NEXAFS

Modern Methods in Heterogeneous Catalysis Research

.....we are done in 2009!

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Abbreviations

XAS: X-ray Absorption Spectroscopy

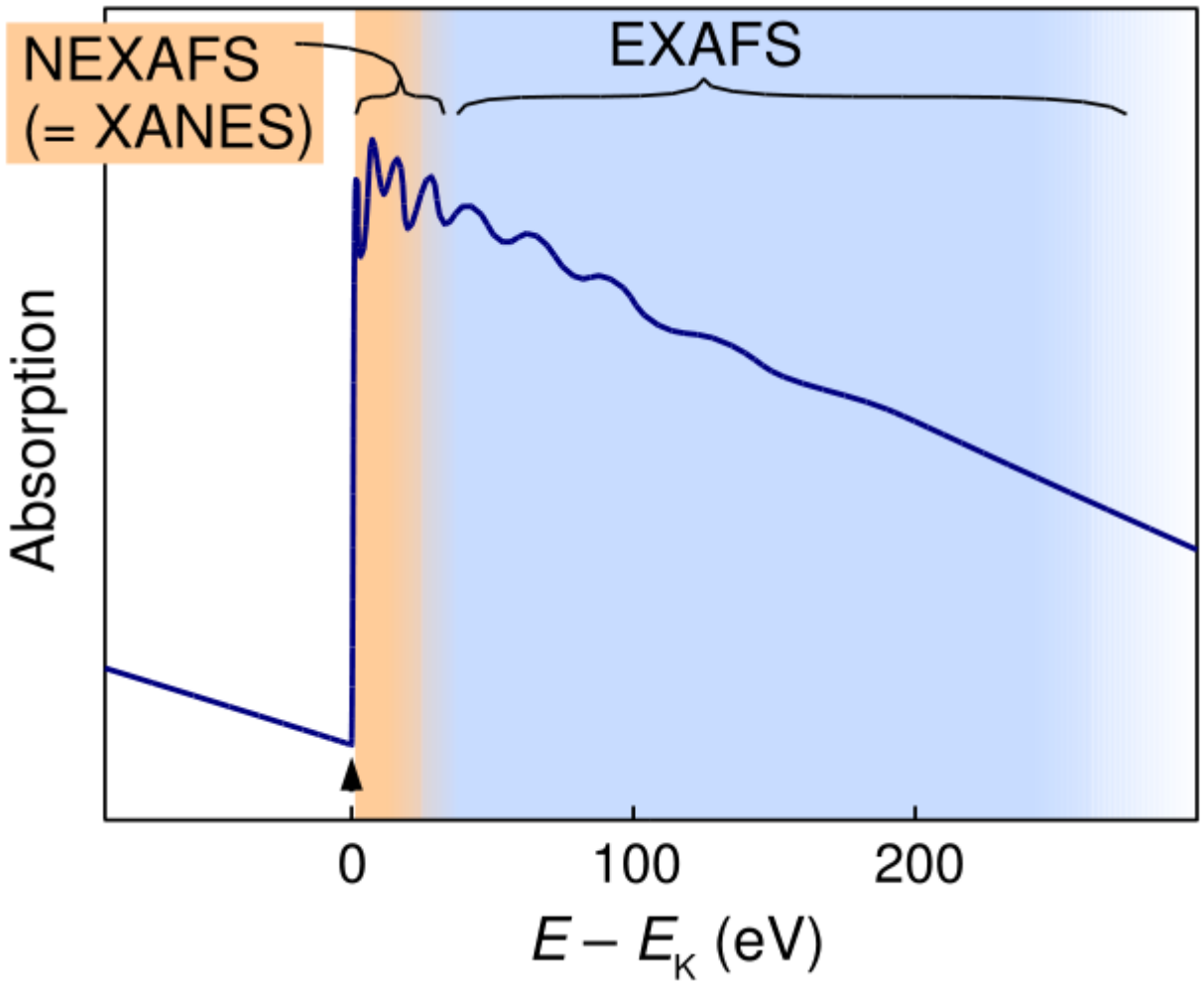
NEXAFS : Near Edge X-ray Absorption Fine Structure
(preferentially used for low Z elements : O, N, C,.....)

XANES: X-ray Absorption Near Edge Structure

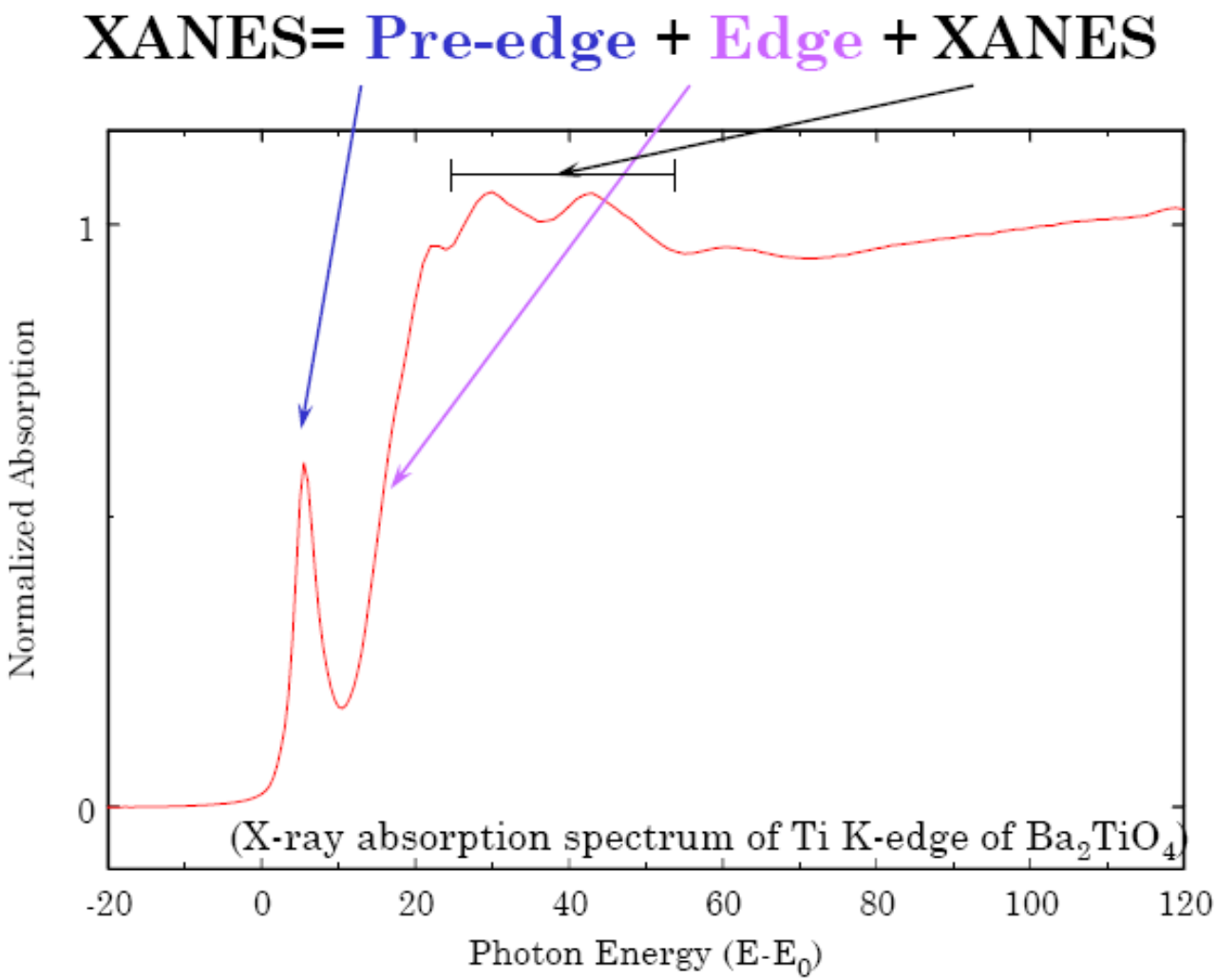
EXAFS: Extended X-ray Absorption Fine Structure

SEXAFS: Surface Extended X-ray Absorption Fine Structure

NEXAFS and EXAFS



What is NEXAFS/XANES?



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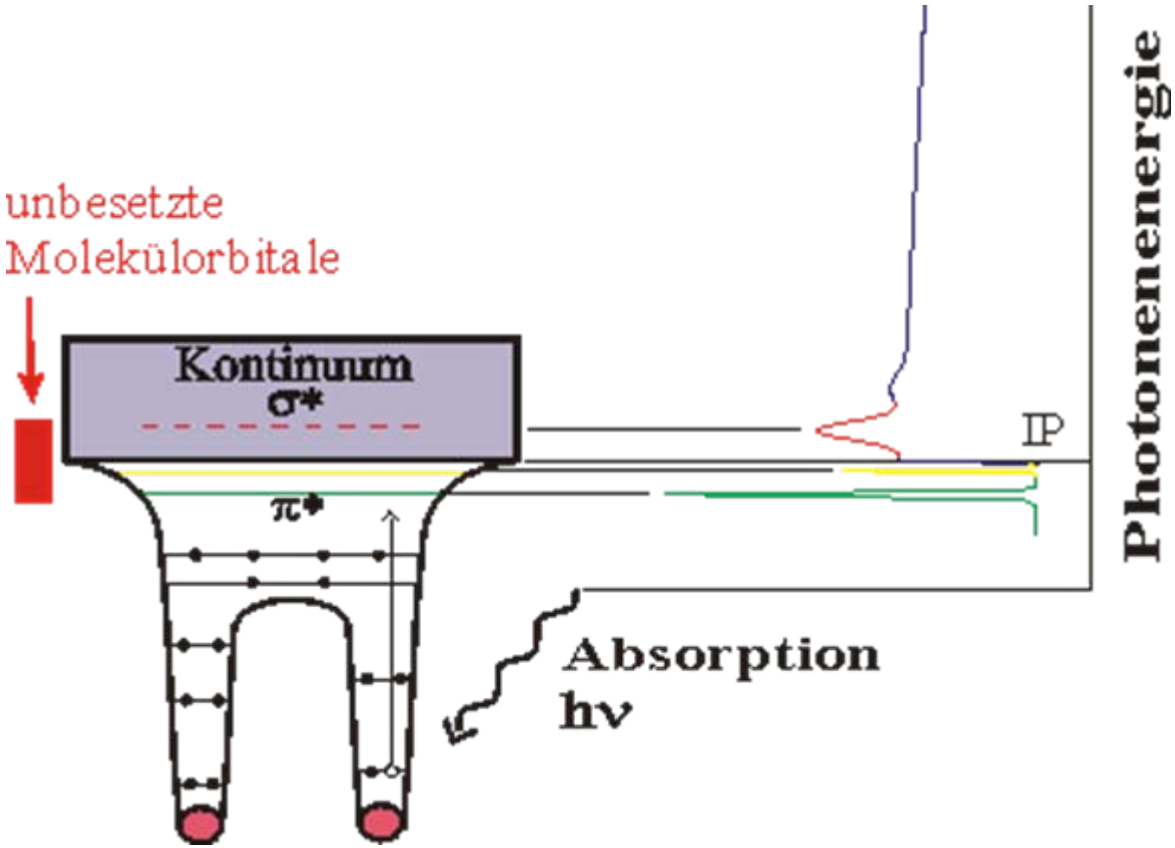
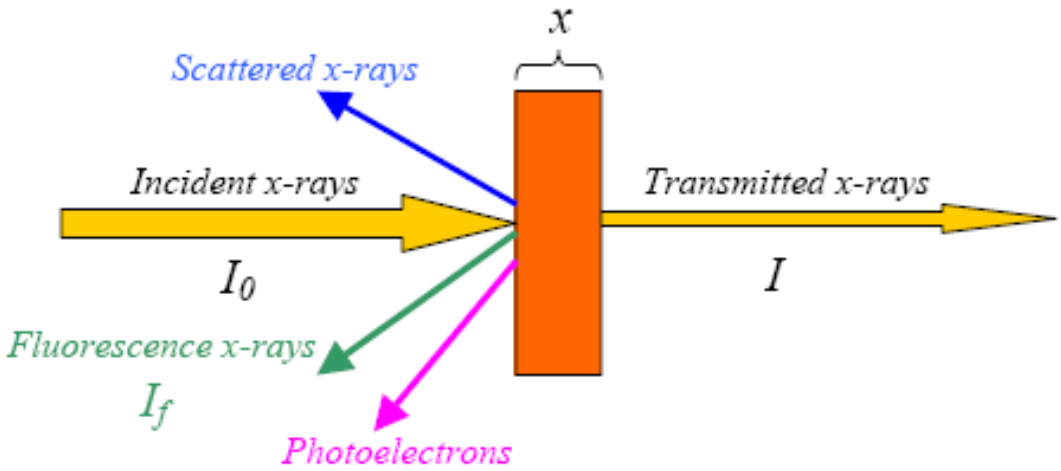
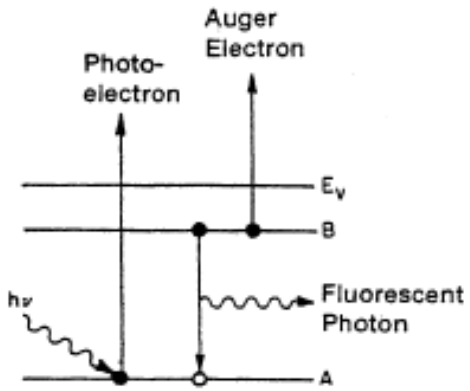
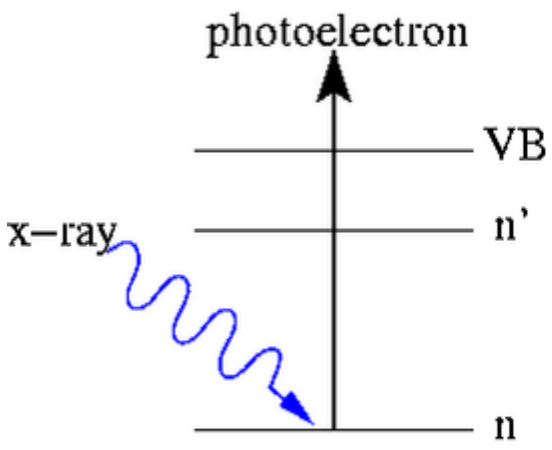
Valence- and Rydberg States in Molecules



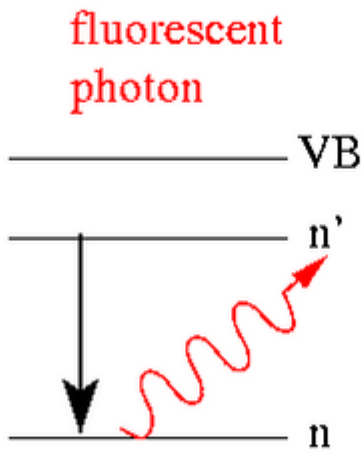
Detection



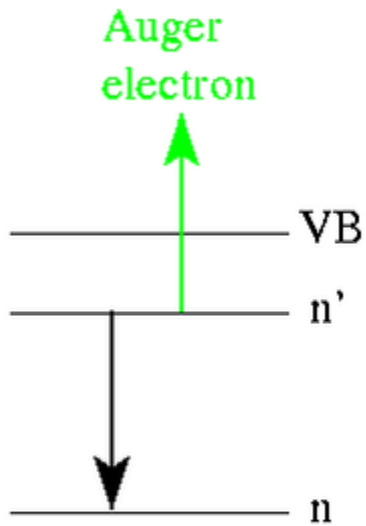




(a)



(b)

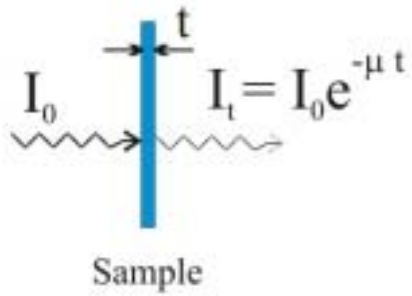


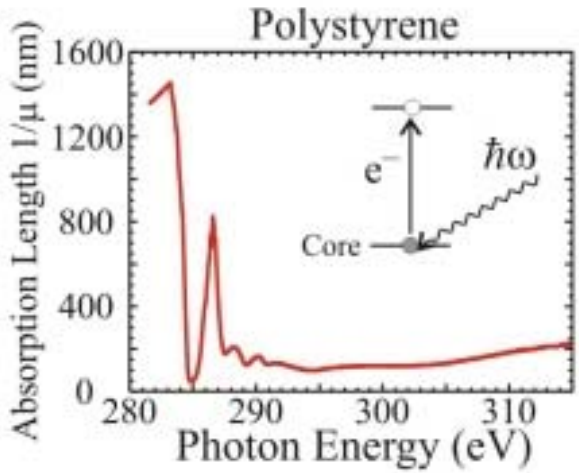
(c)

Detection

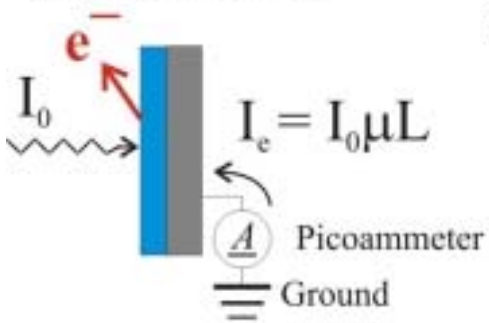
X-Ray Absorption Spectroscopy

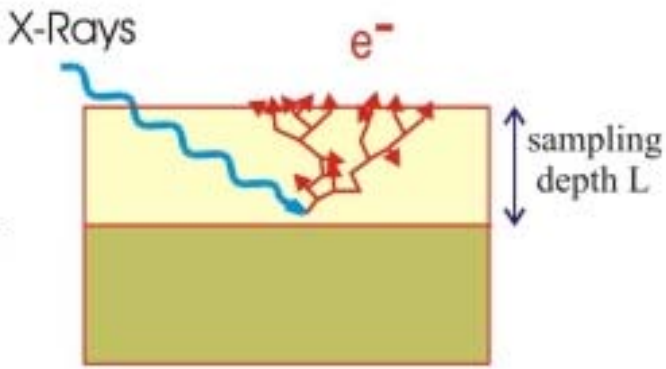
Transmission

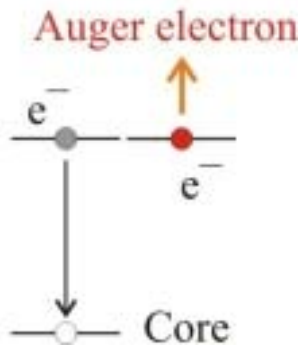




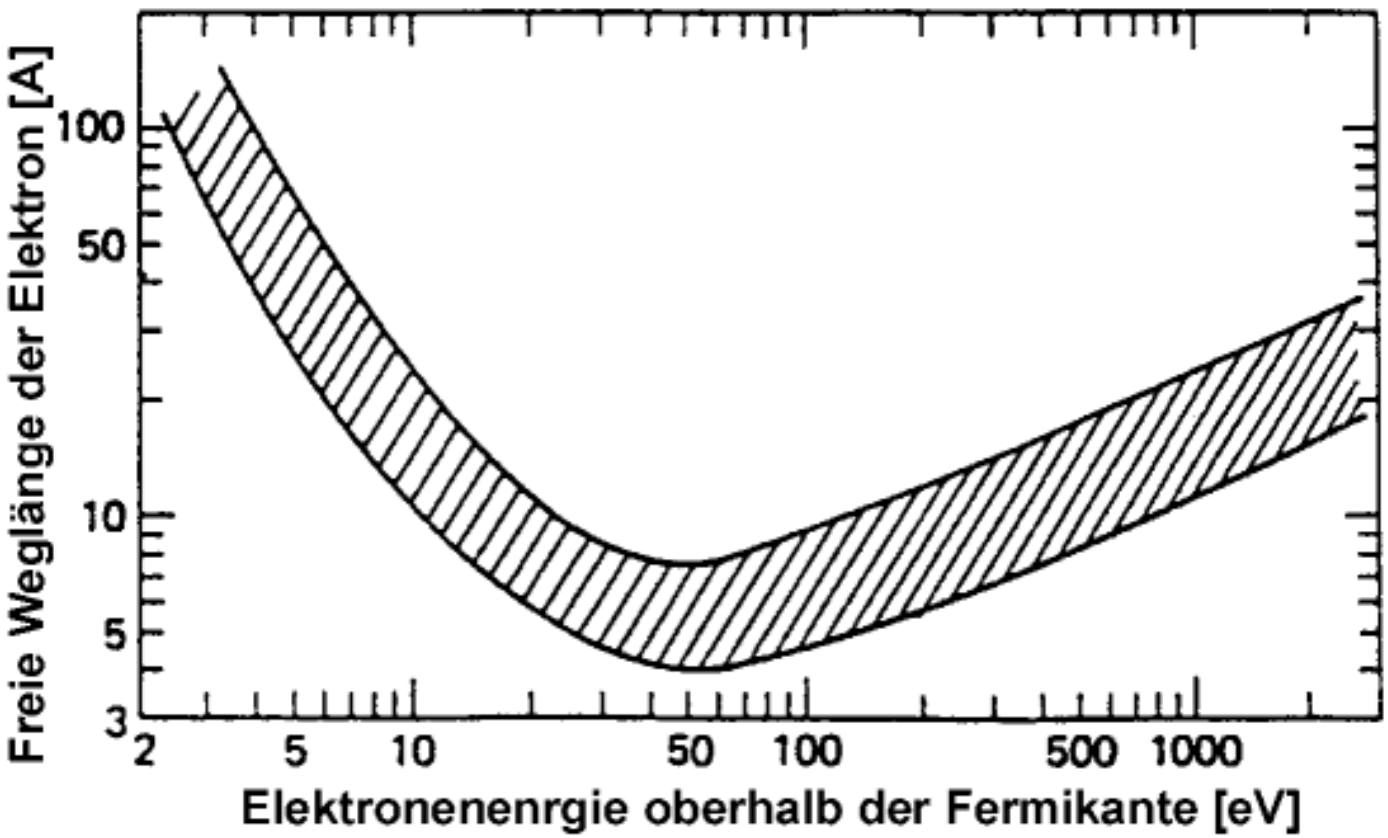
Electron Yield







Mean free path of electron in solids



XANES transitions

- XANES directly probes the angular momentum of the unoccupied electronic states: these may be bound or unbound, discrete or broad, atomic or molecular.
- Dipole selection rules apply*: $\Delta l = \pm 1$, $\Delta j = \pm 1$, $\Delta s = 0$.
- Primary transition will be:
  - $s \rightarrow p$ for K ($1s$ core electron) and L_1 ($2s$ core electron initial state) edges
  - $p \rightarrow d$ for L_2 ($2p_{½}$) and L_3 ($2p_{3/2}$) edges
- But…..final state usually not atomic-like and may have mixing (hybridization) with other orbitals. This is often the interesting part of the XANES!

* Some transitions are true quadrupolar transitions. These are usually very weak.

XANES interpretation

- The EXAFS equation breaks down at low-*k*, which complicates XANES interpretation.
- **We do not have a simple equation for XANES.**

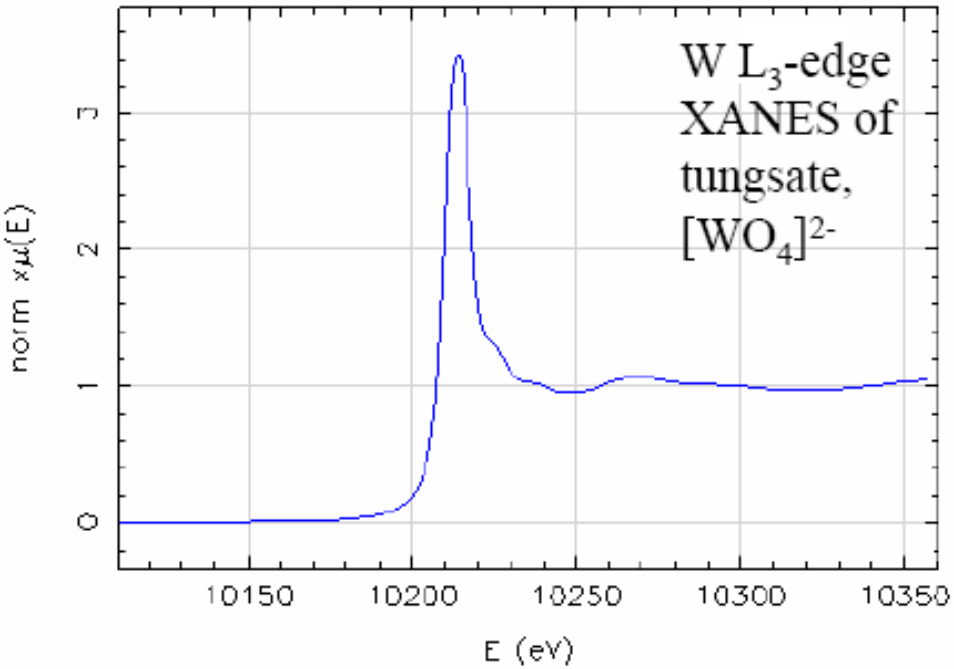
XANES can be described ***qualitatively*** (and nearly ***quantitatively***) in terms of:

coordination chemistry	regular, distorted octahedral, tetrahedral…
molecular orbitals	p-d hybridization, crystal field theory
band structure	the density of available occupied electronic states
multiple scattering	multiple bounces of the photoelectron

- These chemical and physical interpretations are all related:

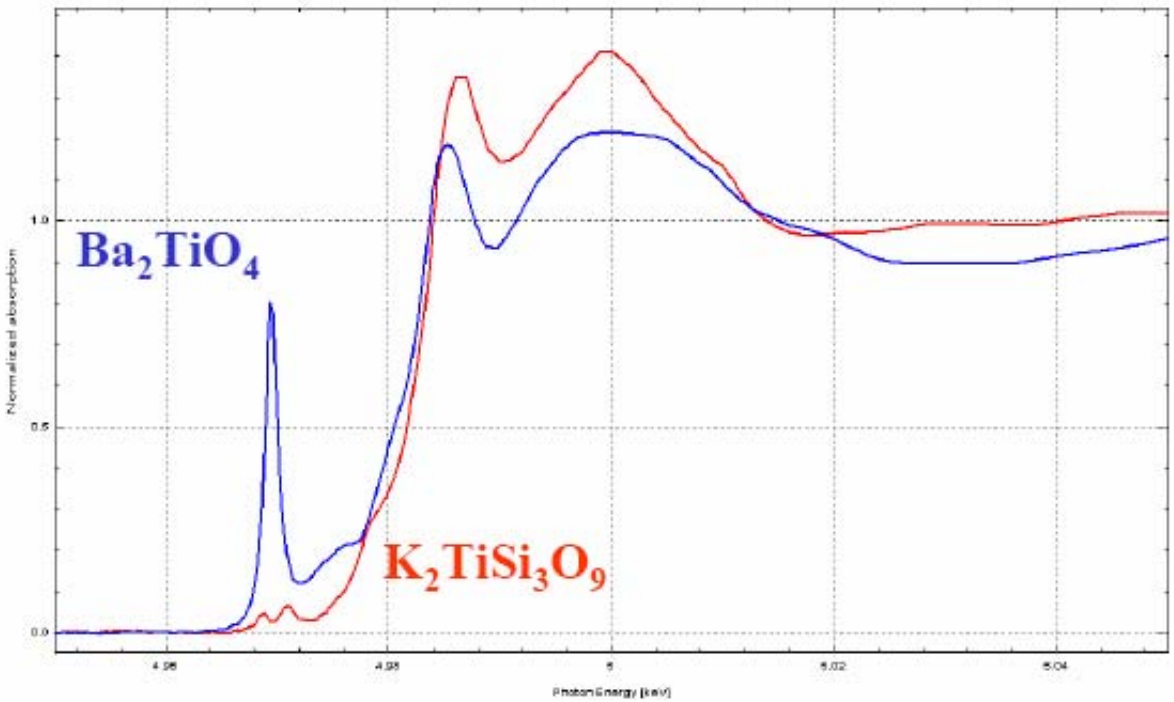
What electronic states can the photoelectron fill?

„White Line“



- In years past x-ray absorption spectra were taken with use of photographic plates.
- Absorption edges appeared as unexposed bands on the plate (developed in negative), or “white lines”.
- Very prominent for L-edges of transition metals in high oxidation states.

Local coordination environment



Both Ti^{4+}

Ba_2TiO_4

$K_2TiSi_3O_9$

- Ti K-edge XANES shows dramatic dependence on the local coordination chemistry.

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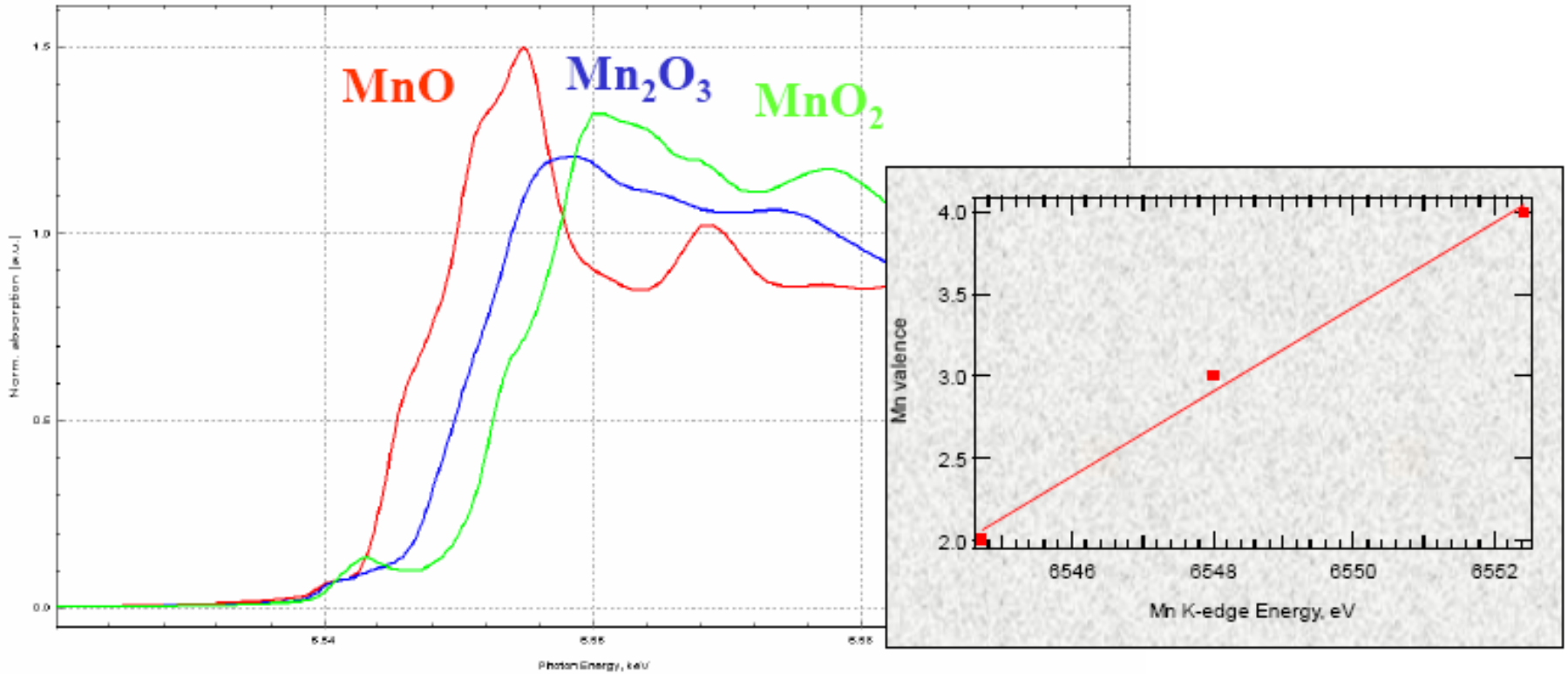
Estimation of the oxidation state



- Many edges of many elements show significant edge shifts (binding energy shifts) with oxidation state.
- First observation was by Berengren for phosphorus in 1920*!

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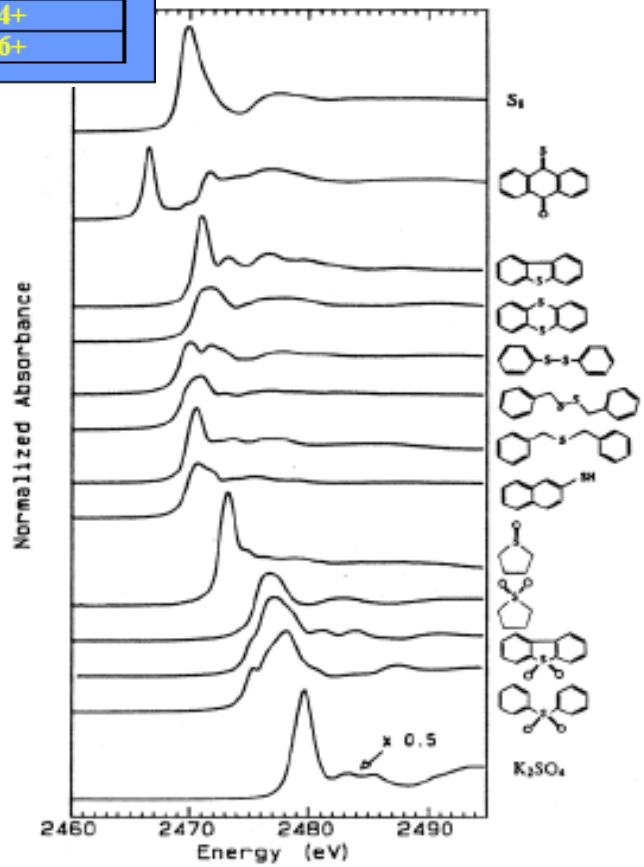
*See "A history of X-ray absorption fine structure", R. Stumm von Bordwehr, Ann. Phys. Fr. 14 (1989) 377-466)

XANES Analysis: Oxidation state of sulfur

Sulfur type	Formal oxidation state
Sulfide	2-
Thiophene	1+
Sulfoxide	2+
Sulfone	4+
Sulfate	6+



Sulfur K-edge XANES used to identify and quantify the form of sulfur in heavy petroleum, coals, soils etc.

11 eV edge shift from S^{2-} to S^{6+}.

Spectra of S in similar environments similar: thiophene, benzothiophene.

Can be used as fingerprint.

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Reference: George and Gorbaty, J. Am. Chem. Soc. 101 (1979) 3182

What do we learn from XANES?

XANES is strongly sensitive to the chemistry (formal oxidation state and geometry) of the absorbing atom.

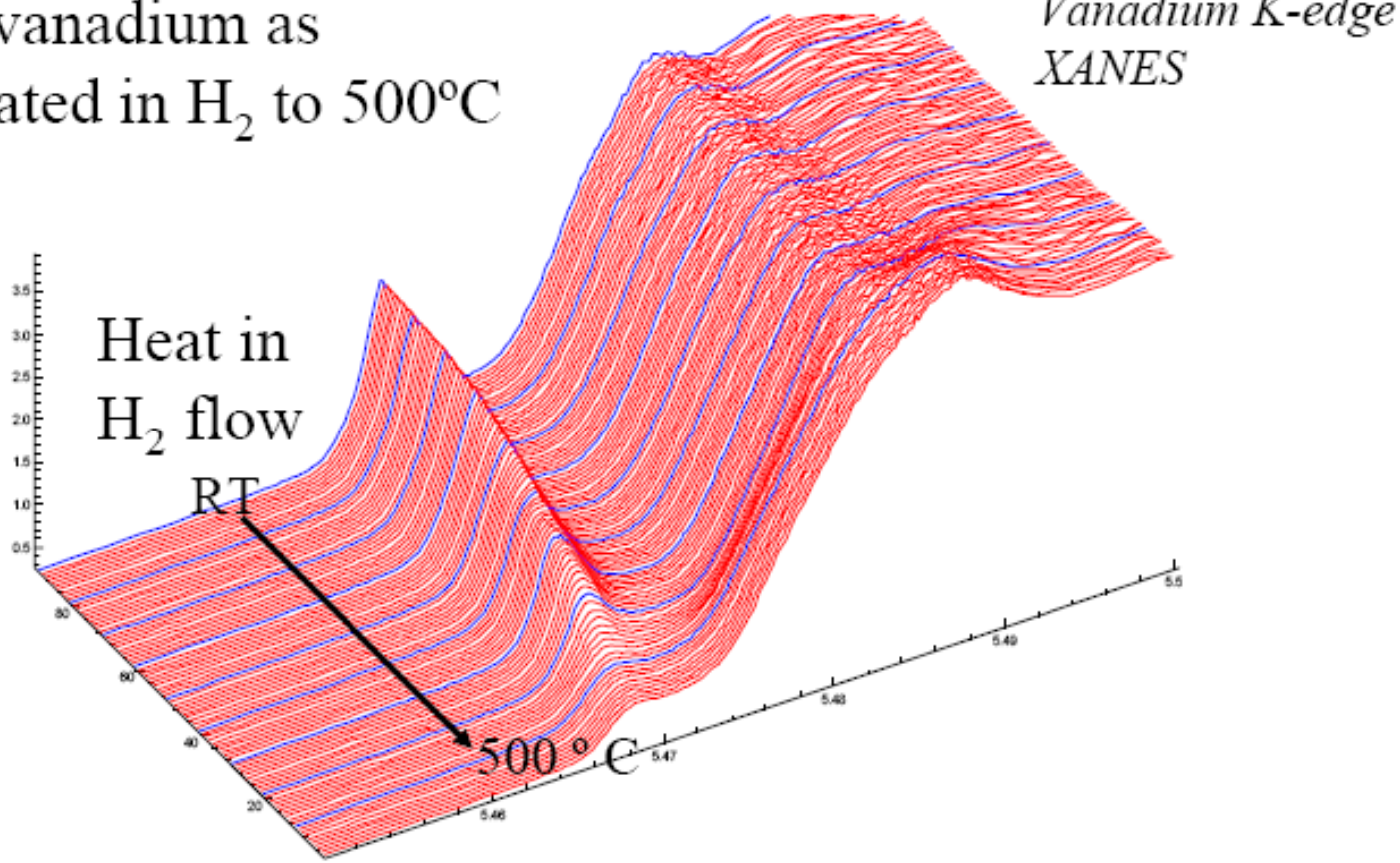
Region	Transitions	Information Content
Pre-edge	Features caused by electronic transitions to empty bound states. Transition probability controlled by dipolar selection rules.	Local geometry around absorbing atom. Dependence on oxidation state and bonding characteristics (chemical shift).
Edge	Defines ionization threshold to continuum states.	Dependence on oxidation state (chemical shift), main edge shifts to higher energy with increased oxidation state. (As much as 5 eV per one unit change).
XANES	Features dominated by multiple-scattering resonances of the photoelectrons ejected at low kinetic energy. Large scattering cross section.	Atomic position of neighbors: interatomic distances and bond angles. Multiple scattering dominates but *ab initio* calculations providing accessible insight (e.g. FEFF8).

Advantages of NEXAFS vs. EXAFS

- Spectra simpler to measure than EXAFS: features intense, concentrated in small energy region.
- Weak temperature dependence (Debye-Waller), so spectra can be recorded at reaction temperature (*in situ*):
  - $\mathrm{Exp}(-2k^2\sigma^2) = \exp(-2(0.5)^2 \times 0.005) \sim 1$
- Faster to measure than full spectrum: <msec demonstrated.
- Sensitive to chemical information: valence, charge transfer.
- Probes unoccupied electronic states: important in chemistry.
- Often used as simple "fingerprint" to identify presence of a particular chemical species.
- Beamlines with micro-probe capabilities can also scan energy and obtain XANES spectra with elemental distribution.

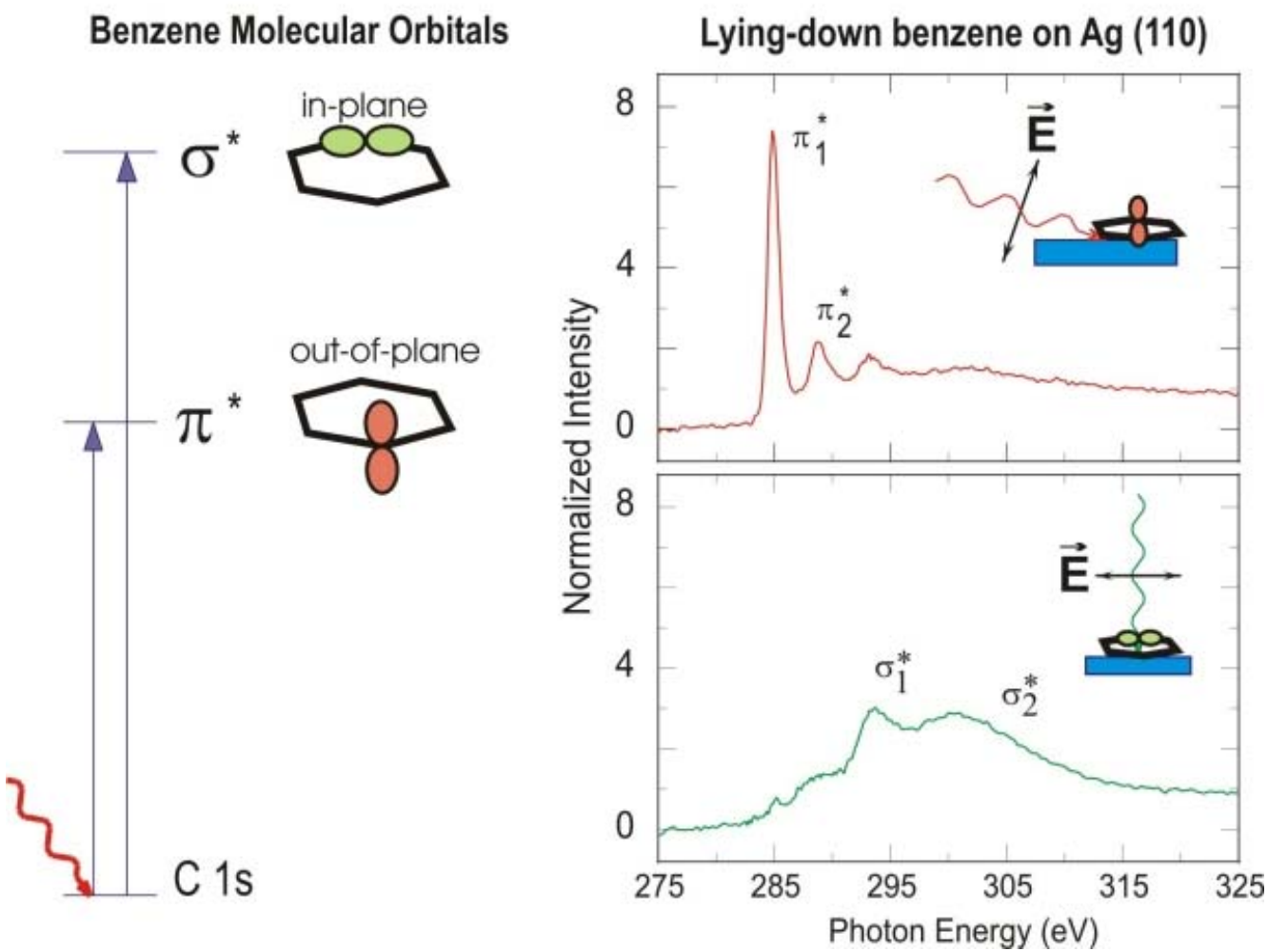
Time Evolution of XANES: Kinetics

TPR-XANES showing reduction of vanadium as catalyst is heated in H_2 to 500ºC



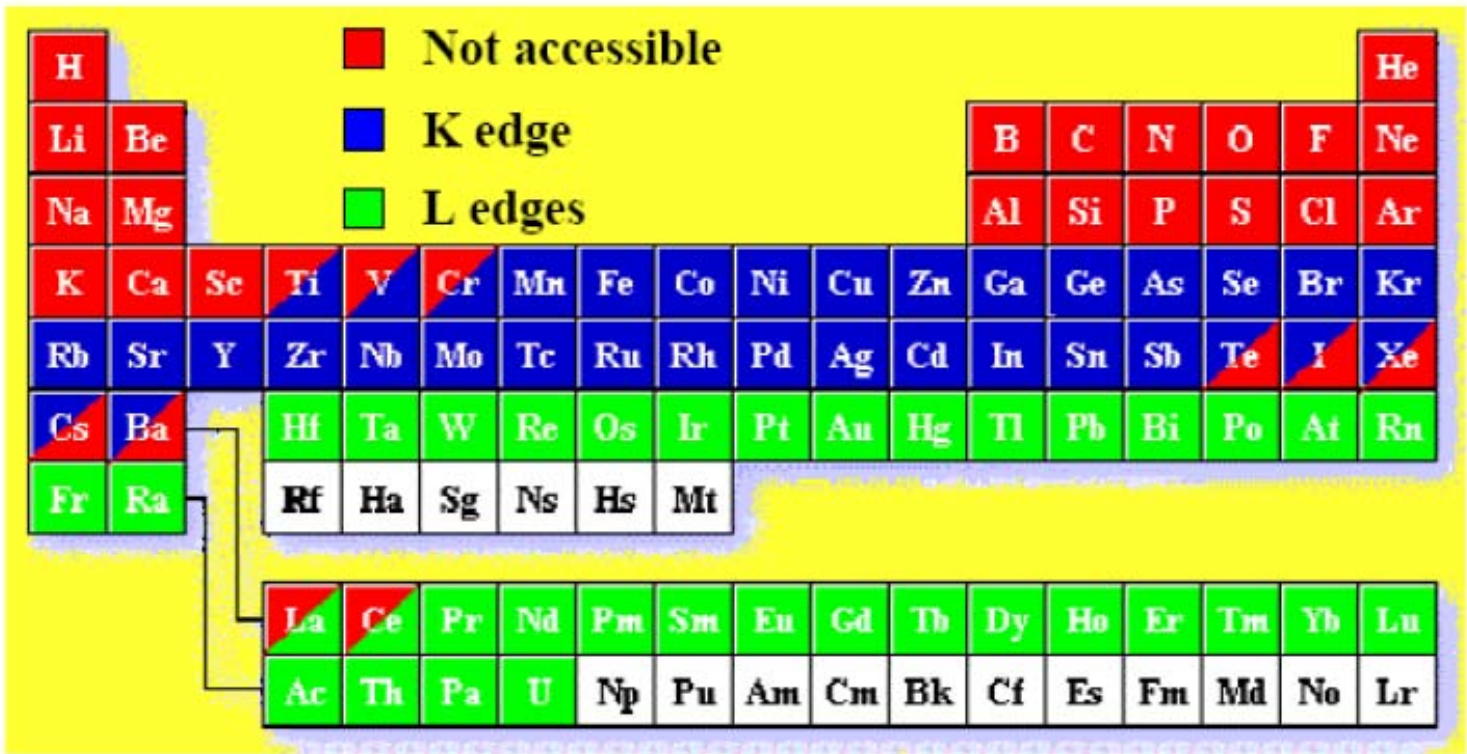
80 sec/scan

Polarisation dependency



This is not completely right!

Elements for EXAFS



Synchrotronradiation Facilities in the soft X-ray range

ALS (LBL, Berkeley CA USA)

Astrid (Aarhus, Dänemark)

BESSY (Berlin, Deutschland)

Elettra (Trieste, Italy)

Superaco (Orsay, France)

Max-Lab (Lund, Schweden)

NSLS (BNL, Brookhaven, NY USA)

PAL (Pohang, Korea)

Photon Factory at KEK (Japan)

SLS (Villingen, Schweiz)

Spring-8 (Japan)

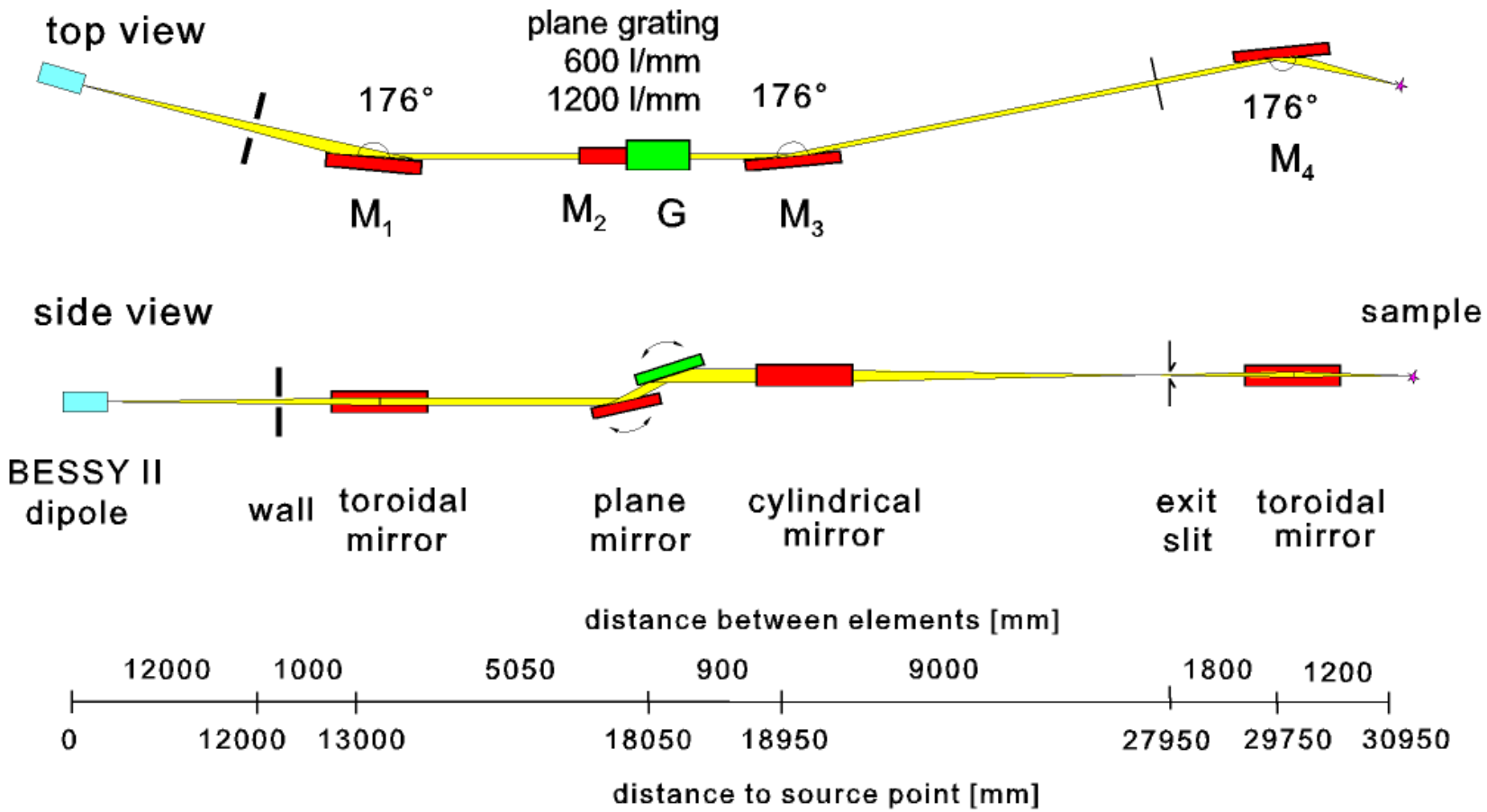
SRC (Staughton, WI USA)

SRS (Daresbury, UK)

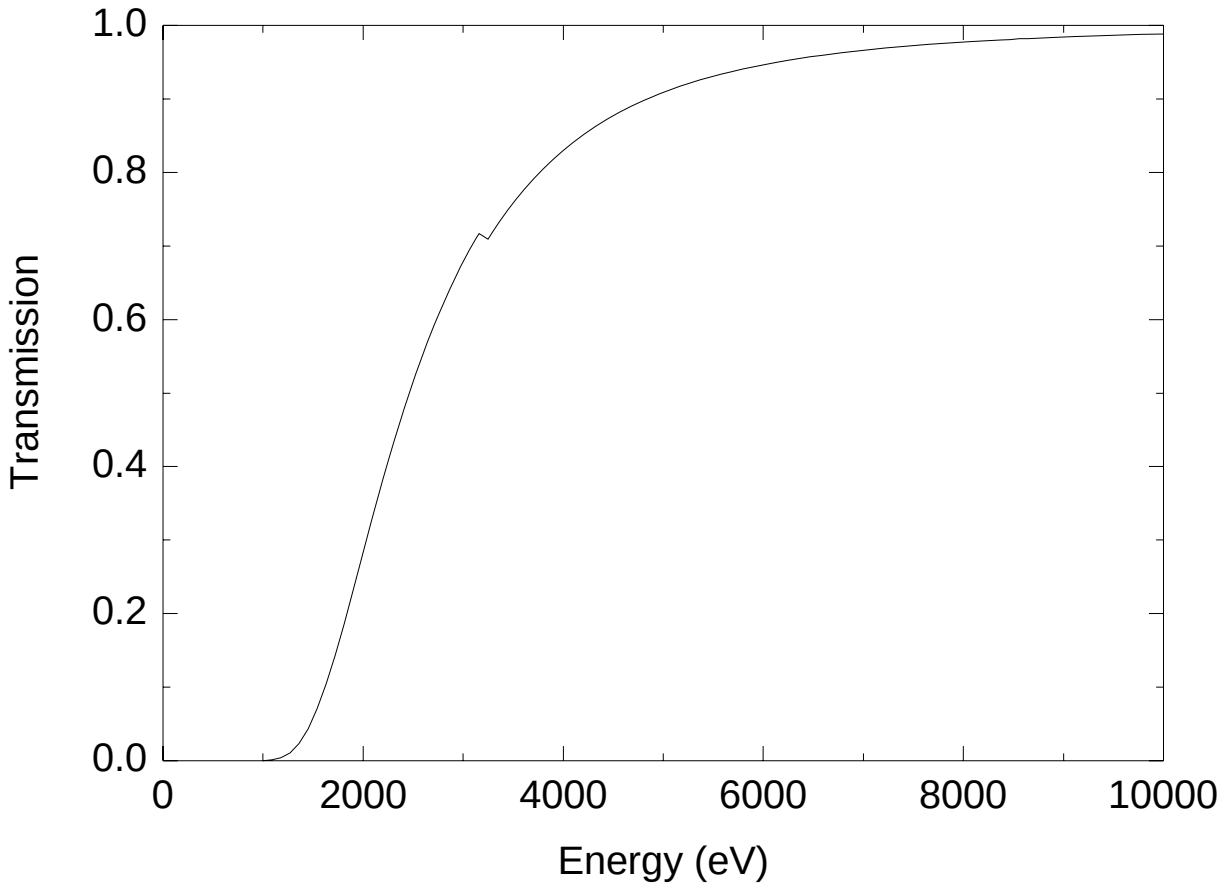
SRRC (Hsinchu, Taiwan)

SSRL (Stanford, USA)

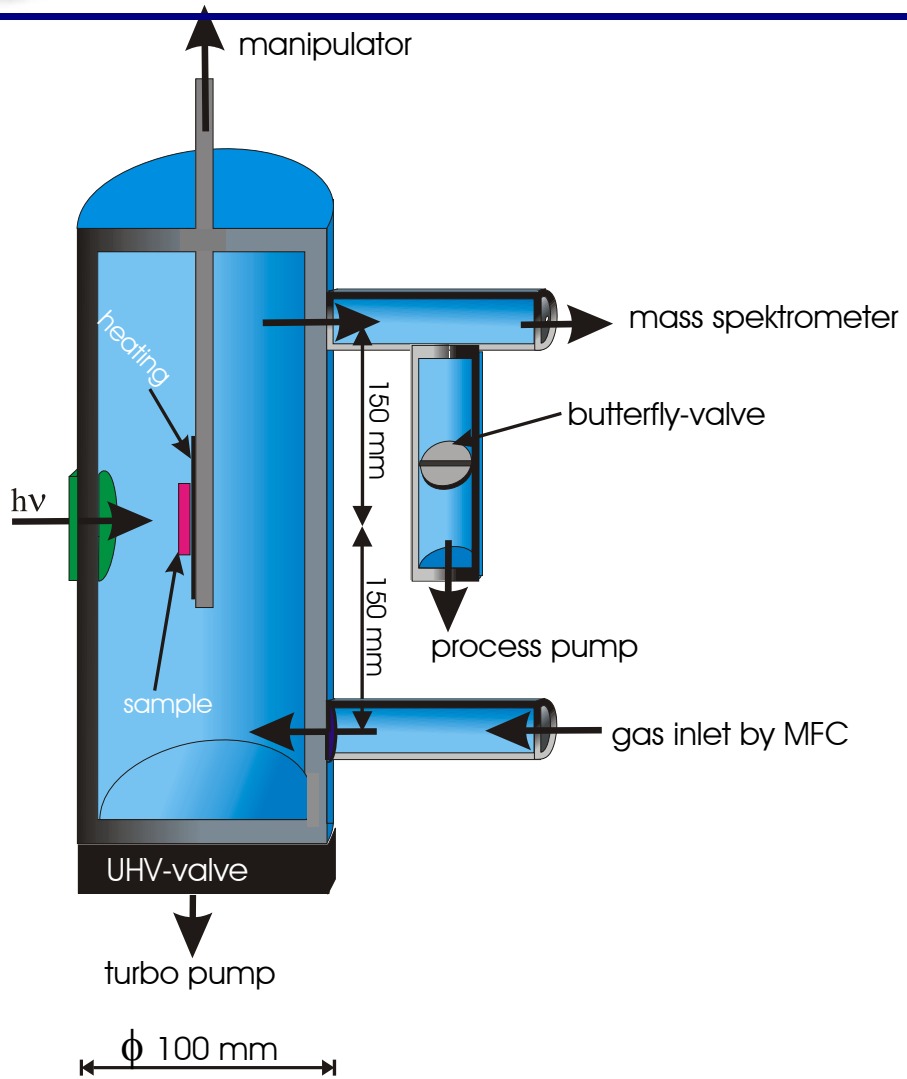
Plane Grating Monochromator Beamline



Transmission von 20 cm air



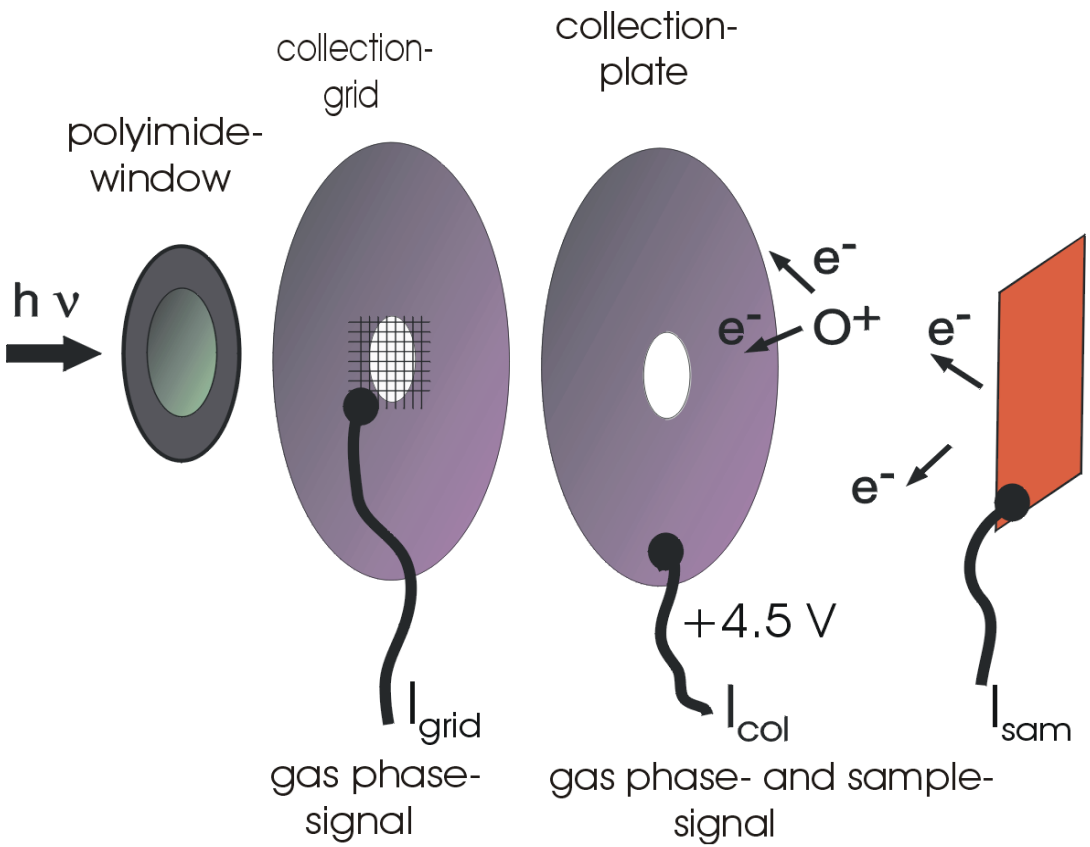
Experimental Set-Up

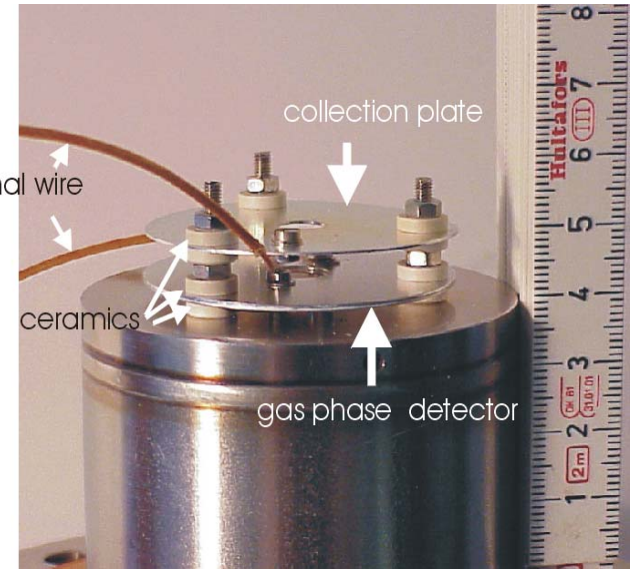


properties of the set-up

- heating up to 900 K
- pressure up to 20 mbar
- batch- and flow-through-mode
- angular dependent measurements

In situ XAS detector system



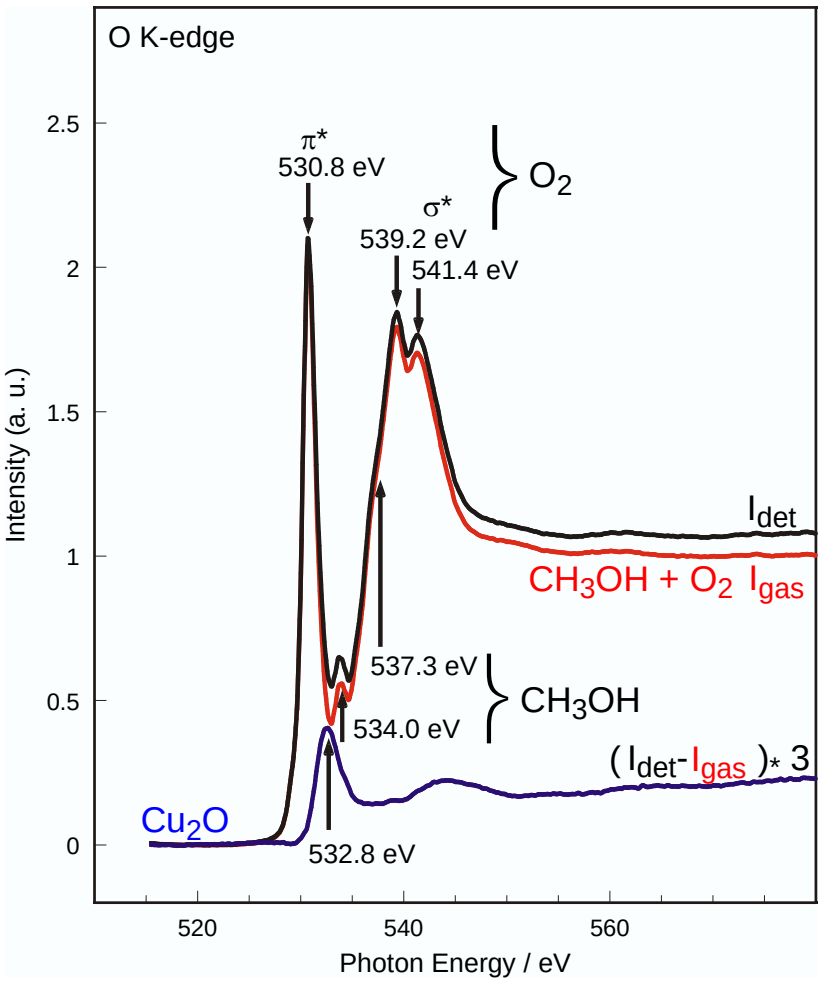


Simultaneous detection of gas phase- and sample signal

A. Knop-Gericke et al

Gas phase subtraction

Analysis of the Near **E**dge **X**-ray **A**bsorption **F**ine **S**tructure (NEXAFS)

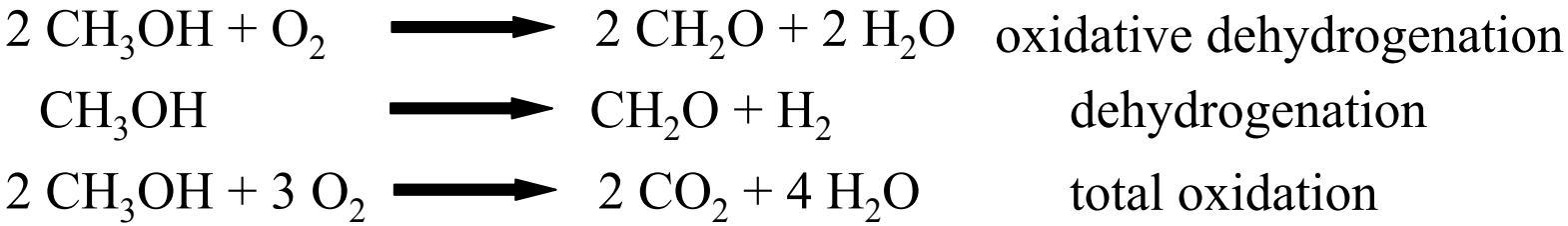


NEXAFS of the O K-edge

- Total electron yield of the gas phase dominates all signals, therefore only small differences in the detector signals
- Substraction allows to separate the absorption signal of the surface of the catalyst

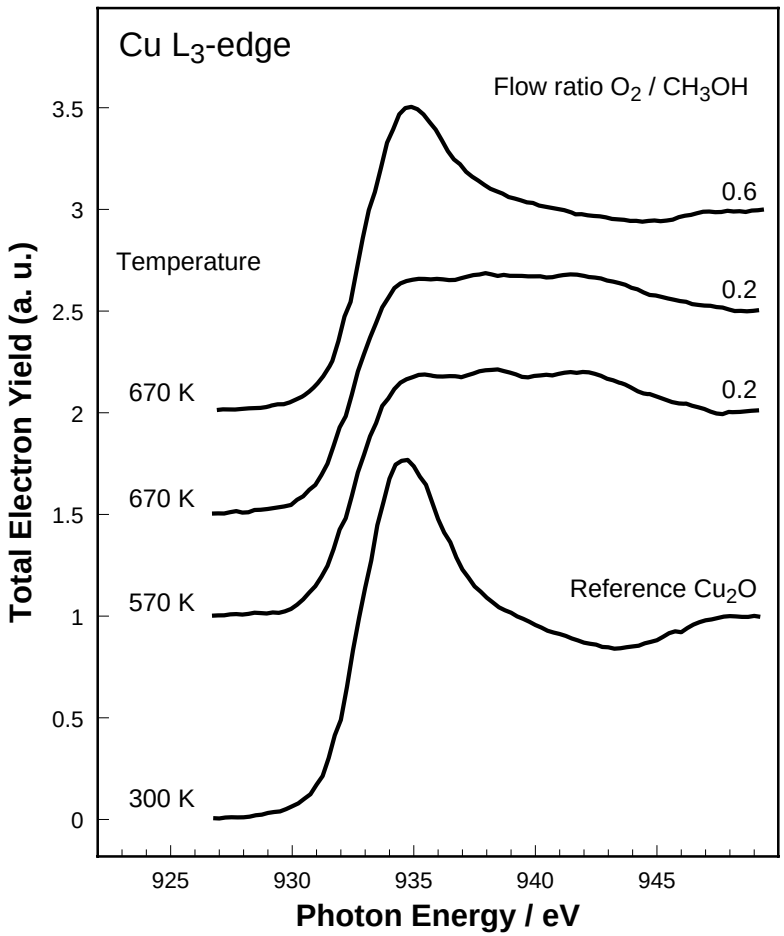
A. Knop-Gericke et al

Methanol Oxidation

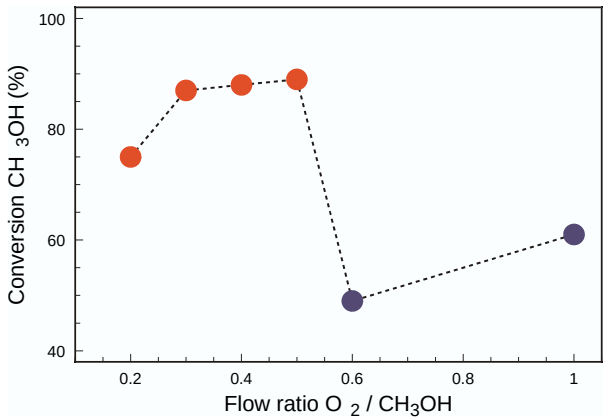


Cu L_3- NEXAFS

NEXAFS at the Cu L_3-edge



Catalytic Activity

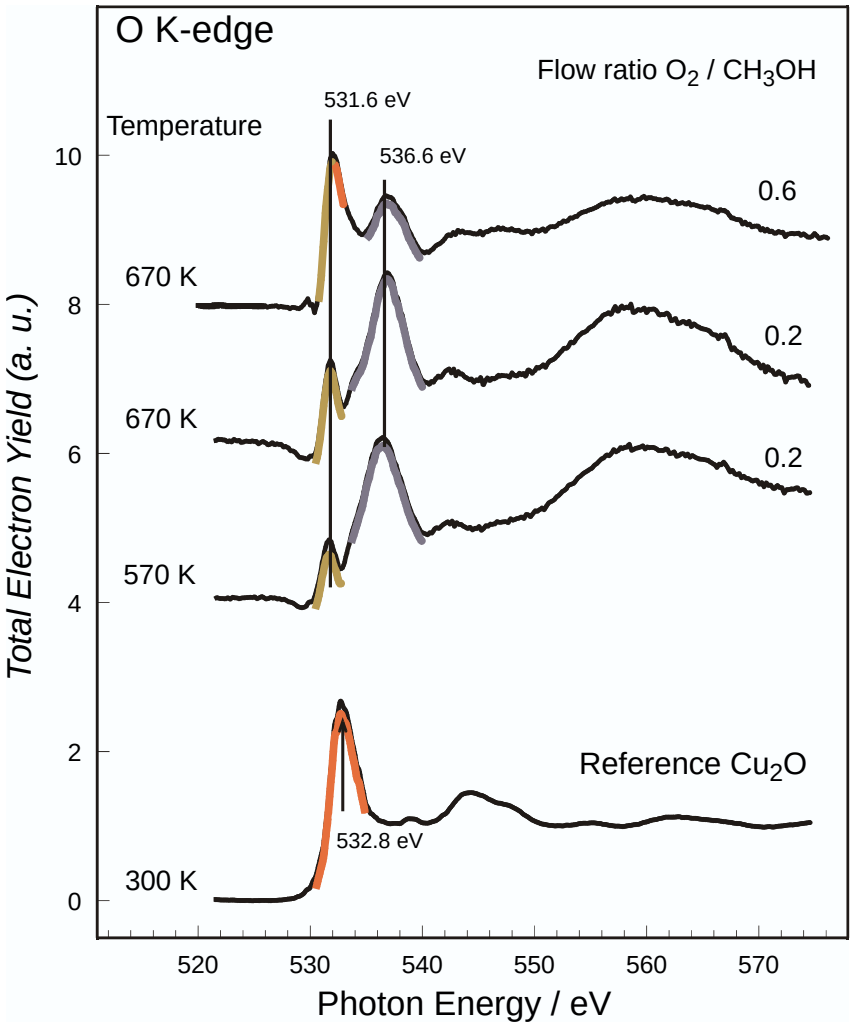


Increased activity for gas flow ratios:
O_2 / CH_3OH < 0.5

Transition from an oxidic copper-phase to the metallic state

A. Knop-Gericke et al

NEXAFS at the O K-edge



less active

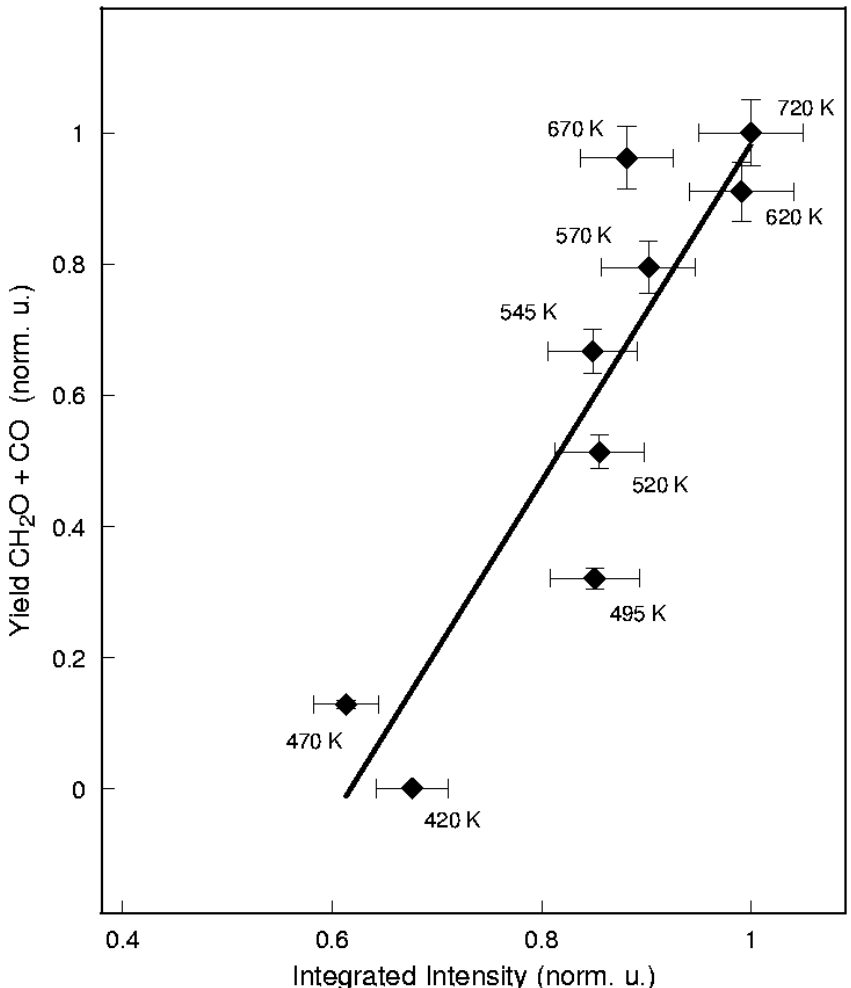
very active

- NEXAFS of the active state is completly different from the NEXAFS of the known copper-oxides
- 2 oxidic- and 1 suboxidic species can be distinguished

A. Knop-Gericke et al

Correlation between the SuboxideSpecies and CH_2O-Yield

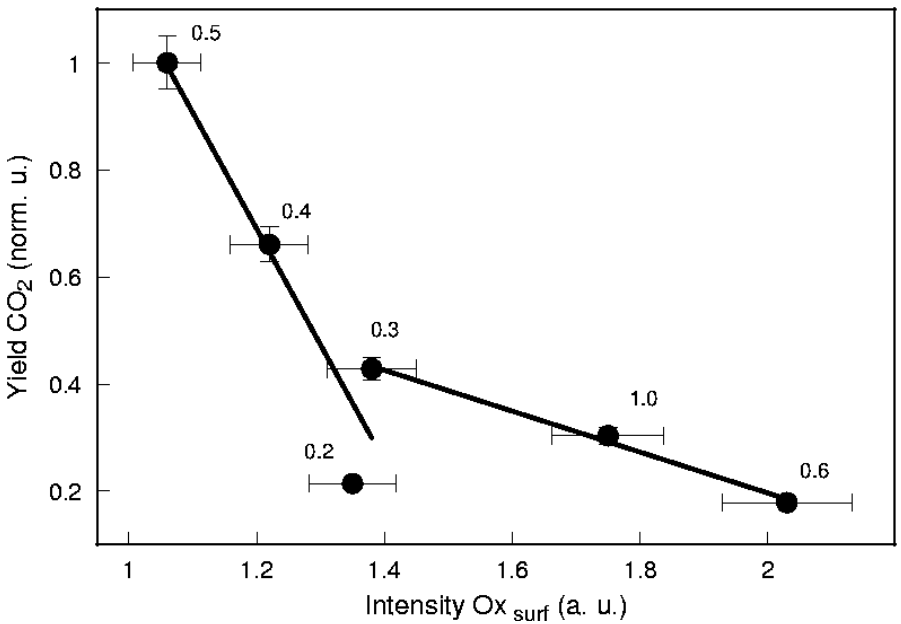
Variation of temperature at O_2 / CH_3OH = 0.2

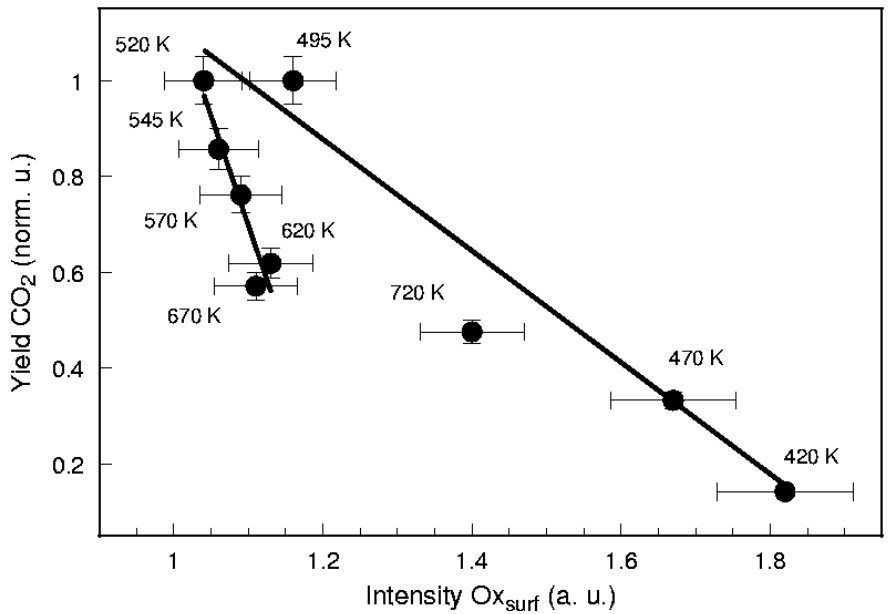


- Intensity of the suboxide species increases with increasing temperature
- Intensity of the suboxide species is positively correlated to the yield of CH_2O and CO

A. Knop-Gericke et al

Correlations between oxidic species and CO_2



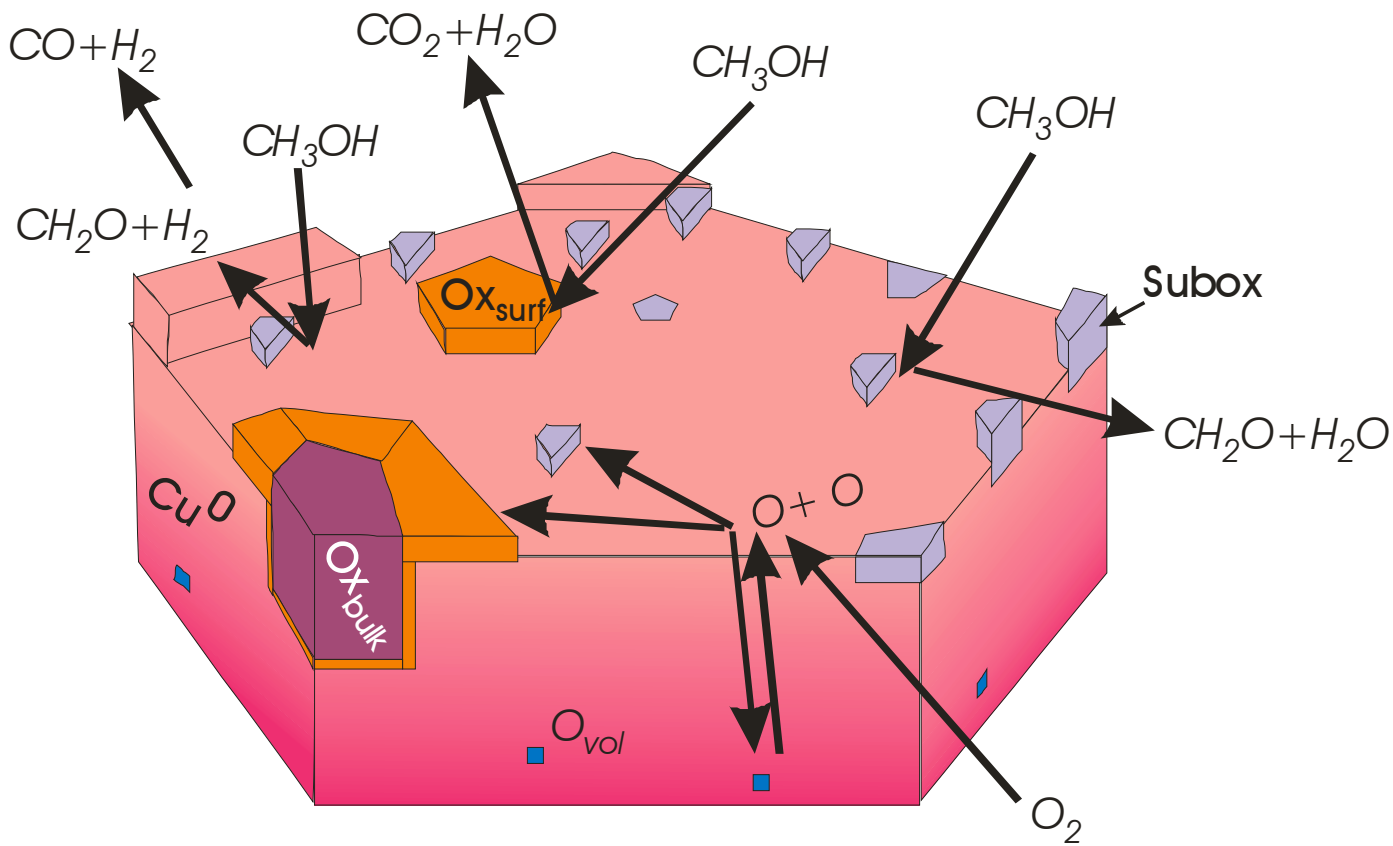


- Intensity of the oxidic species Ox_{surf} decreases with increasing CO_2-yield
- 2 areas of activity can be distinguished

A. Knop-Gericke et al

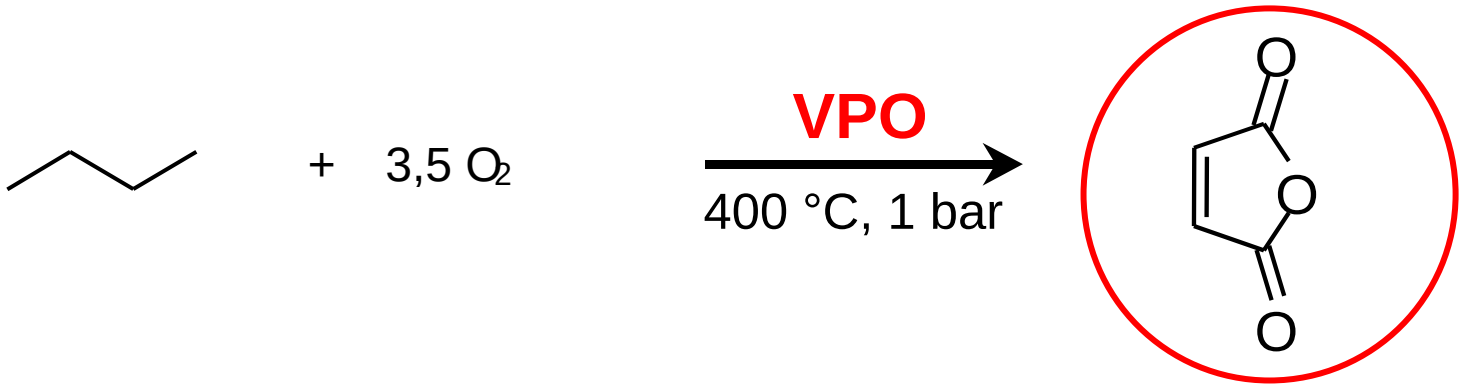
Model

Proposed model of the copper surface under reaction conditions for methanol oxidation



A. Knop-Gericke et al

n-Butane Oxidation to MA by Vanadium Phosphorus Catalysts



1,5 Vol% air

Maleic Anhydride (MA)

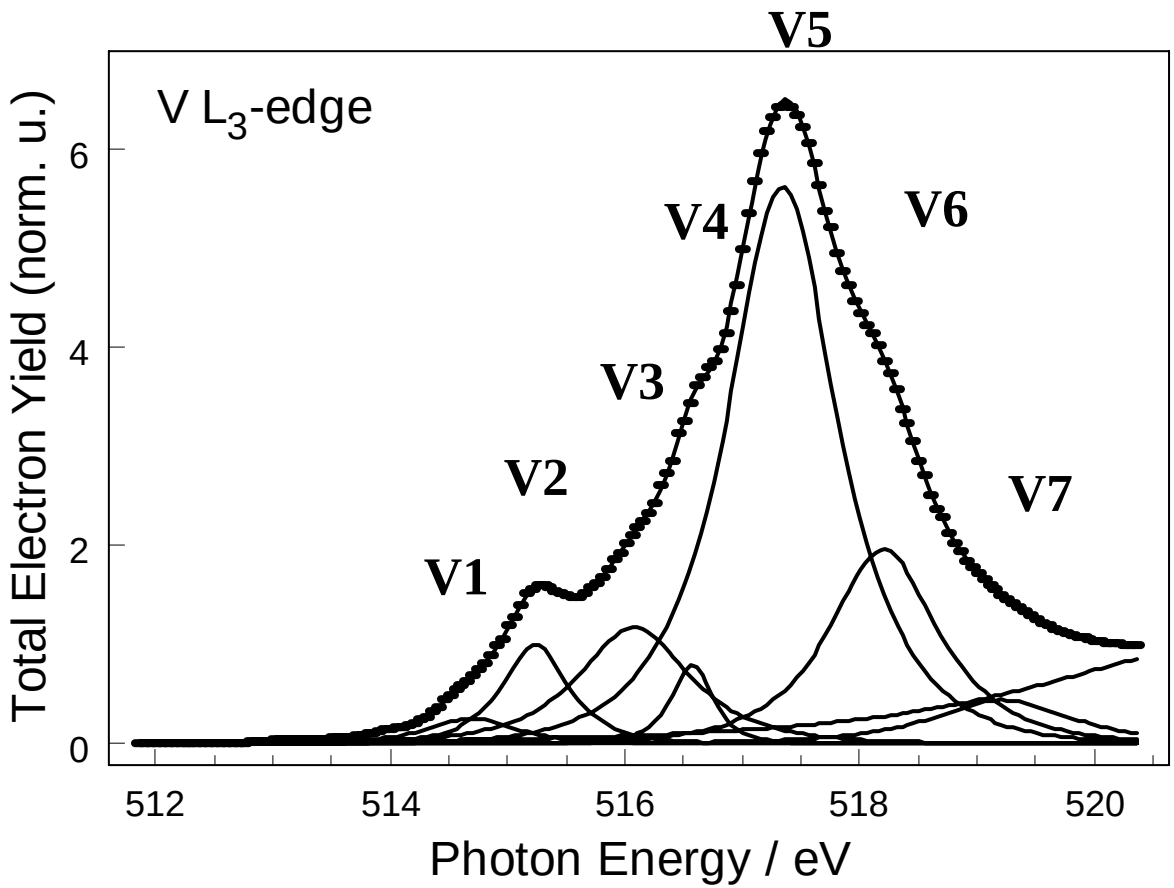
C_4H_{10} + 6,5 O_2 → 4 CO_2 + 5 H_2O

C_4H_{10} + 4,5 O_2 → 4 CO + 5 H_2O

Active phase: highly ordered vanadyl pyrophosphate $(VO)_2P_2O_7$ **?**

The VPO V L_3-NEXAFS

Analysis of spectral shape by unconstrained least squares fit

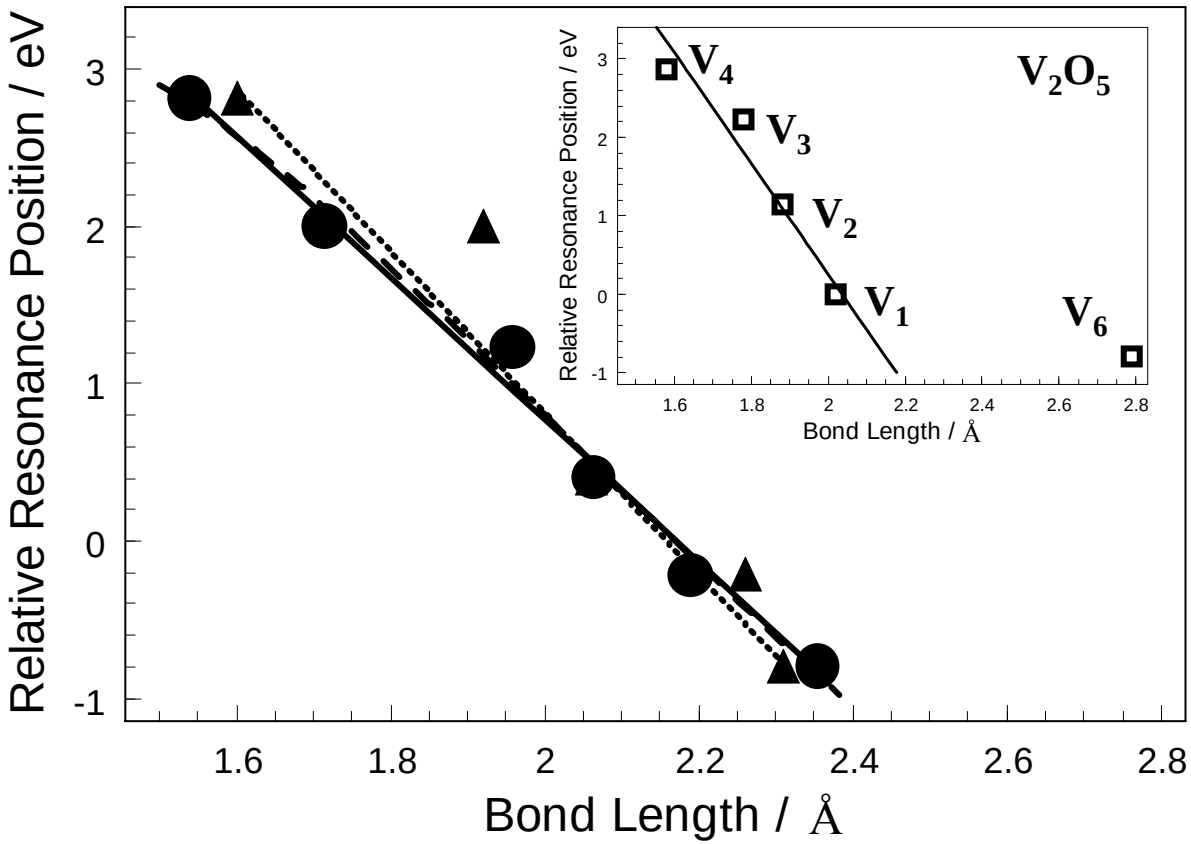


- V valence
- Details of the local chemical bonding
- Local geometric structure

M. Hävecker et al.

Interpretation of V L_3 NEXAFS

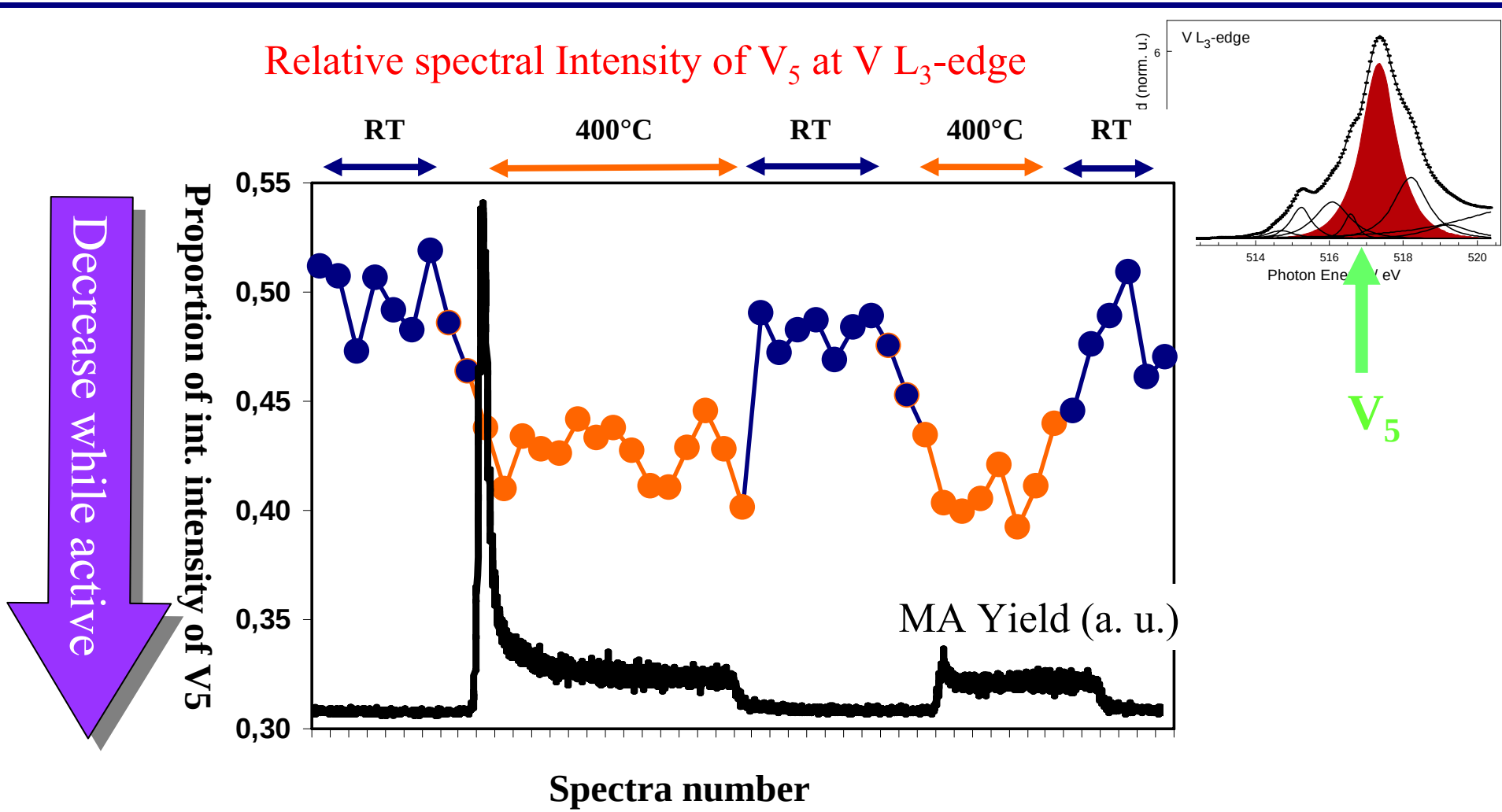
Experimental finding:



⇒ NEXAFS resonances appear in a sequence of V-O bond lengths

M. Hävecker et al.

Changes of NEXAFS while heating



M. Hävecker et al.

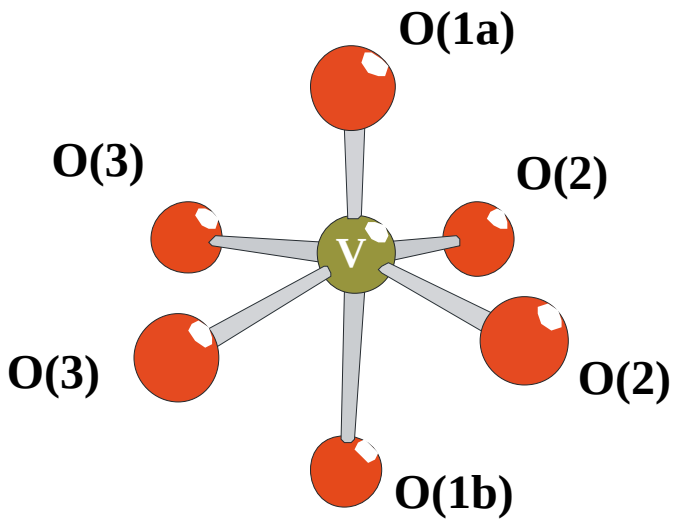
Interpretation of V L_3 NEXAFS

Identification of resonances (V5, V6):

V_2O_5 as model substance for VPO

DFT calculation of DOS (V_2O_5 !)*:

V_2O_5: Close relationship between geometric and electronic structure at V L_3-absorption edge



⇒ main contributions to NEXAFS resonances appear in a sequence of V-O bond length

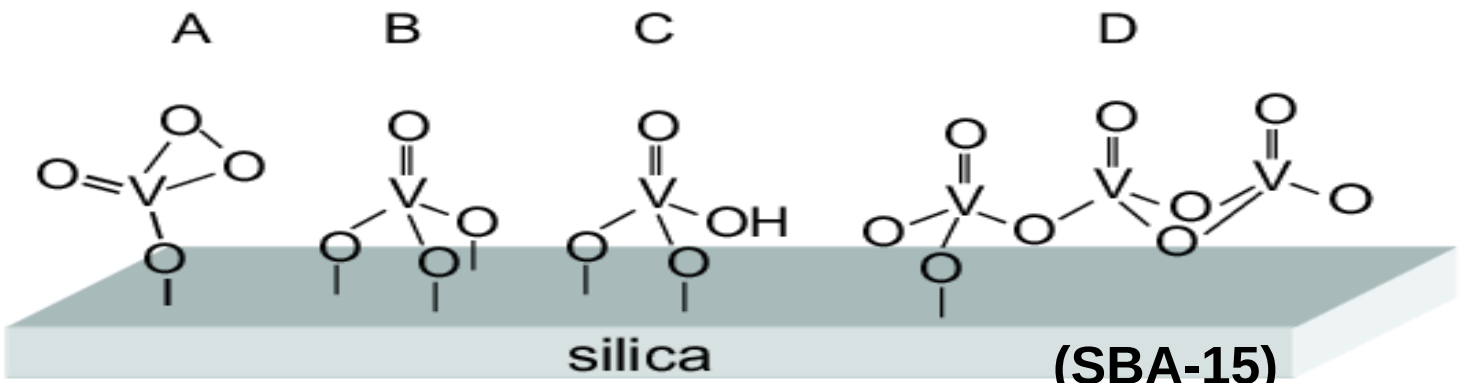
⇒ V6: O(1a)
⇒ V5: ? (estimated value of bond length between O(2) and O(1a): 1.72 Å)

System: VO_x on silica support (SBA-15)

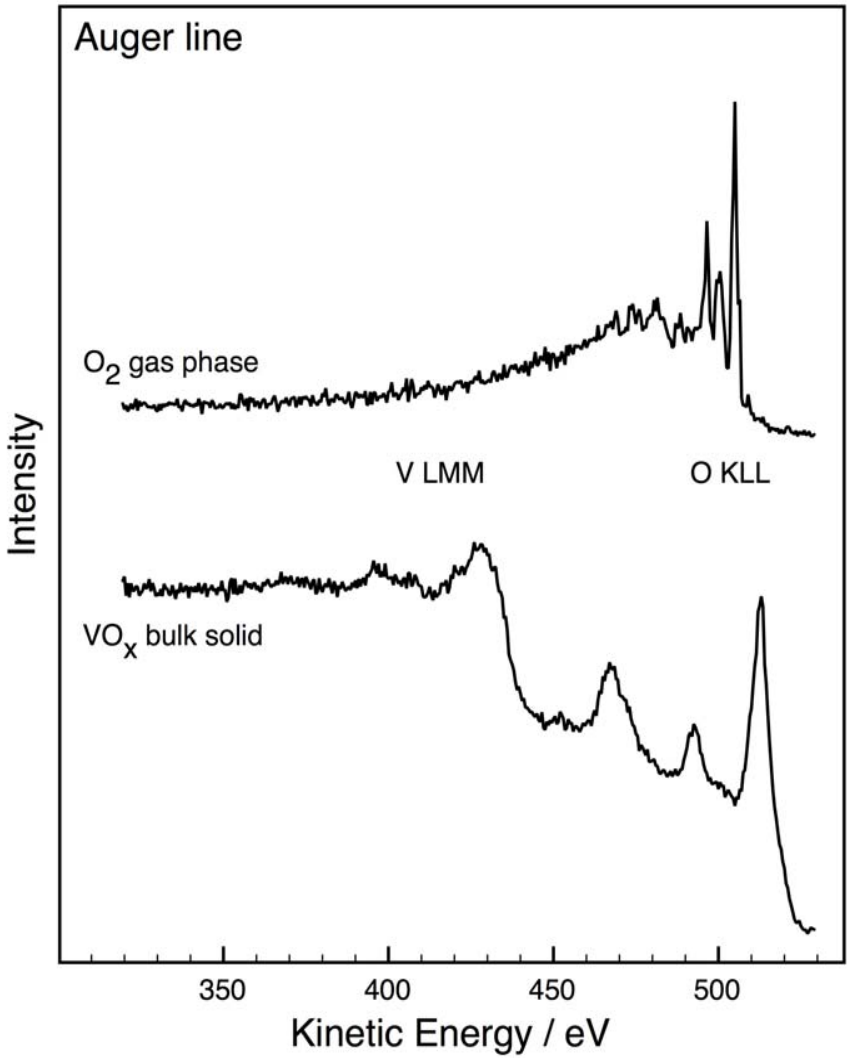
Objective: What is the molecular structure of dehydrated VO_x species (monomer vs. polymer)?

Methodology: In situ NEXAFS in combination with DFT cluster calculations

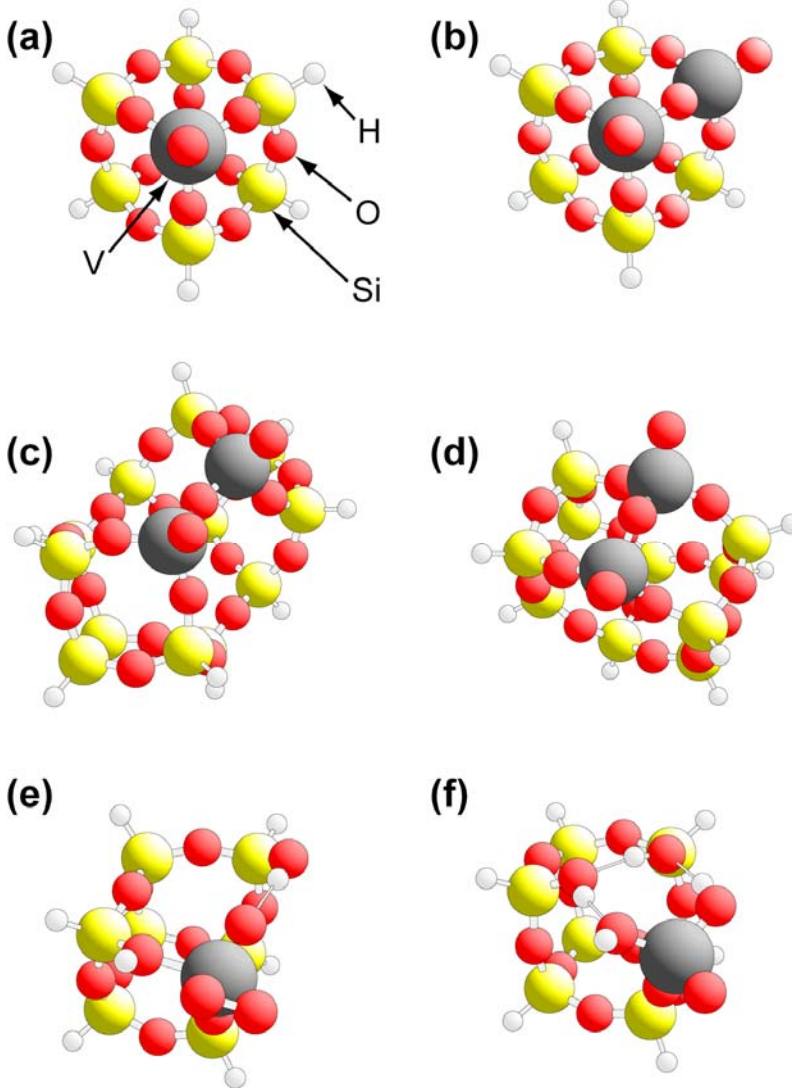
Question: Spectroscopic evidence for V-O-V bonds?

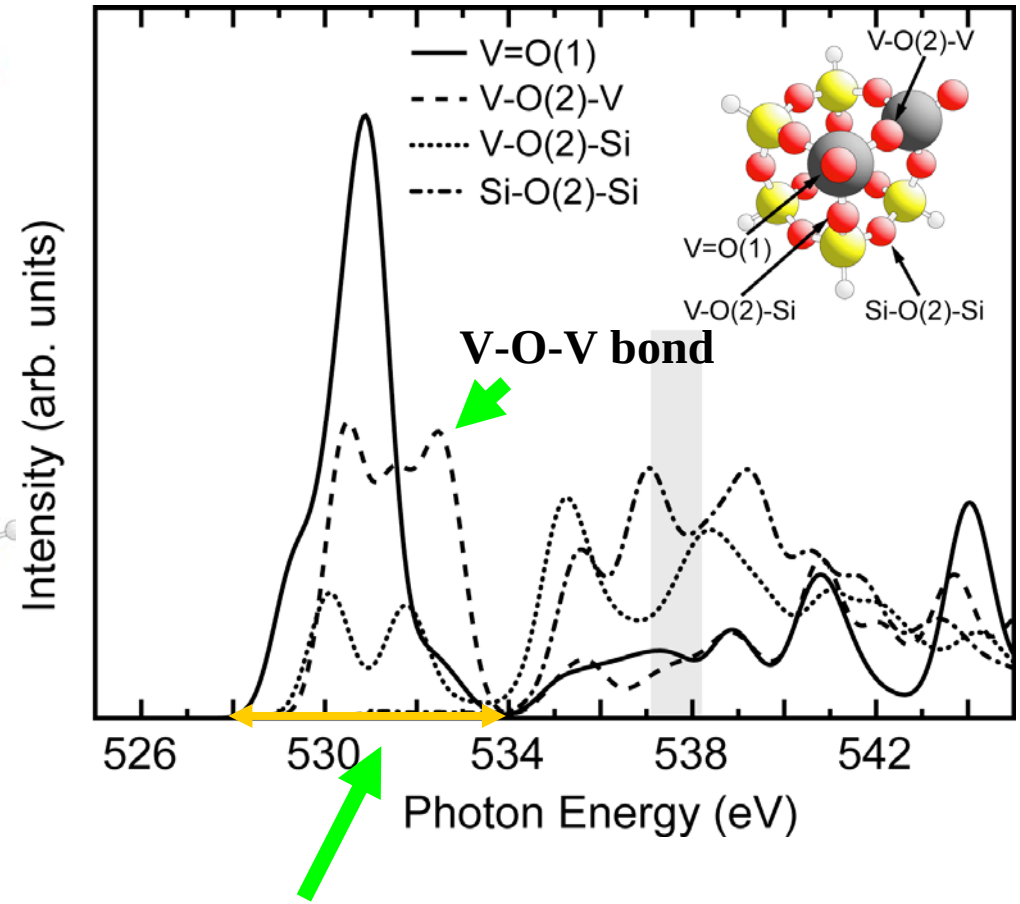


Differentiation between gas phase and surface contribution by proper selection of the Auger-window



Simulation of O K-NEXAFS for various VOx clusters on silica





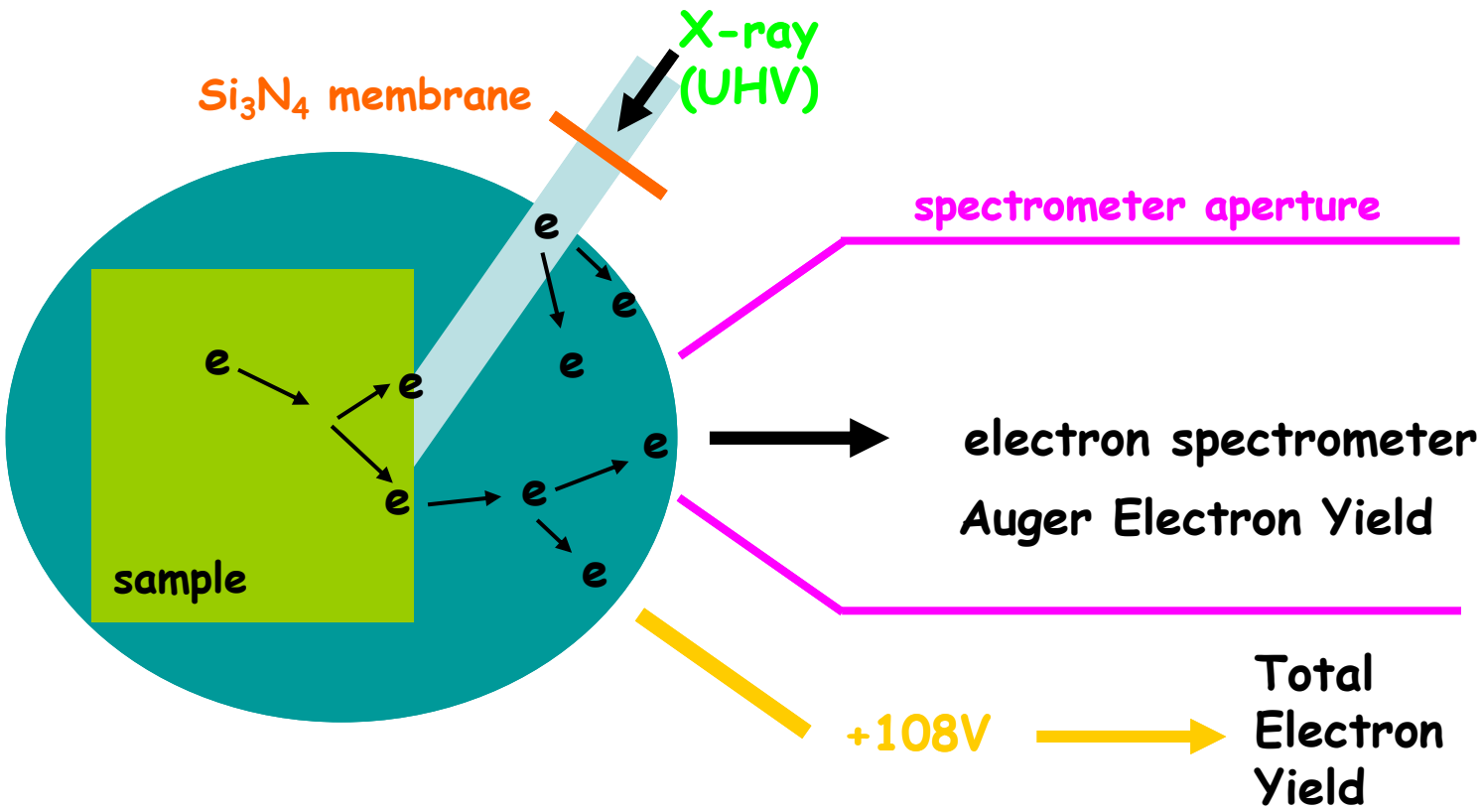
***no* signature of Si-O-Si bonds**

M. Cavalleri et al., J. Catal. 262 (2009) 215

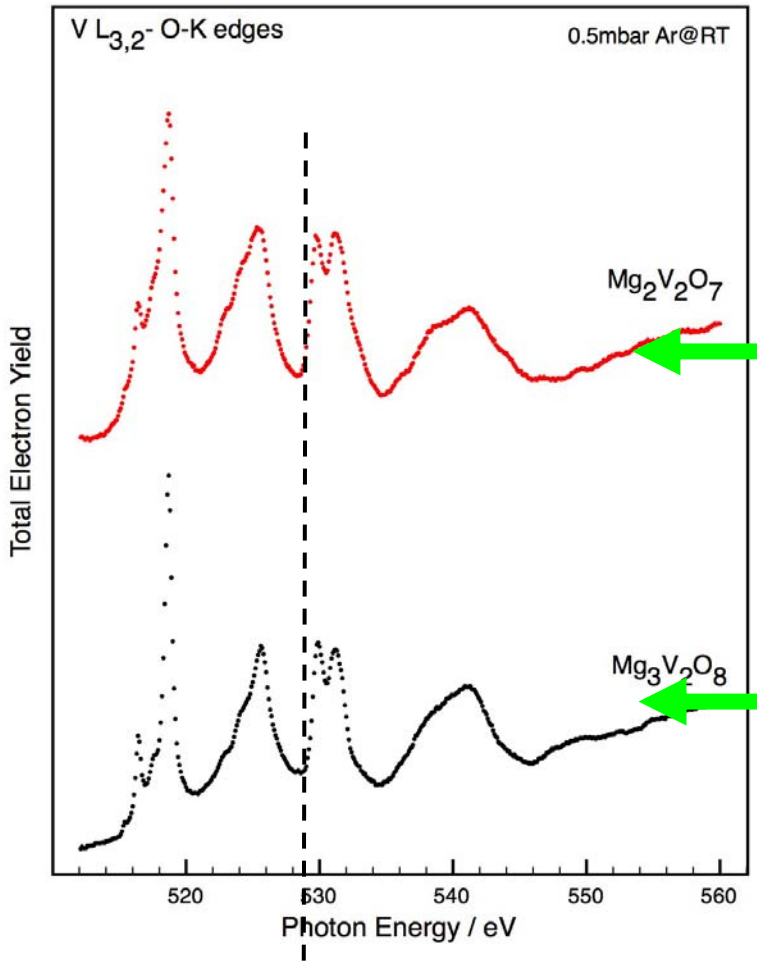
Experimental: In situ soft X-ray NEXAFS

Electron yield technique: (secondary) de-excitation process (Auger decay) as measure for absorption cross section σ :

$N_{abs} = c^*(1-e^{-\sigma\rho}) \approx c^*\sigma\rho$ $\quad \sigma \propto N_{hole} \rightarrow \sigma \propto I_{EY} \rightarrow I_{EY} \propto N_{abs}$



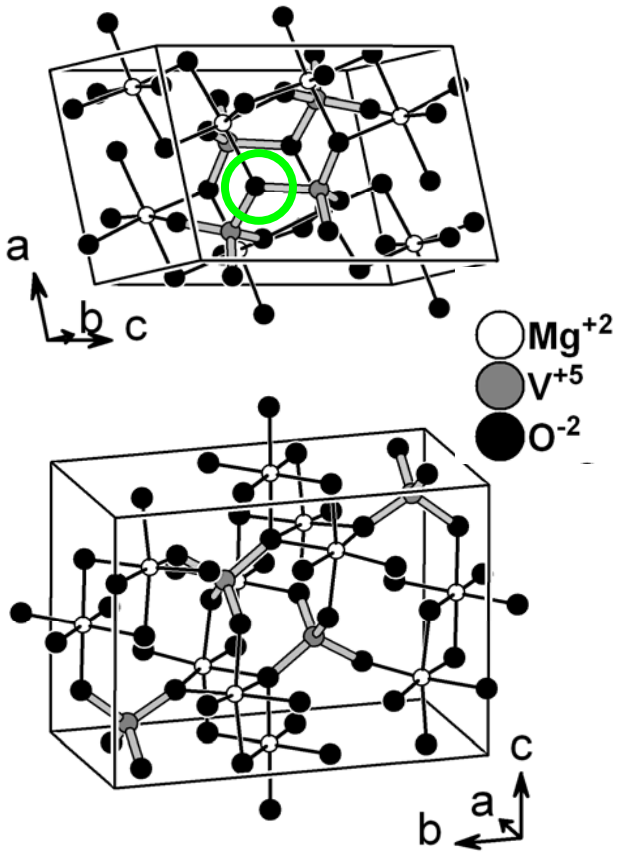
Experimental O K-NEXAFS of Mg vanadate reference compounds



V-O-V bond

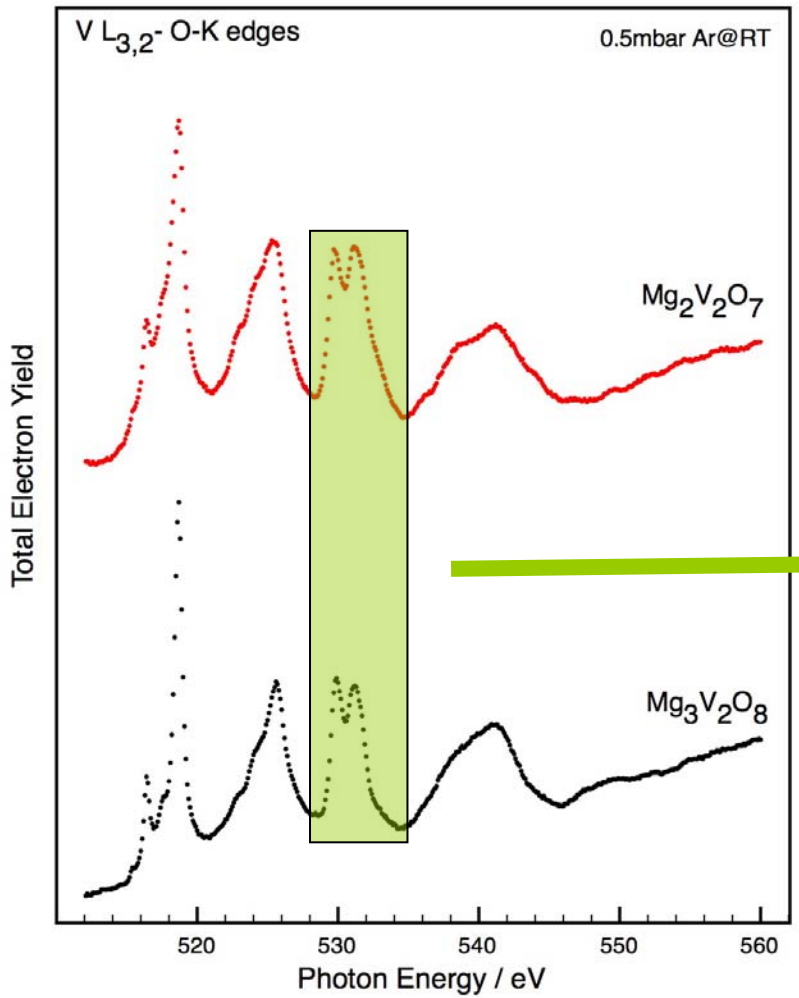
no V-O-V bond

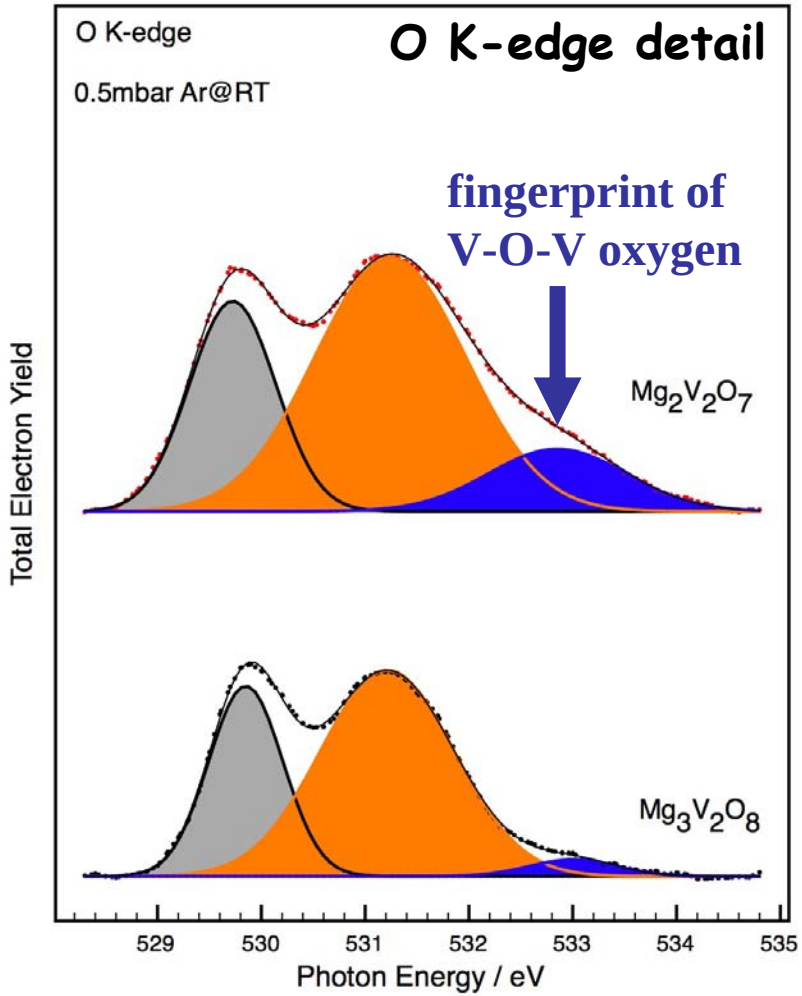
Crystal structure



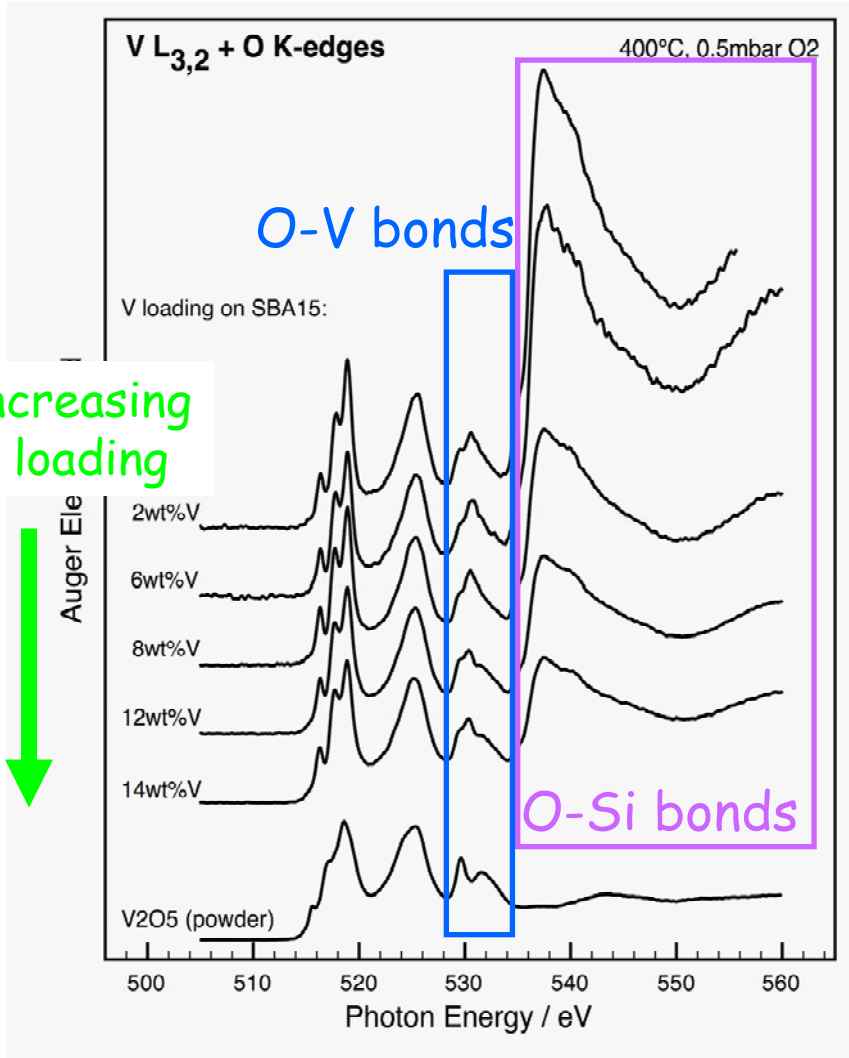
V2p → V3d O1s → O2p

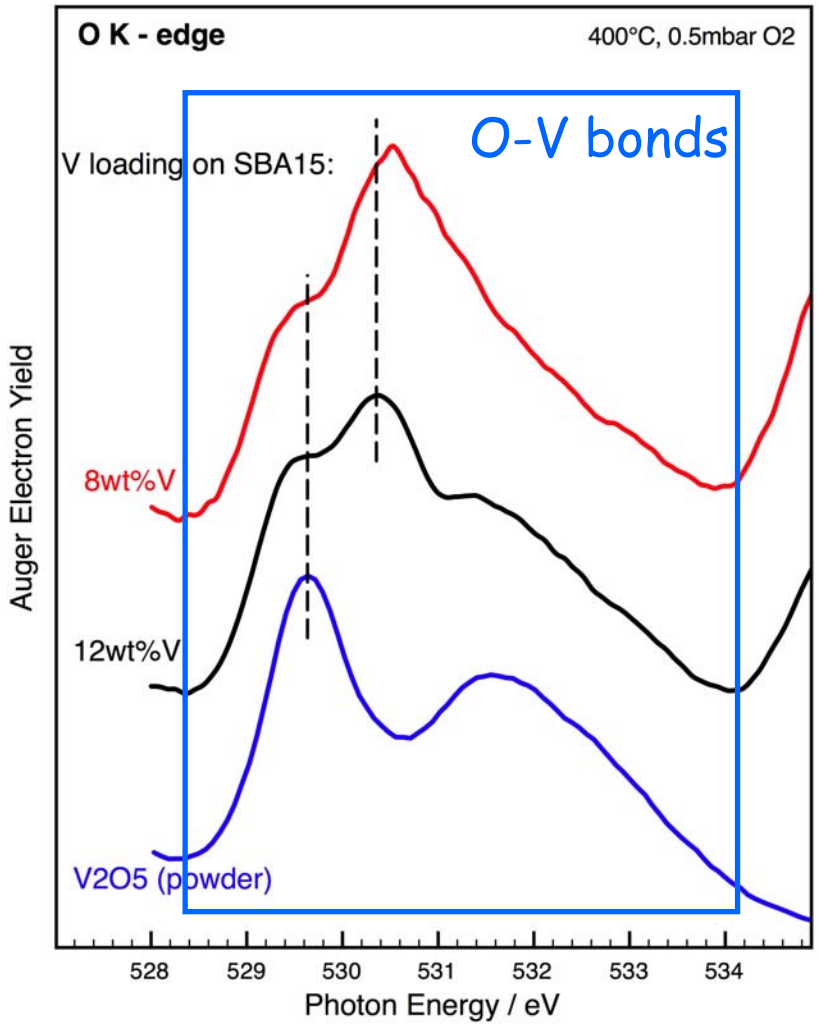
Fingerprint of V-O-V bonds



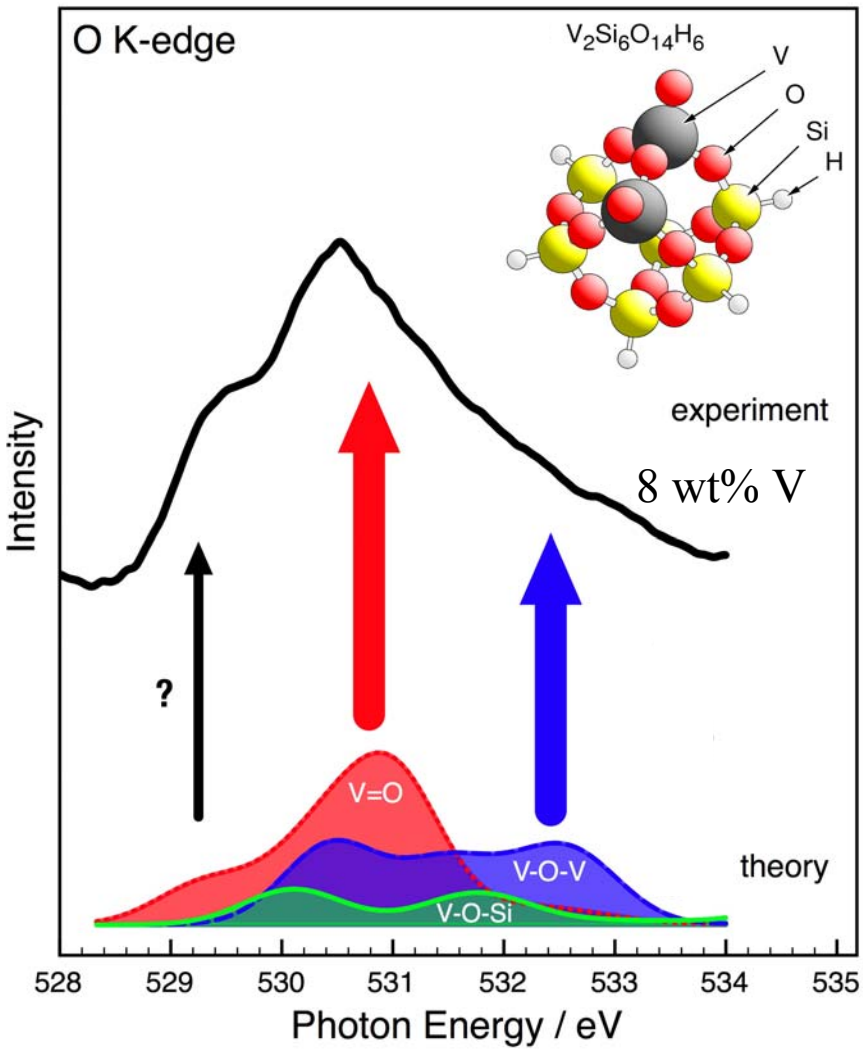


Experimental O K-NEXAFS of VOx/SBA-15 in O_2 gas at 400°C (after correction for gas phase transmission)





Comparison of experimental O K-NEXAFS with theoretical cluster simulation



Comparison with theory allows to differentiate between different V-O bonding configurations

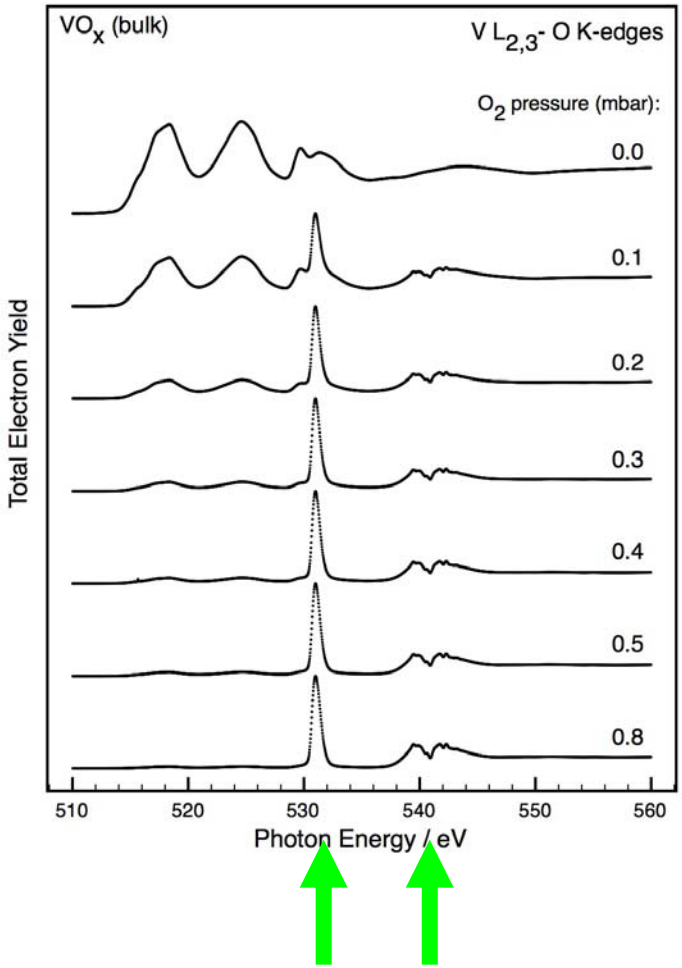
A distribution of vanadia species is present including non-monomeric species

M. Hävecker et al., pss(b) 246 (2009) 1459

M. Cavalleri et al., J. Catal. 262 (2009) 215

Why Auger Electron Yield?

Total Electron Yield

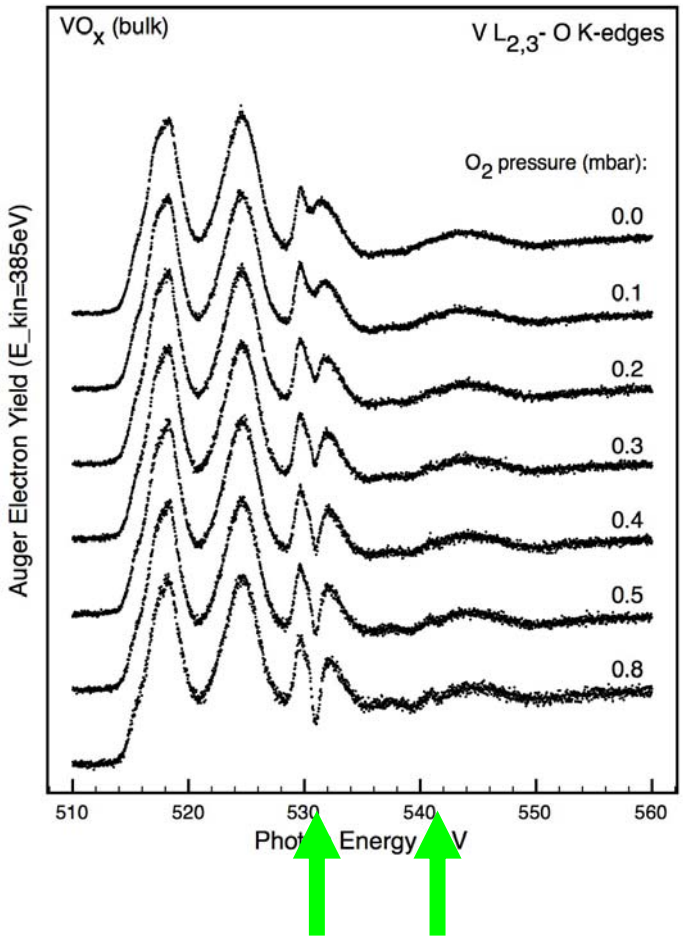


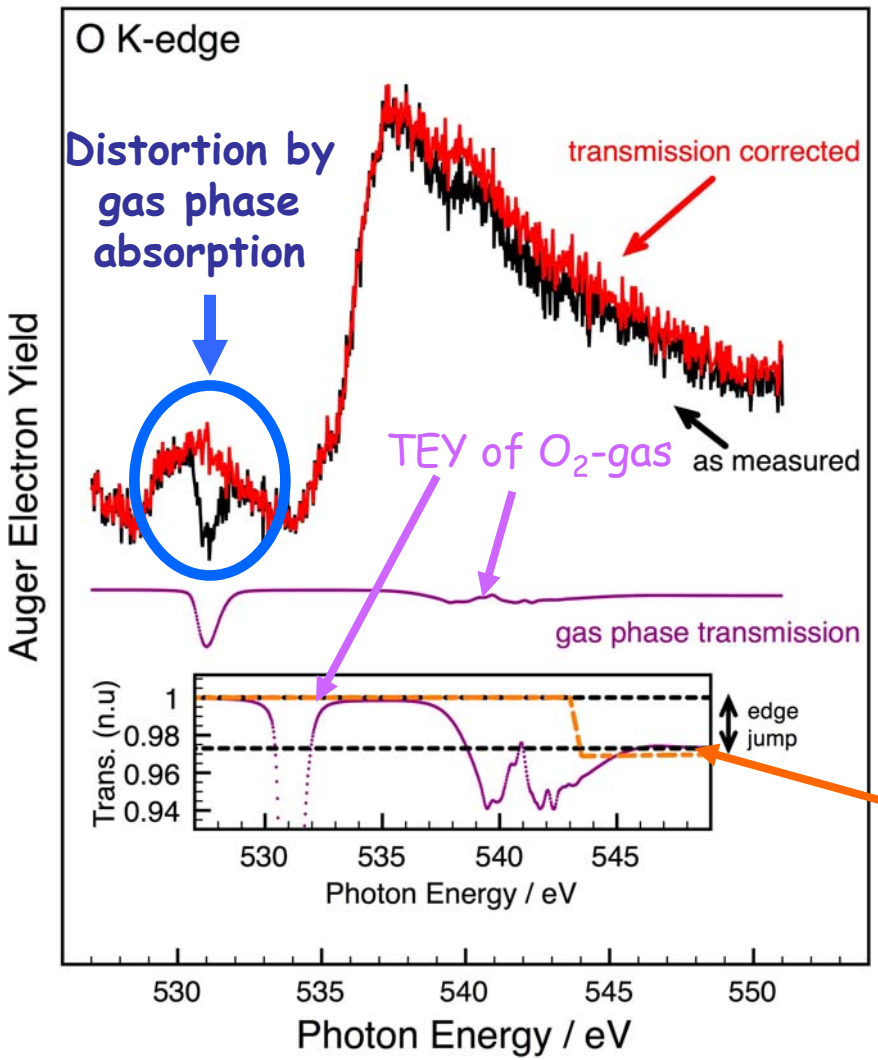
O_2 pressure varied

vacuum

0.8 mbar O_2

Auger Electron Yield

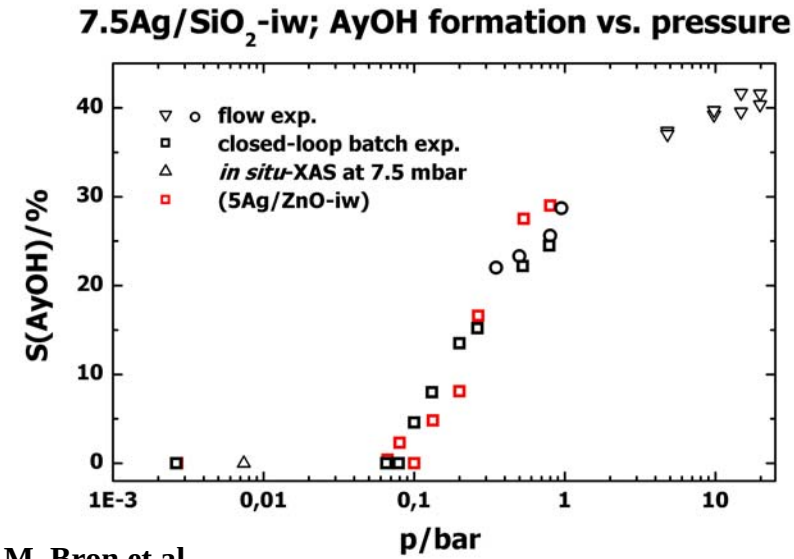




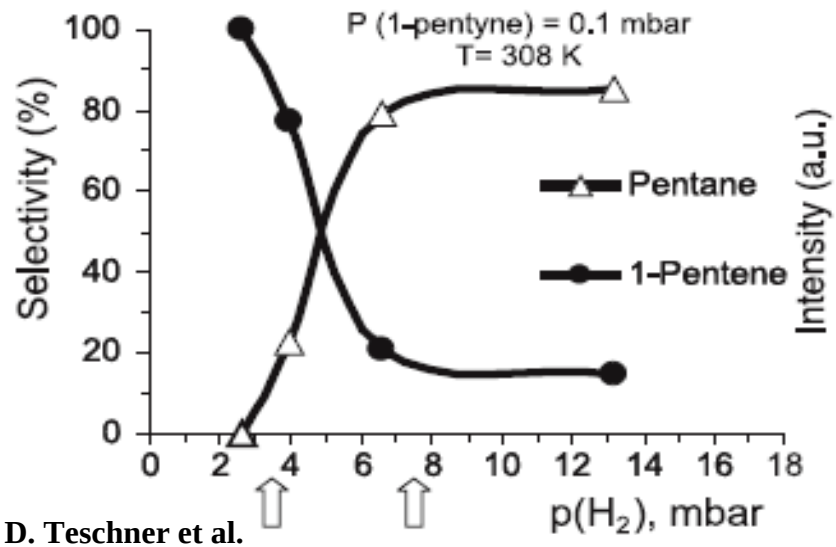
Simulation of photon absorption of O_2 (24mm, 0.5mbar, 20°C)

Outlook / Future plans

How relevant are results obtained in 0.5 mbar reaction atmosphere for "the real world"?



M. Bron et al.



D. Teschner et al.

Selective hydrogenation of acrolein to allyl alcohol over Ag

Selective hydrogenation of Pentyne over Pd

Outlook / Future plans

How relevant are results obtained in 0.5 mbar reaction atmosphere for "the real world"?

Strategies:

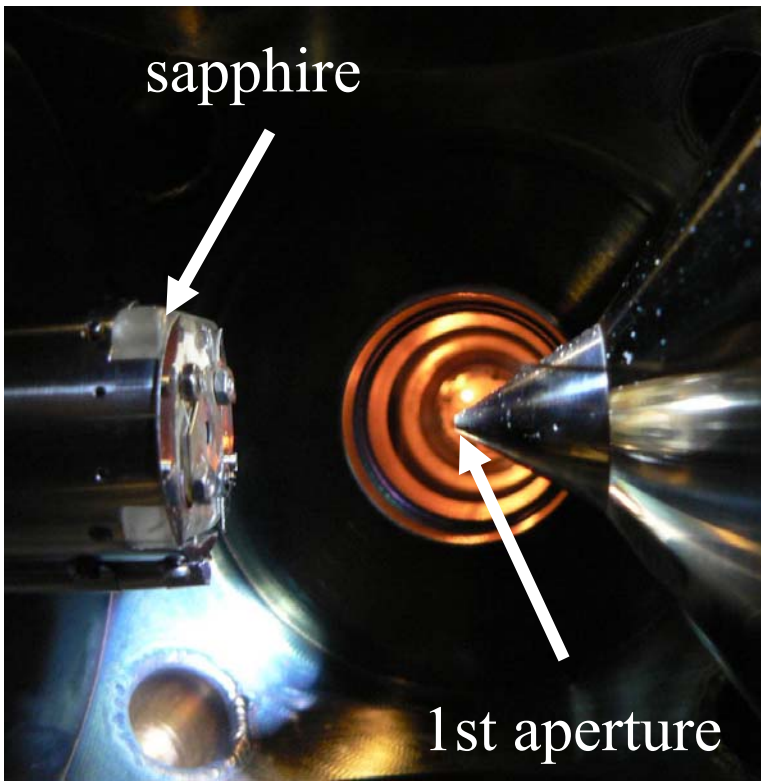
verify gas atmosphere composition during experiments (selectivity!)

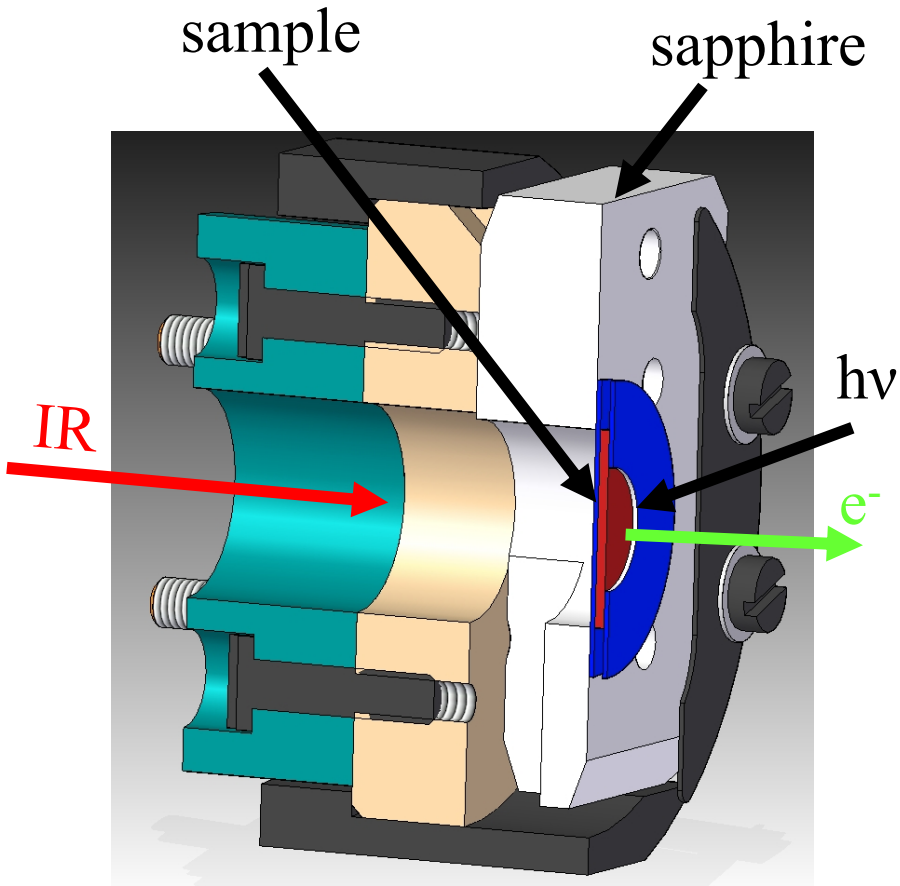
construction of fixed bed reactor at 1<p<1000mbar to perform kinetic measurements

construction of soft-XAS cell operated in electron yield mode at 1<p<1000mbar

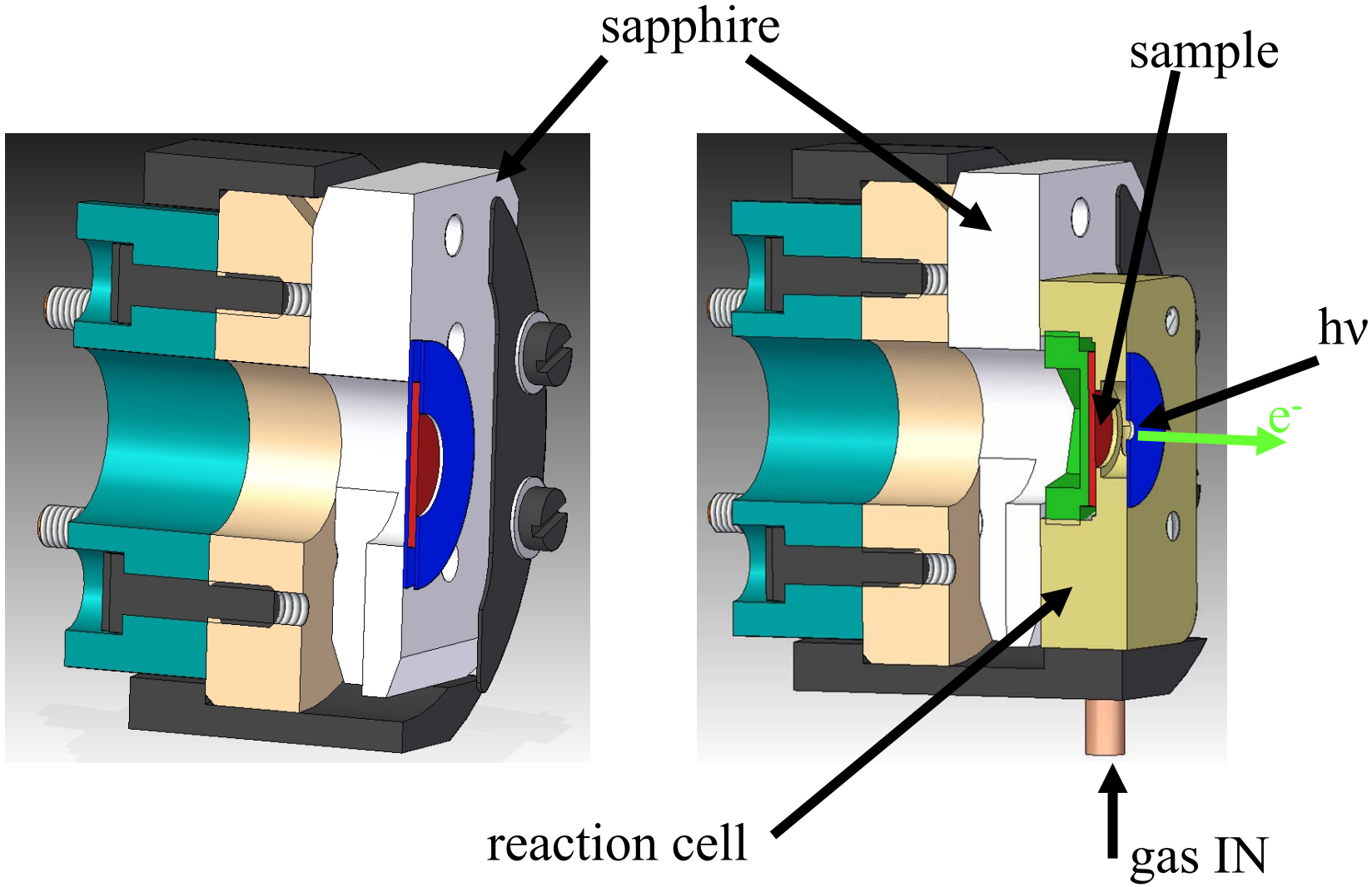
Theory to explore extended regime of $\mu(T,p)$

Outlook / Future plans





Outlook / Future plans



Literature:

Joachim Stöhr: "NEXAFS Spectroscopy", Springer 1992

Jochen Haase: "SEXAFS und NEXAFS – Röntgen-Absorptionsspektroskopie an Adsorbat-bedeckten Oberflächen", Chemie in unserer Zeit, 26. Jg 1992, Nr. 5, pp. 219-231.