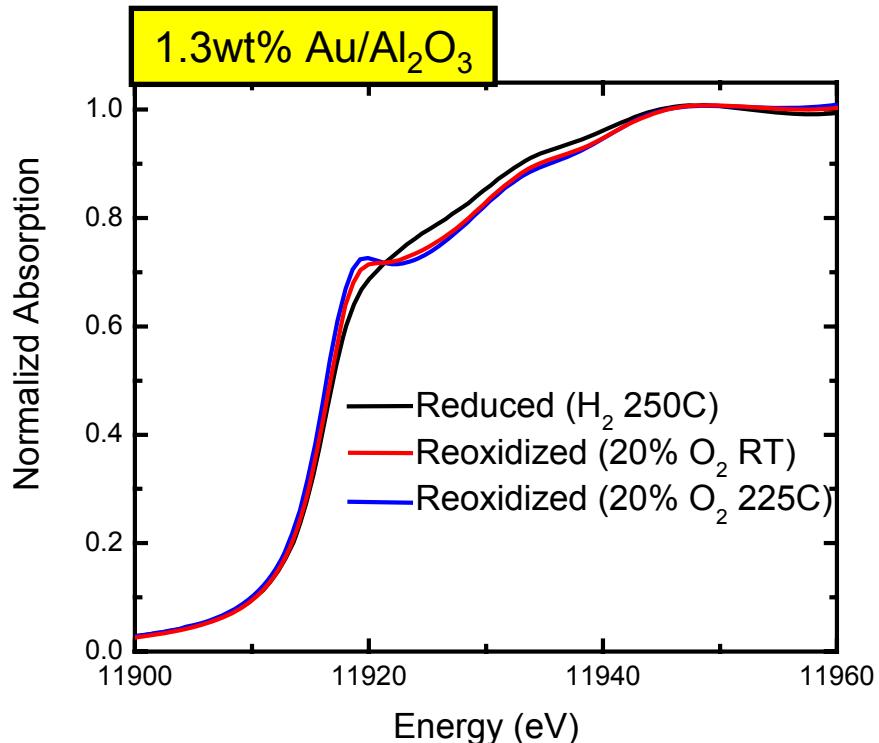
# EXAFS Fitting Results of Reduced Catalysts



*Strong reduction in Au-Au distance with particle size  
No visible influence of support*



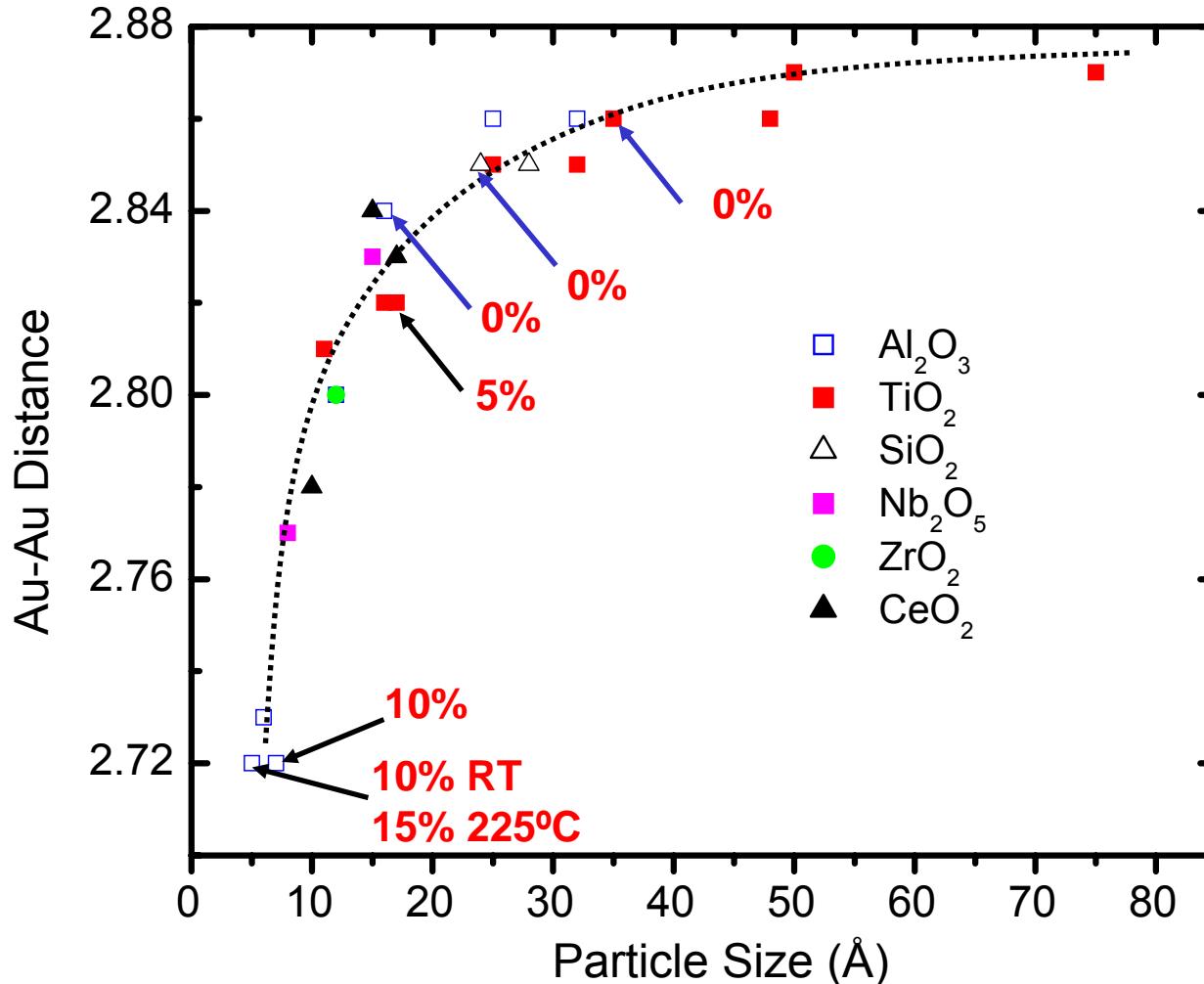
# Exposure to 20% O<sub>2</sub>



	CN	R(Å)	%Au(III)
Reduced	3.6	2.72	0
Reox. RT	3.6 / 0.3	2.72 / 2.04	10
Reox. 225C	2.7 / 0.5	2.71 / 2.04	15



# Gold Oxidation under Oxygen

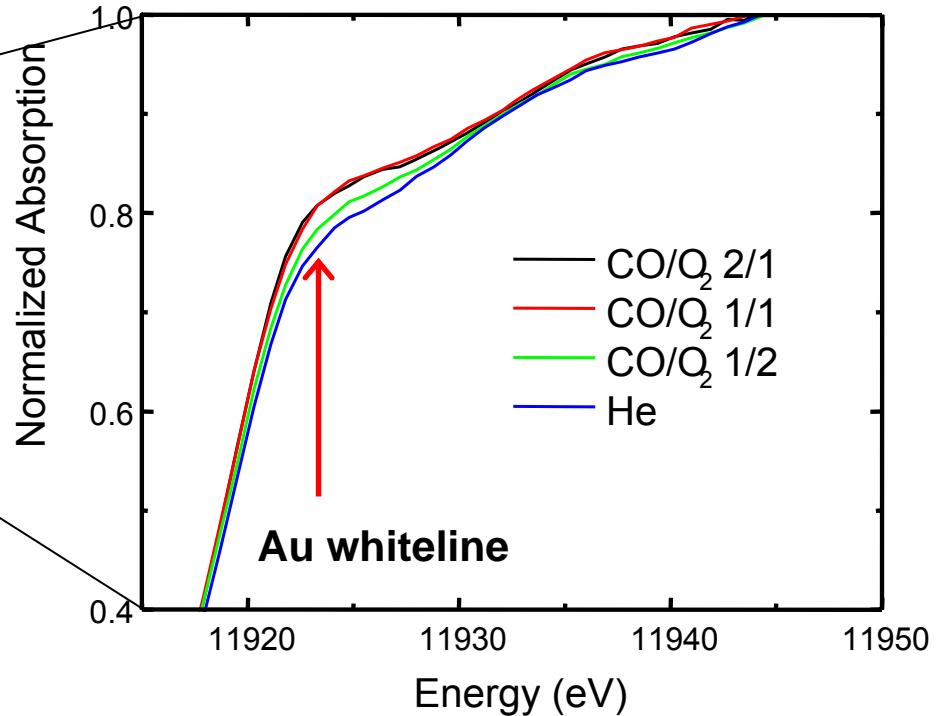
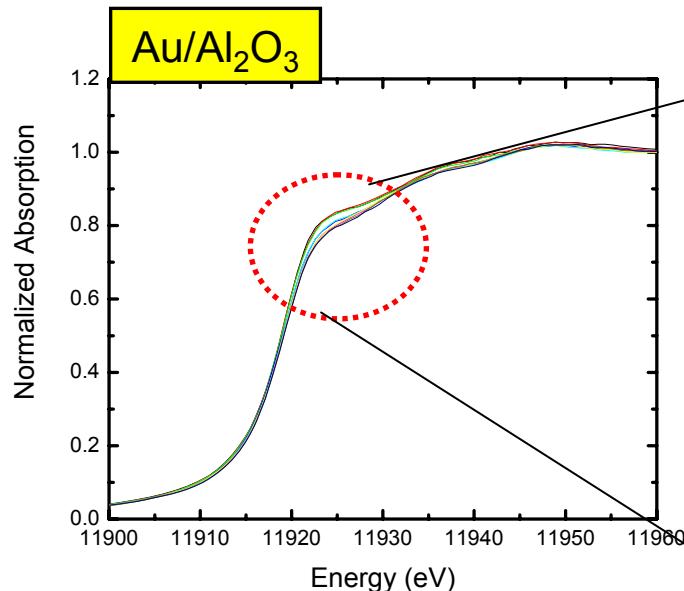


*At most 10-15% reoxidation*



**ETH**

# XAS during CO Oxidation



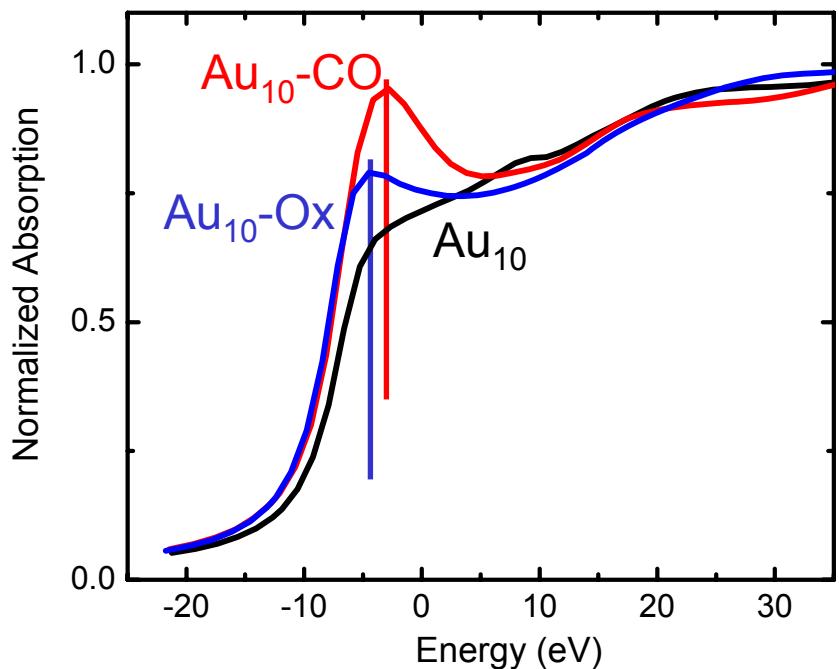
	CN(Au)	R(Au)
He	6.5	2.77
1:1	5.3	2.73
2:1	5.7	2.73
1:2	5.2	2.77

*Small oxygen contribution*

*More intense with more CO:  
holes in the d-band (anti-bonding states)*



# Au L<sub>3</sub>: spectra simulation



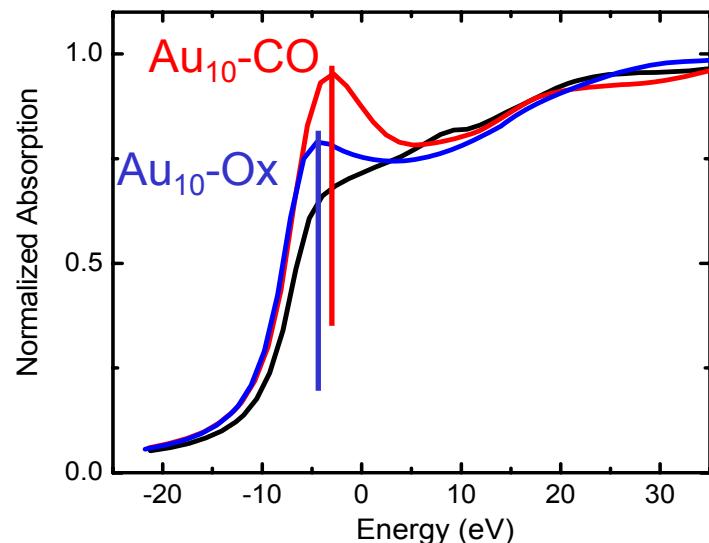
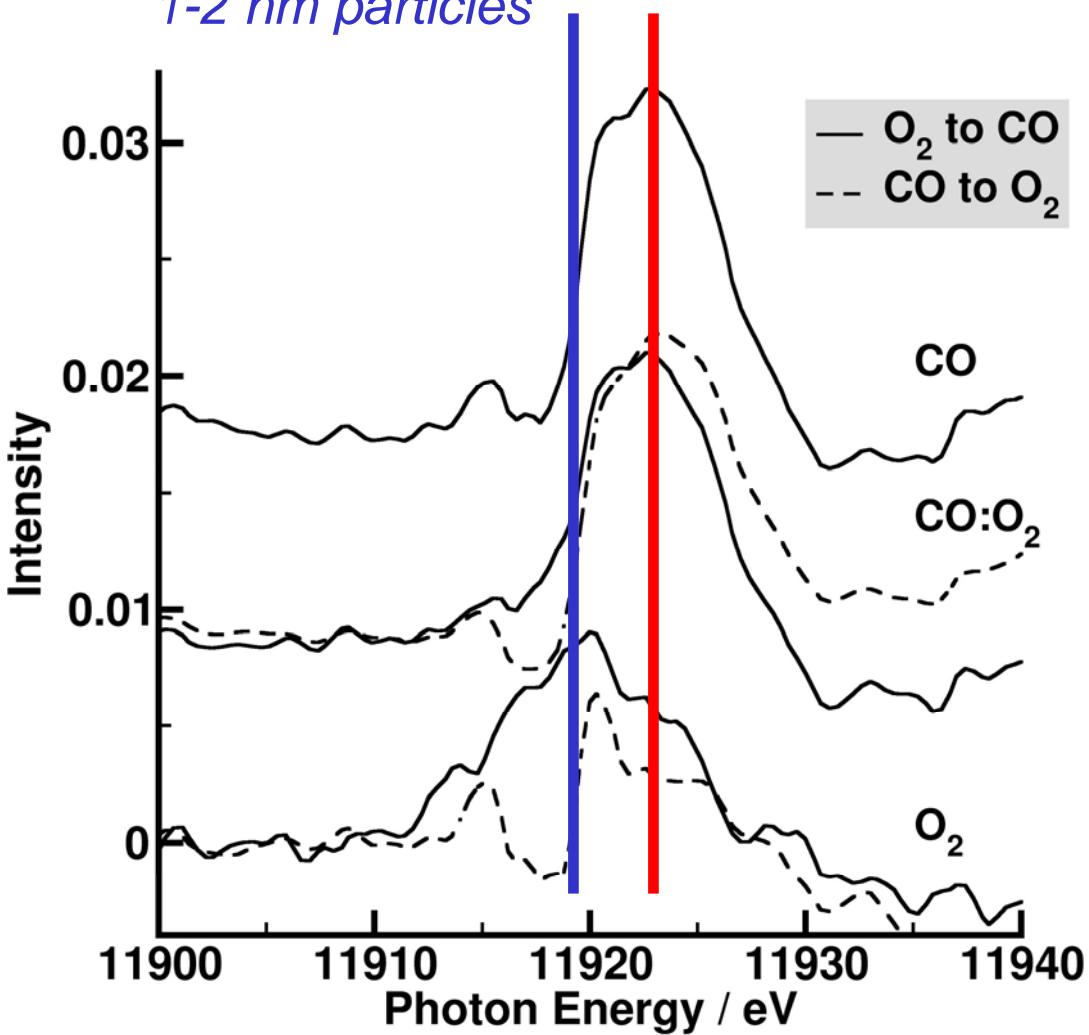
*Charge transfer: d-band holes  
CO different from oxygen*

Full multiple scattering calculations (FEFF8)



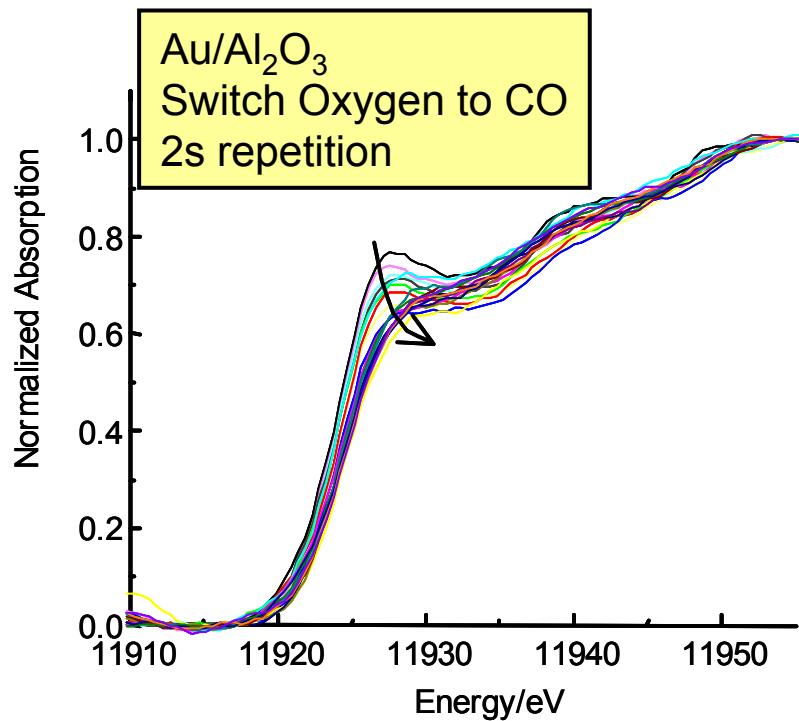
# Au / TiO<sub>2</sub>

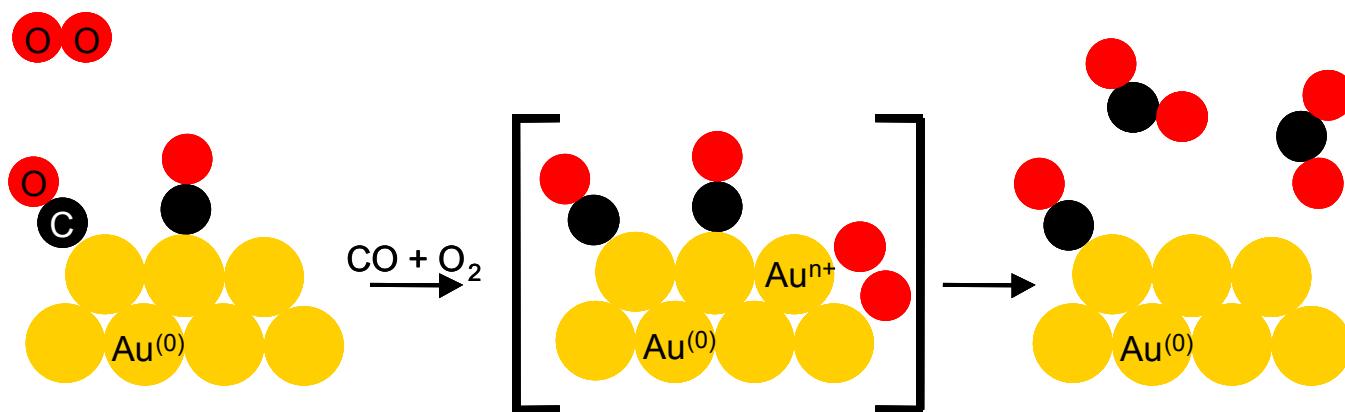
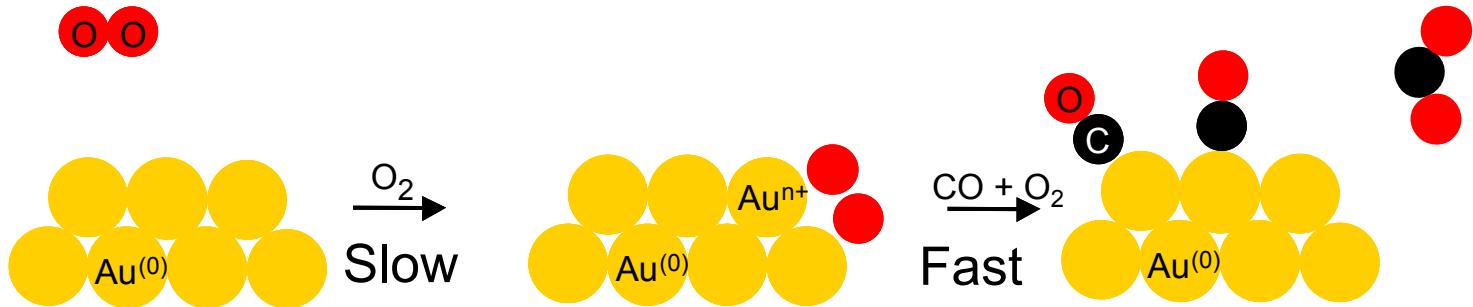
*Difference spectra with reduced Au / TiO<sub>2</sub>  
1-2 nm particles*



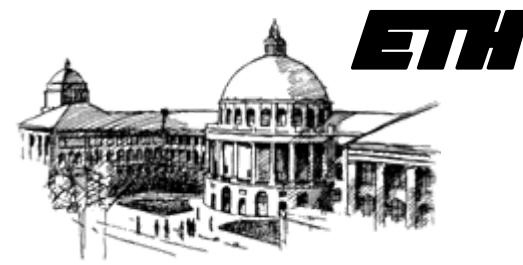
# Gold catalysts and activation of oxygen

- Under (diluted)  $O_2$ : surface oxidation ( $Au/Al_2O_3$  &  $Au/TiO_2$ )
- Switch to  $CO/O_2$ :  $CO$  keeps gold reduced



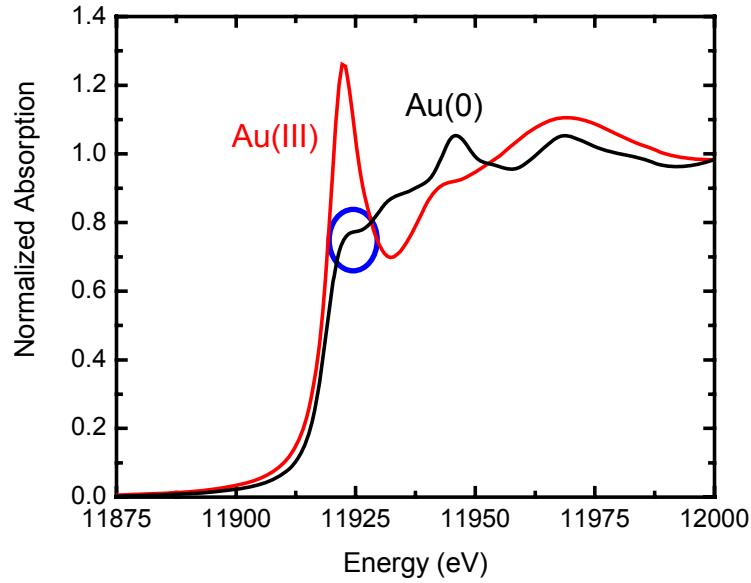


*Reduced gold is active phase*  
*Gold participates in oxygen activation*



Bulk gold is most inert metal: Single Au crystals are unreactive

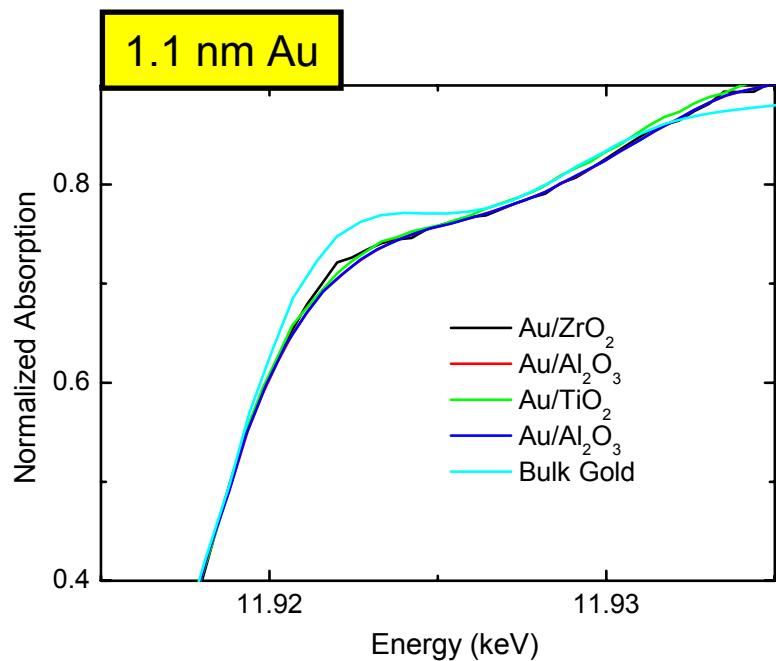
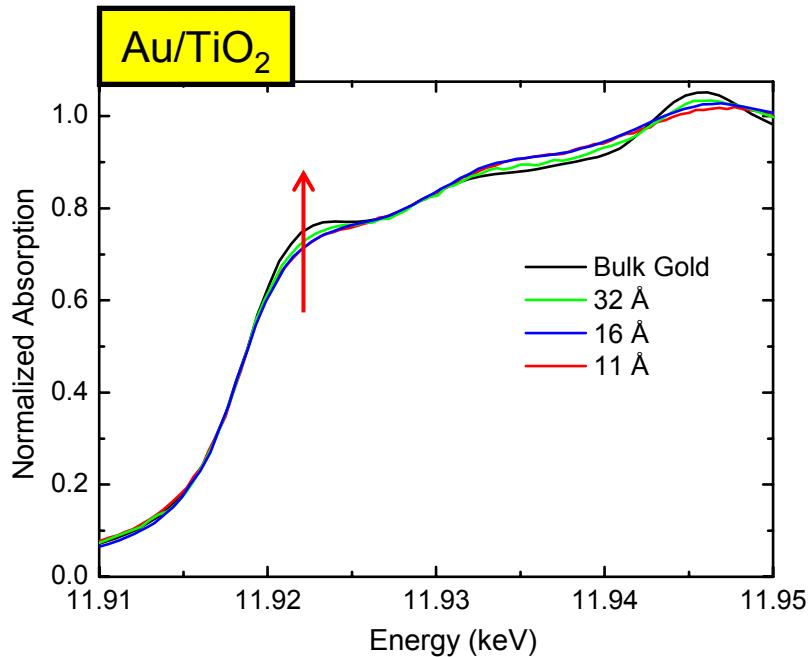
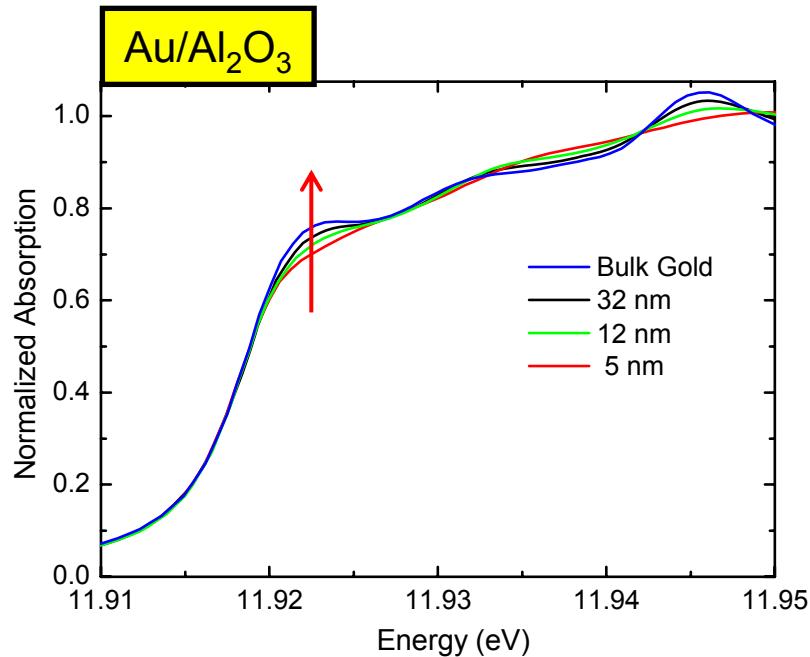
What is different in small particles?



*Whitelines reflect number of holes in the d-band*

*Gold whiteline: spd-rehybridization results in  $5d^{10-x}6sp^{1+x}$*

# Whitelines reflect number of holes in the d-band

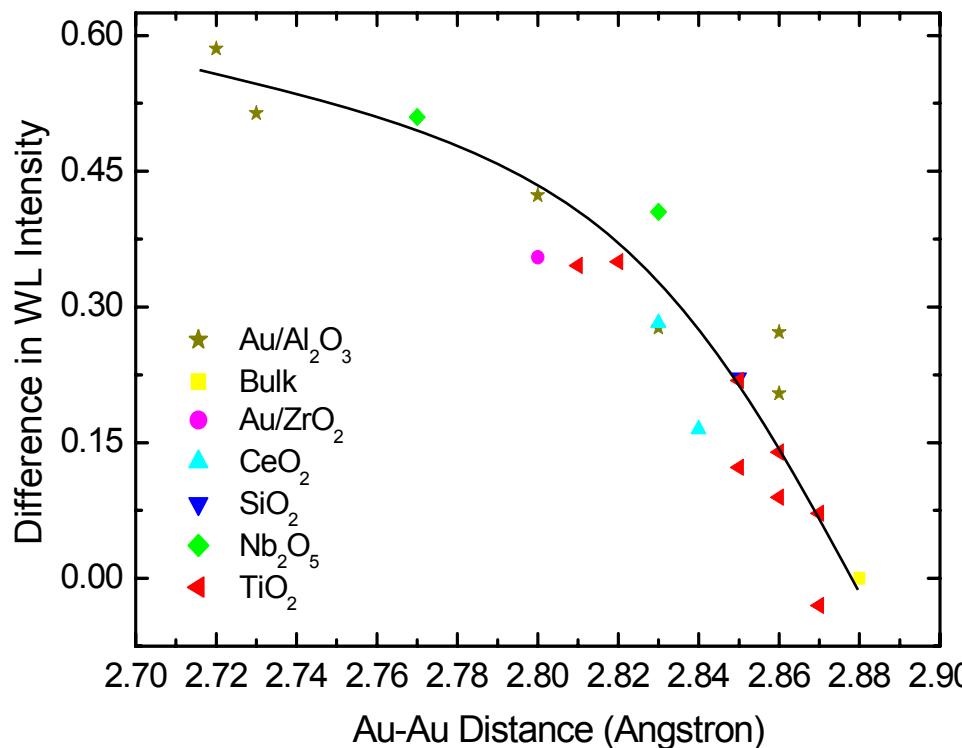
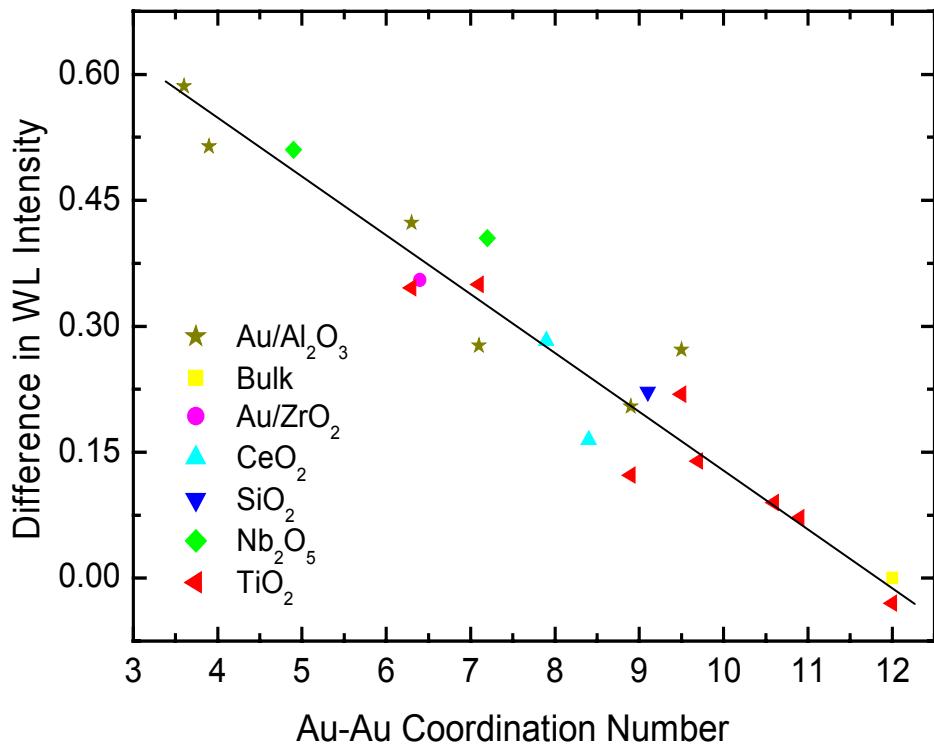


*Whiteline is particle-size dependent*



# Whiteline intensity versus particle size

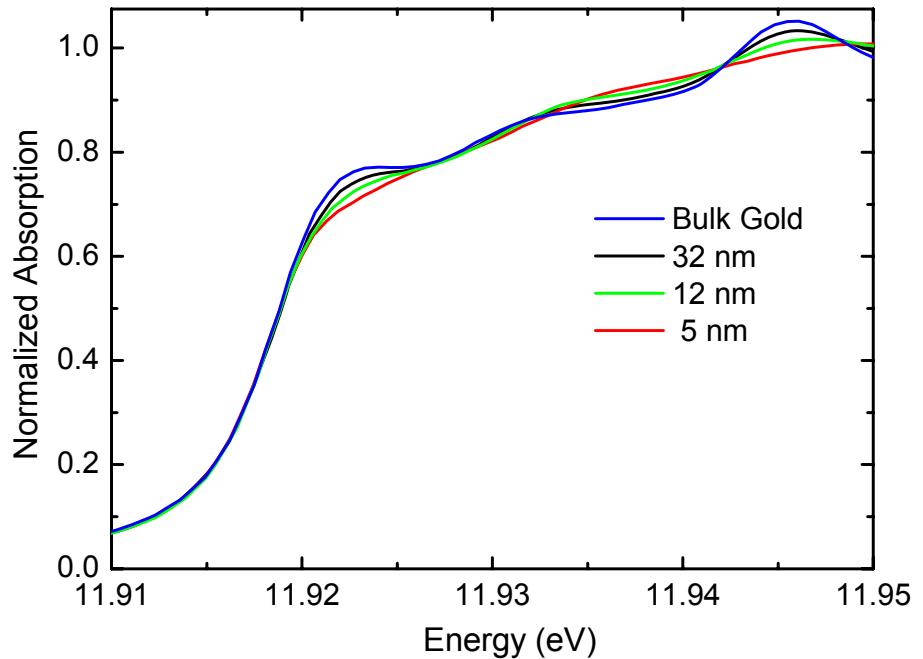
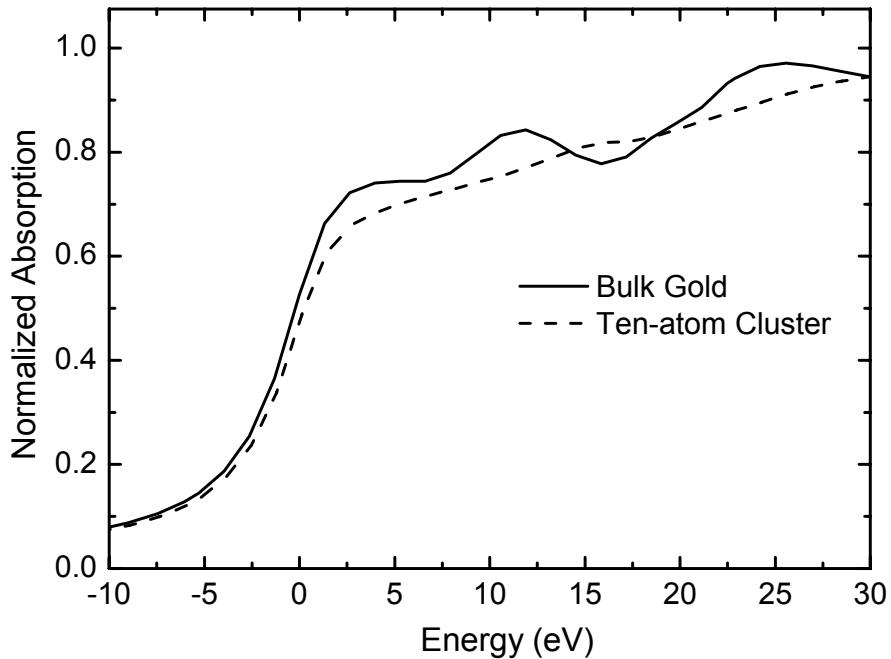
## *Difference intensity with bulk*



*Six supports, one trend  
Larger particles fewer d-electrons*



# FEFF8 simulations

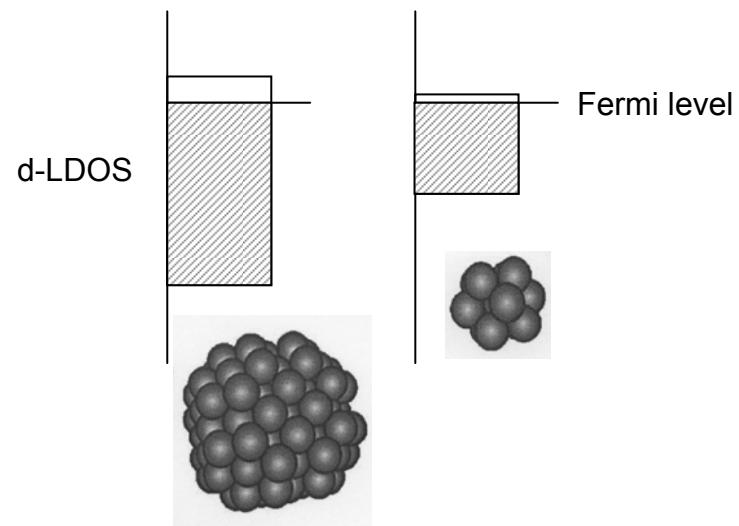
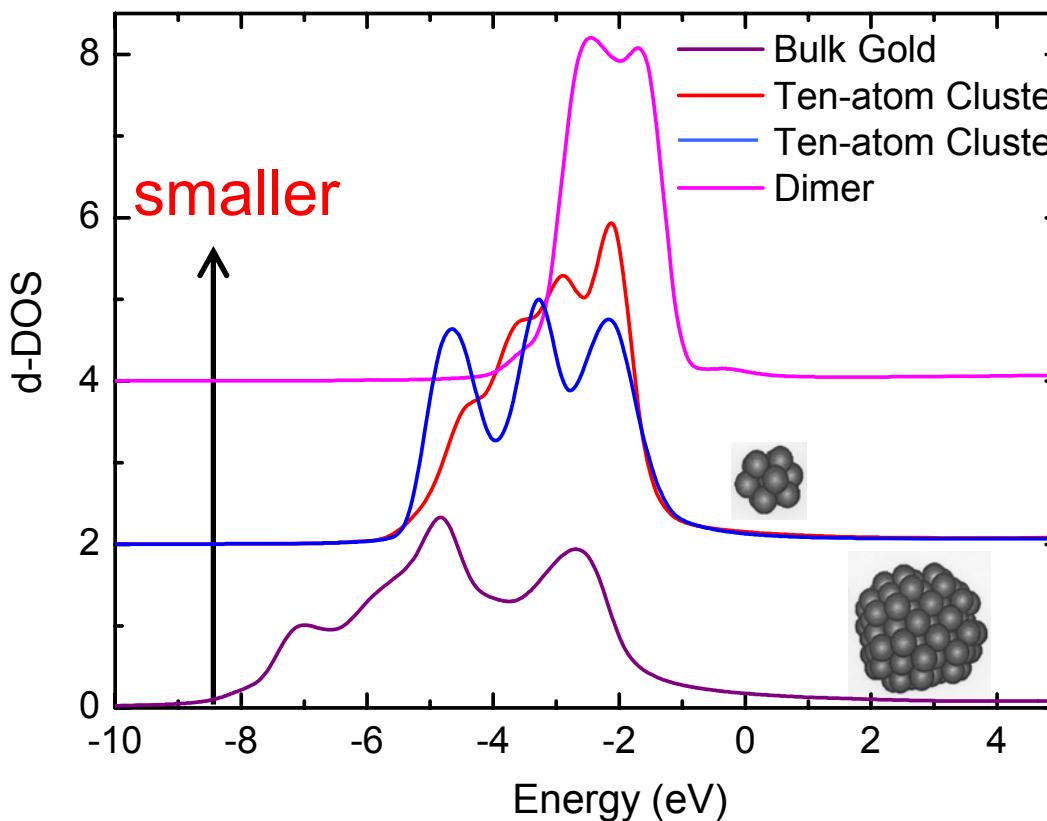


*Smaller particles have different electronic structure  
affected by coordination number and s,p,d-bands*

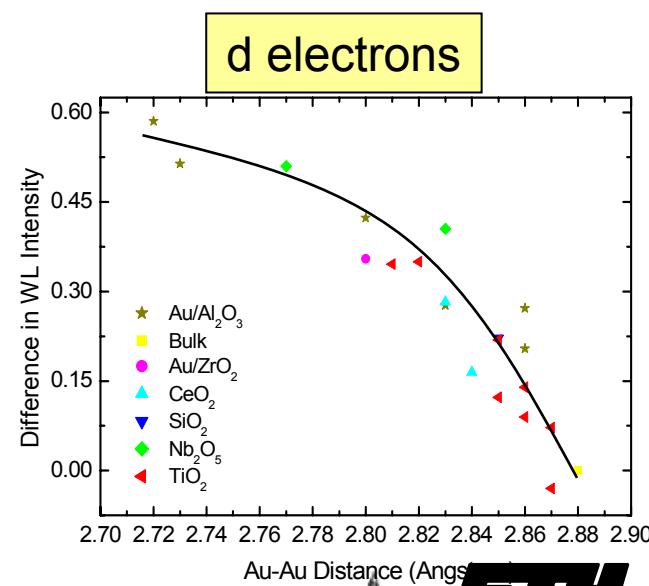
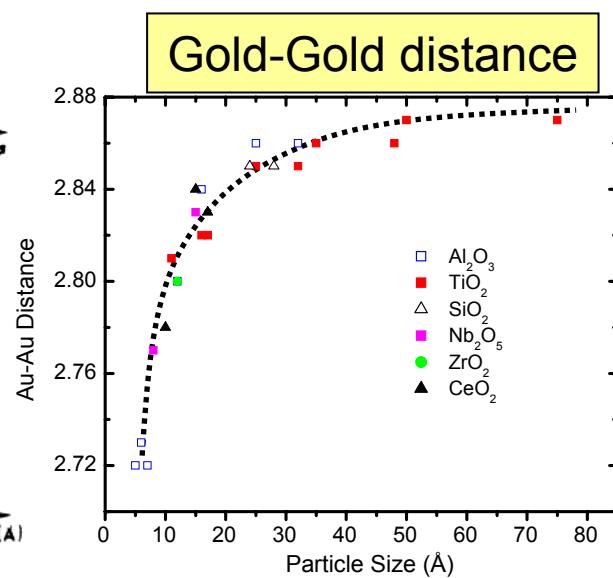
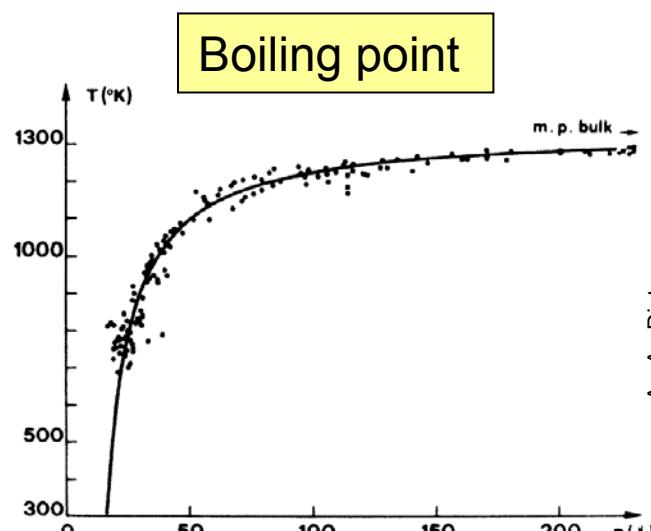
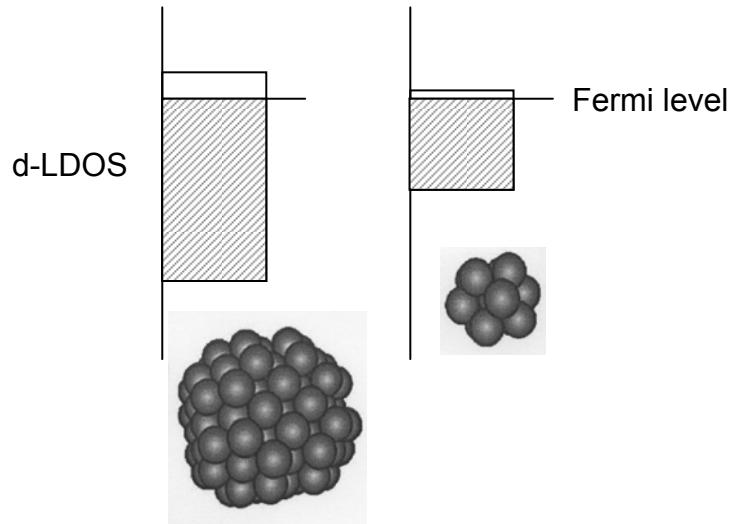
*No support effect on number of d-electrons*



# Projected DOS



- Rehybridization of spd-orbitals ( $5d^{10-x}6sp^{1+x}$ )
- Smaller particles have fewer holes in the d-band
- Particle size dominates support-effect
- Oxygen is activated on gold particle



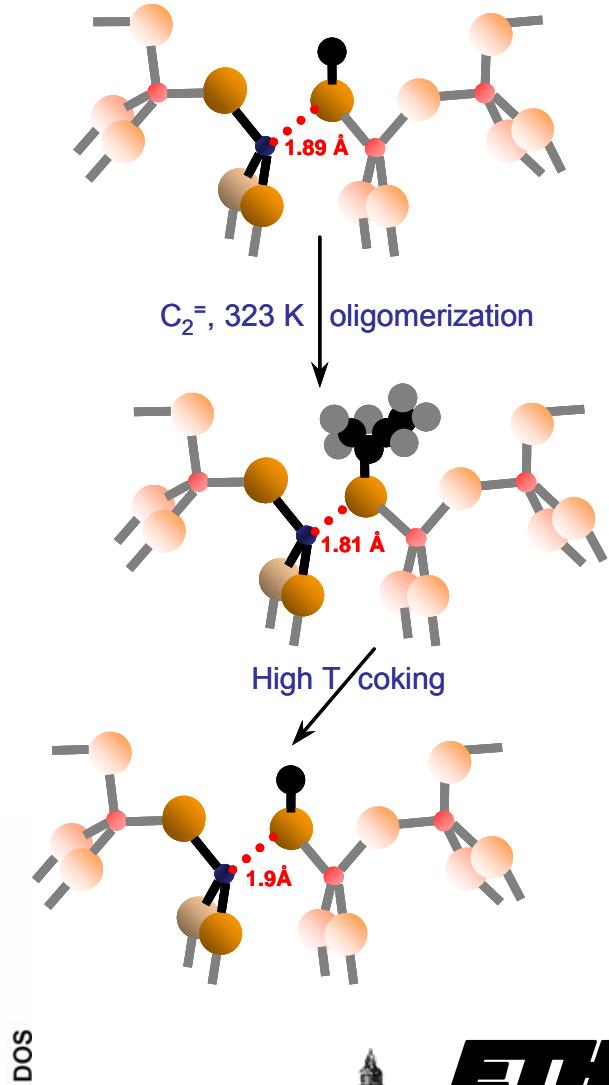
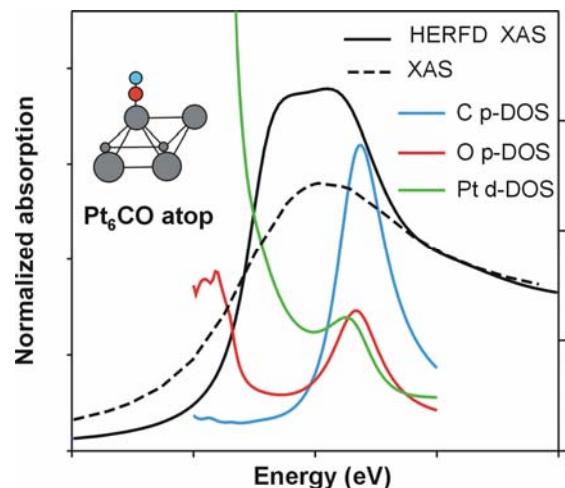
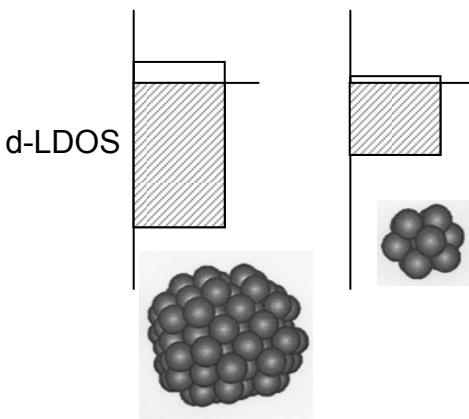
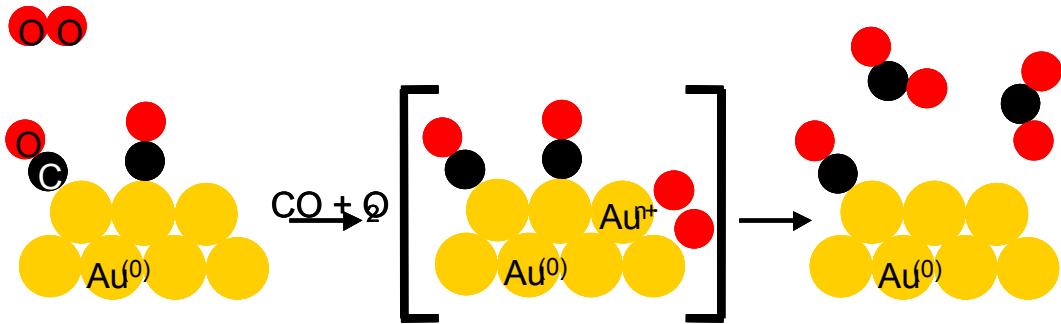
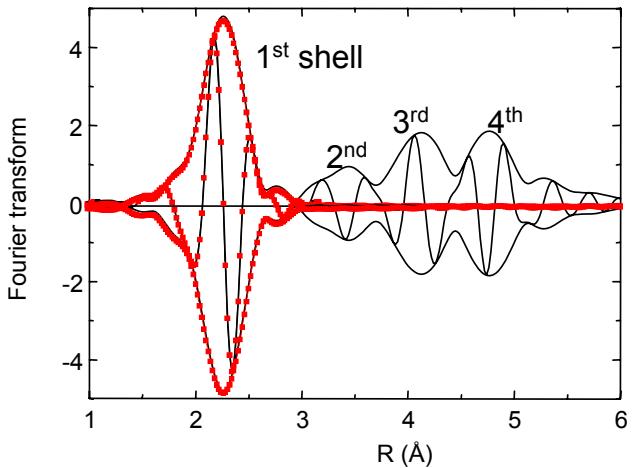
# XAS

- Structure: bond lengths, coordination numbers, DWF
- Geometry
- Oxidation states
- In-situ conditions
- Element specific

Sample damage  
Model free data fitting  
Asymmetric distribution functions  
Mixtures (Bulk technique)  
....



# Summary



ETH

# Acknowledgement

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