In situ X-ray Absorption Spectroscopy in Heterogeneous Catalysis

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- **Introduction to XAS**

  (Synchrotron Radiation, Experimental Set-up,

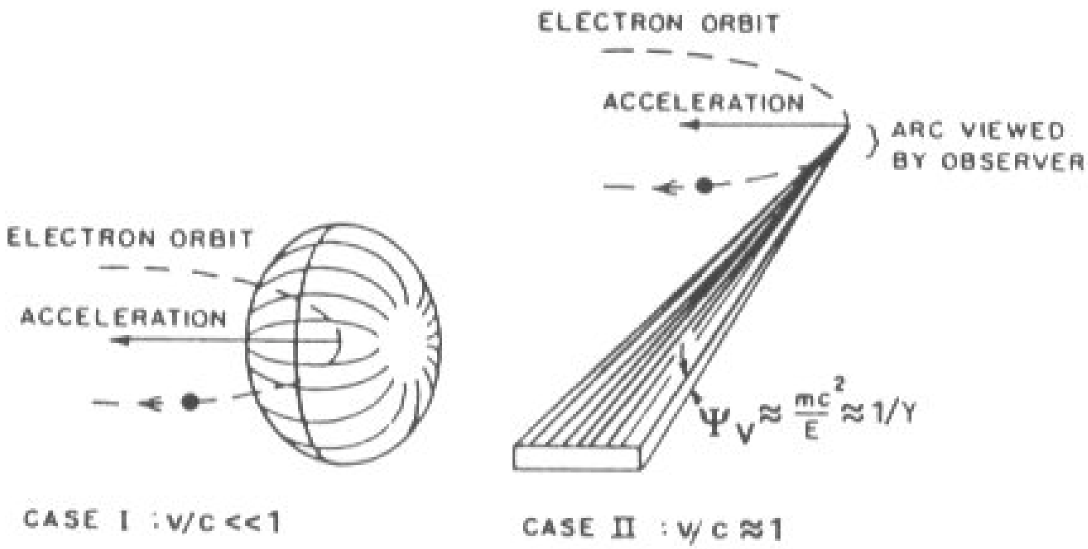
  Data aquisition, data reduction and data analysis)

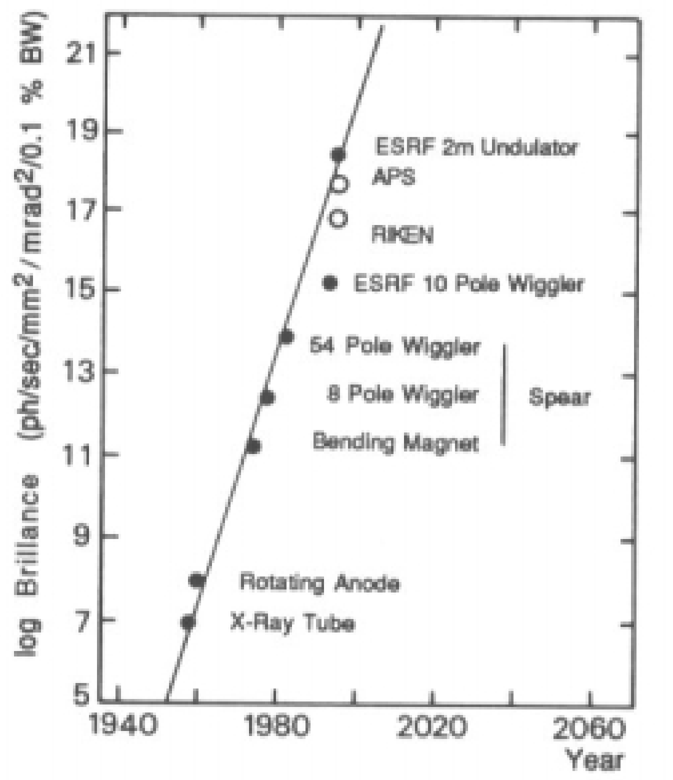
- **XAFS – Examples: Molybdenum oxides and Cu metal**

- **Data analysis**

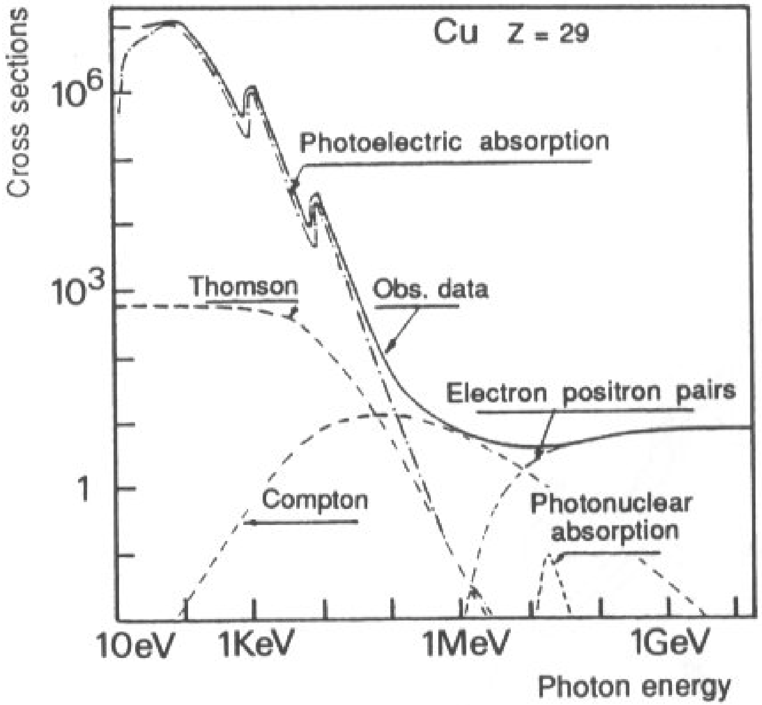
Introduction

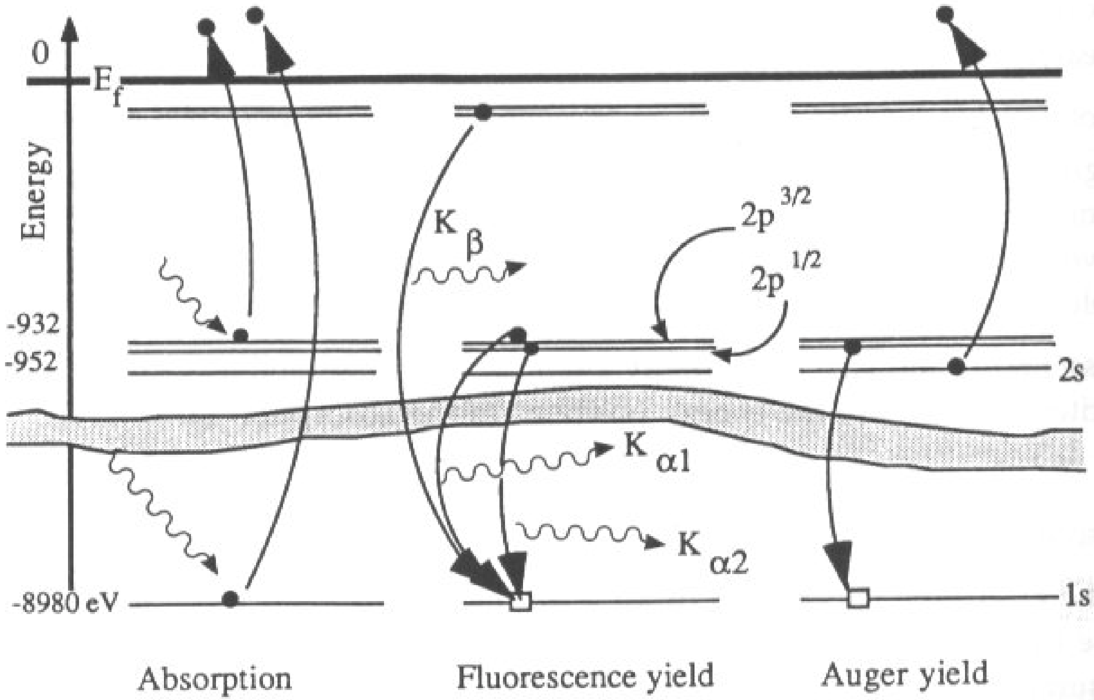
Synchrotron Radiation



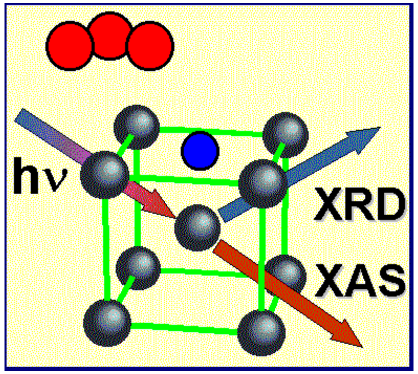


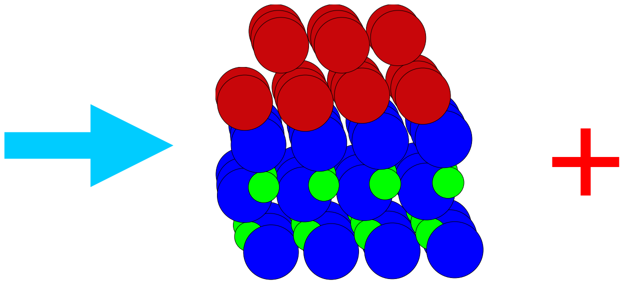
X-ray Absorption Spectroscopy

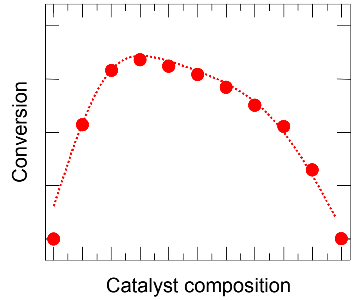


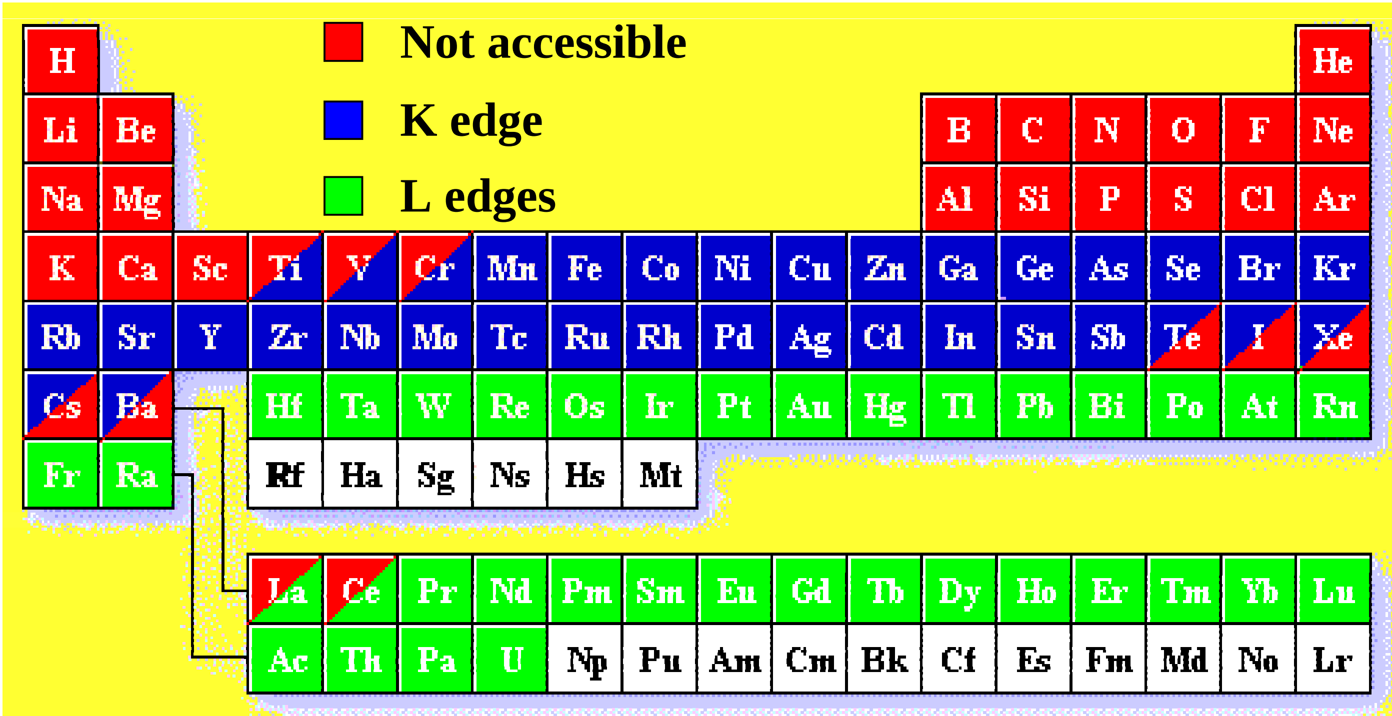


Accessible Elements for TR-XAS Studies at 5 – 30 keV

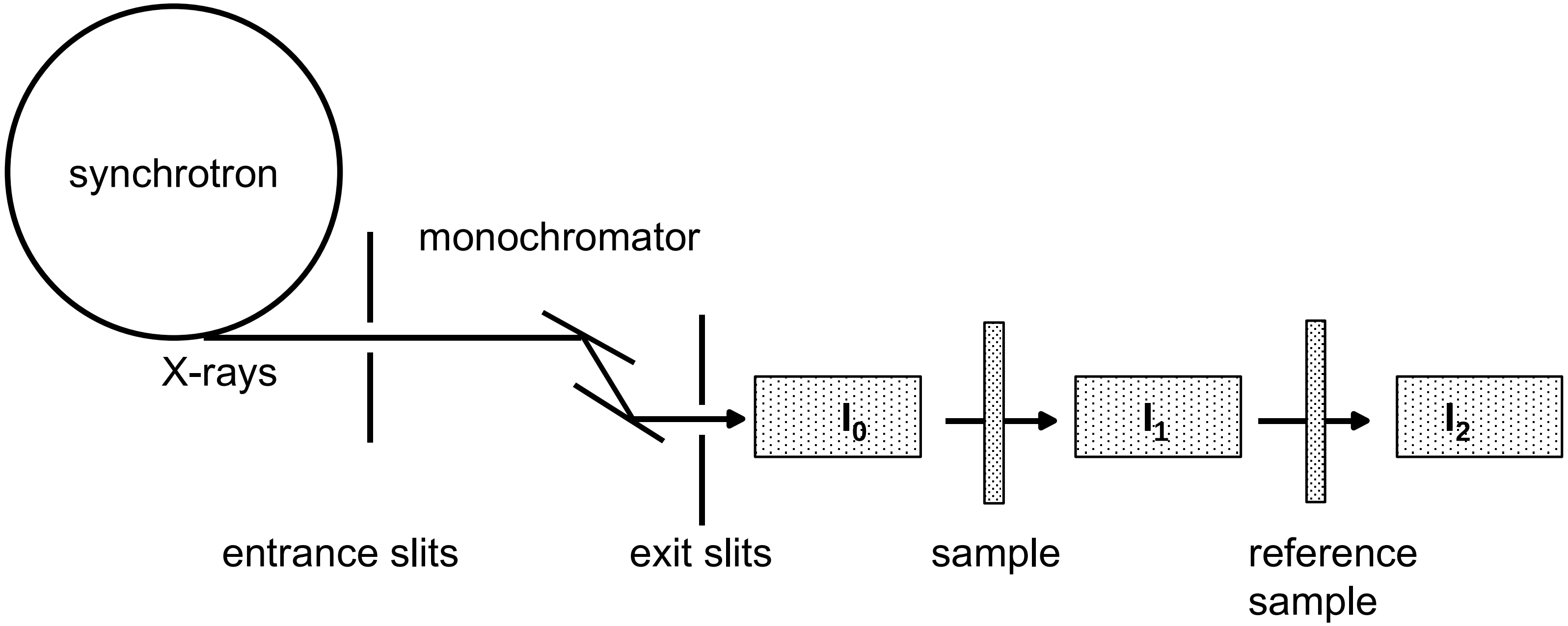






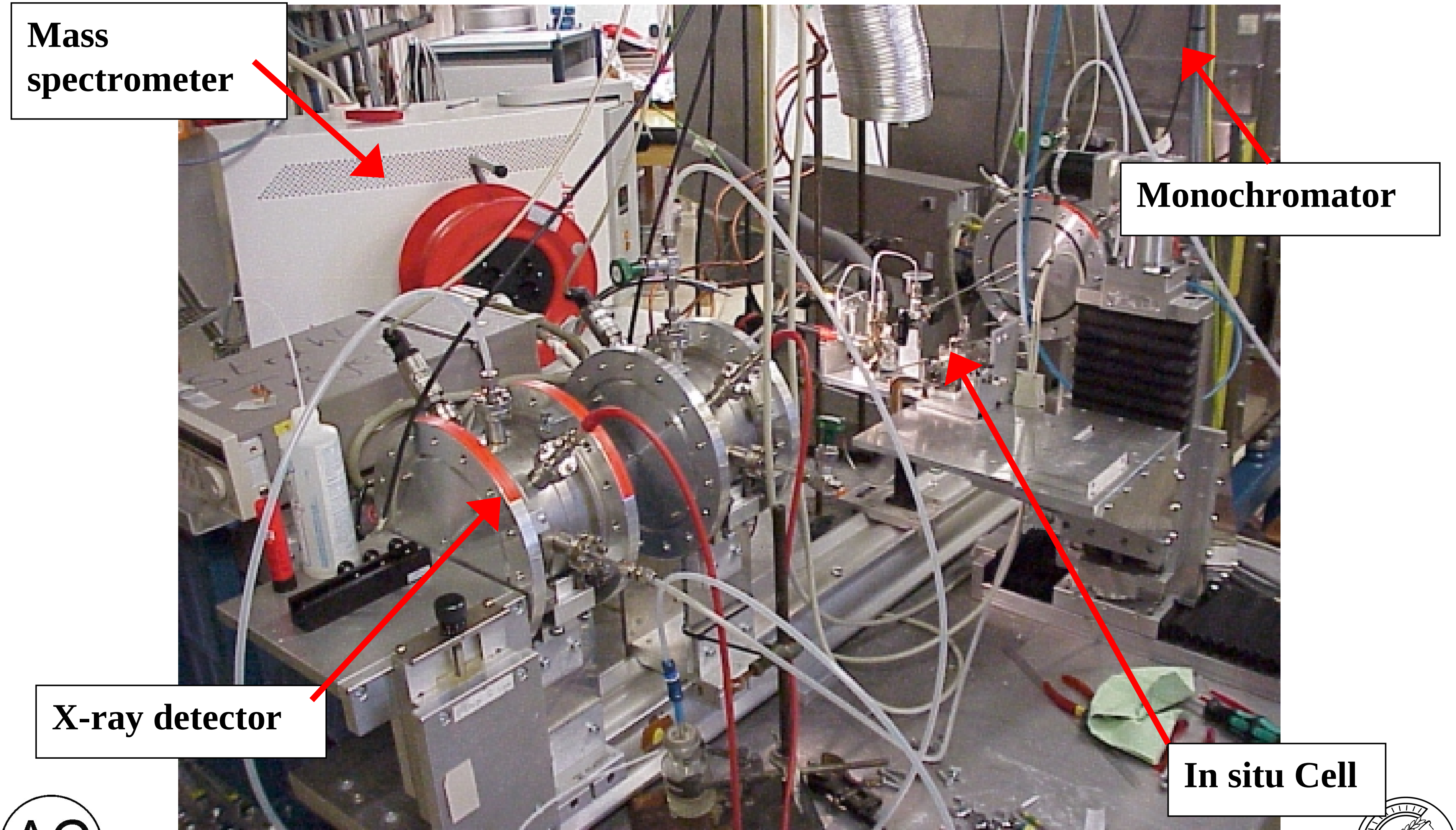


Instrumentation for Conventional XAS Studies

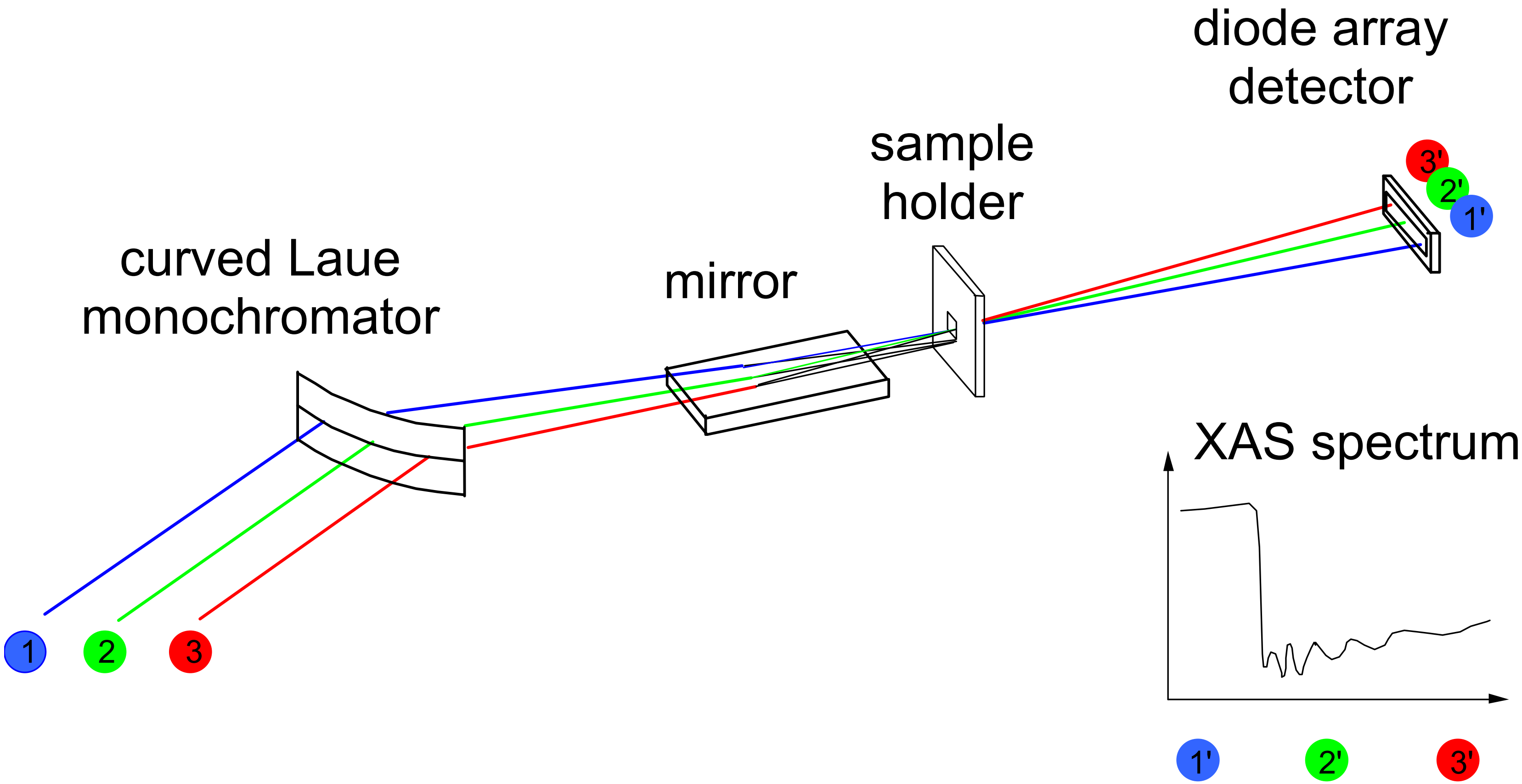


Quick-EXAFS (QEXAFS), (Hasylab, X1), ~ min/spec

Experimental Set-up for in situ XAS in Transmission

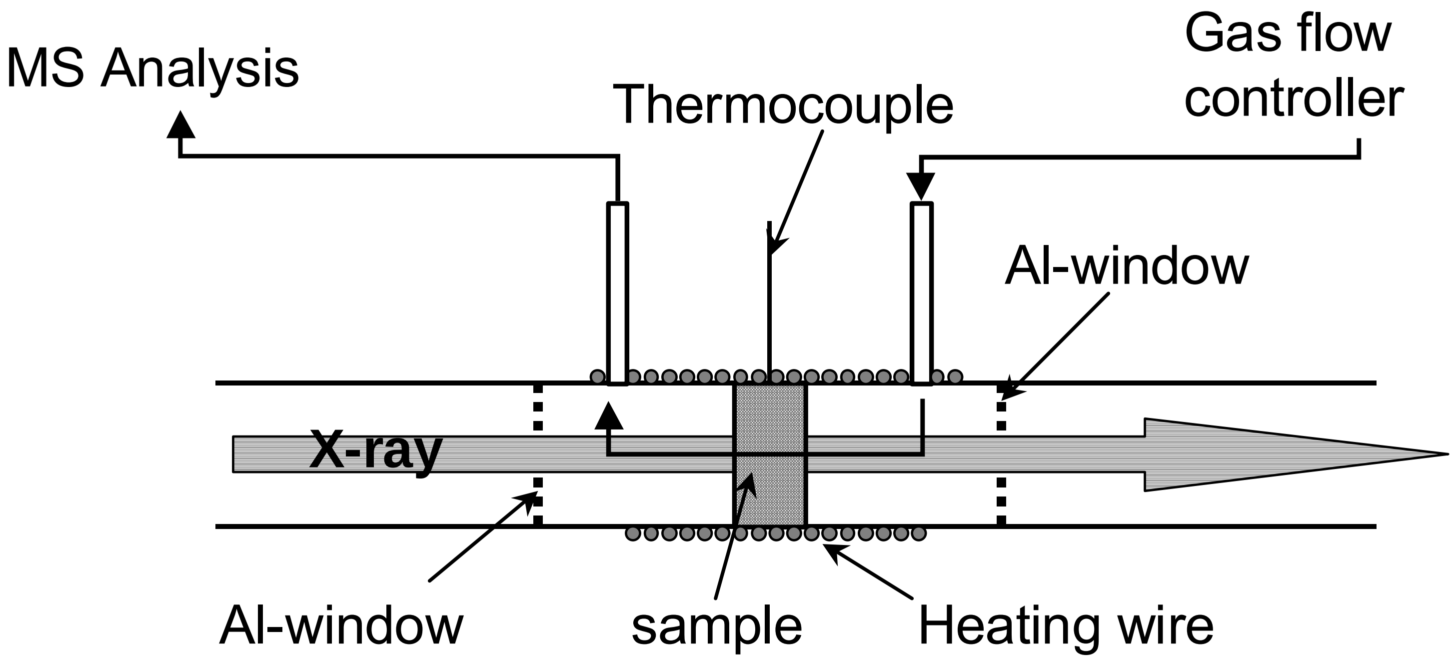


Instrumentation for Time-resolved XAS Studies

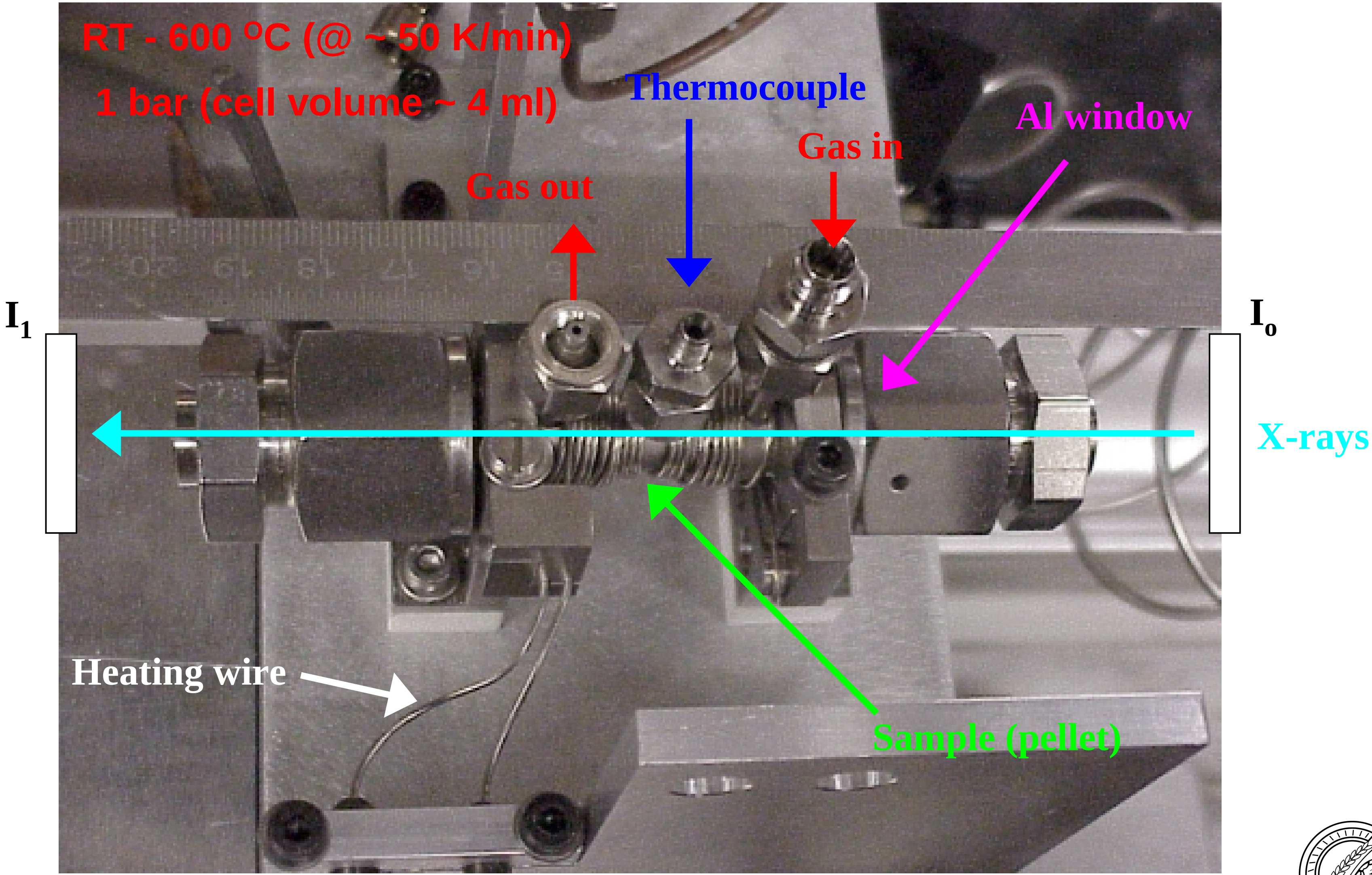


Energy-dispersive XAS (DXAFS), (ESRF, ID24), ~ s/spec

In situ Cell for XAS Studies in Transmission Mode



In situ Cell for XAS Studies in Transmission Mode



Data reduction and analysis

Structural Data from XAFS

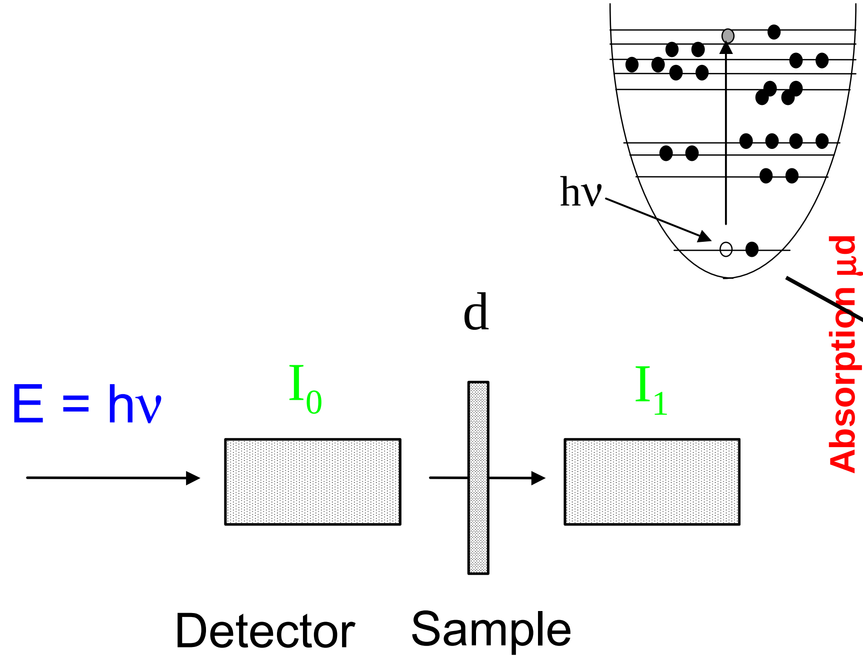
XANES (X-ray absorption near edge structure)

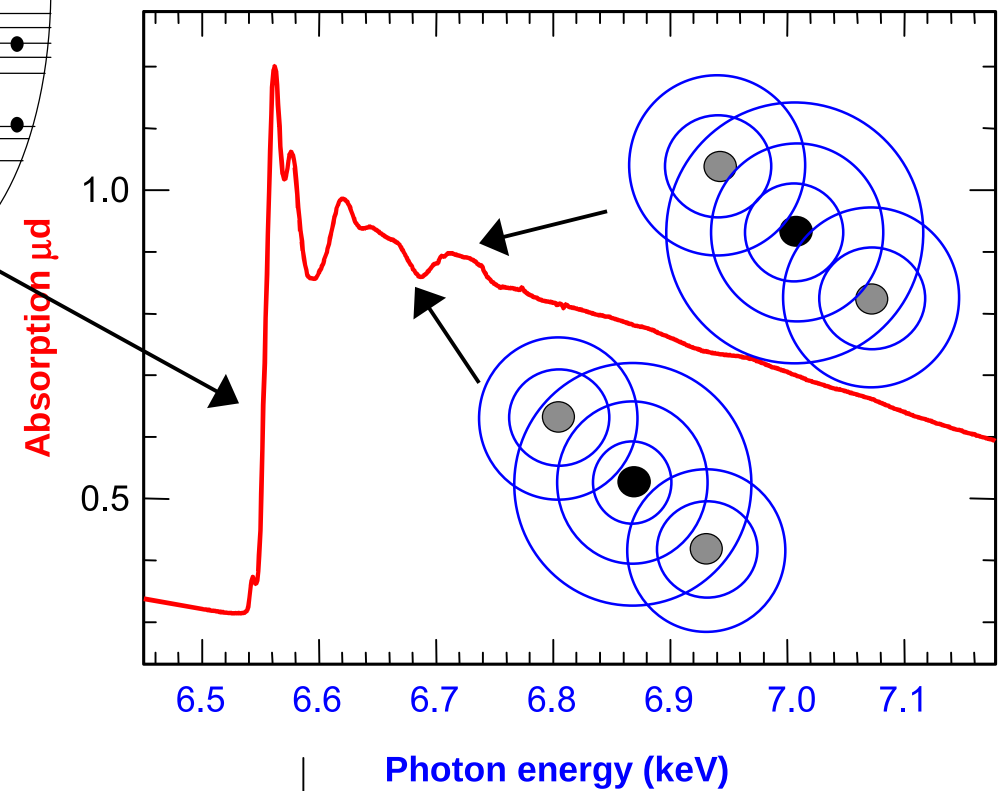
- **Valence** ☺
- **Coordination geometry**
- **Quantification of phase mixtures (PCA)** ☺
- **No reliable codes for theoretical calculations available (yet)**

EXAFS (Extended X-ray absorption fine structure)

- **Nearest neighbour**
- **Type of nearest neighbours**
- **Distance of nearest neighbour shells** ☺
- **Coordination number [and geometry (bond angle)]** ☺
- **Theoretical calculations become standard for data analysis**

X-ray Absorption Spectroscopy - Origin

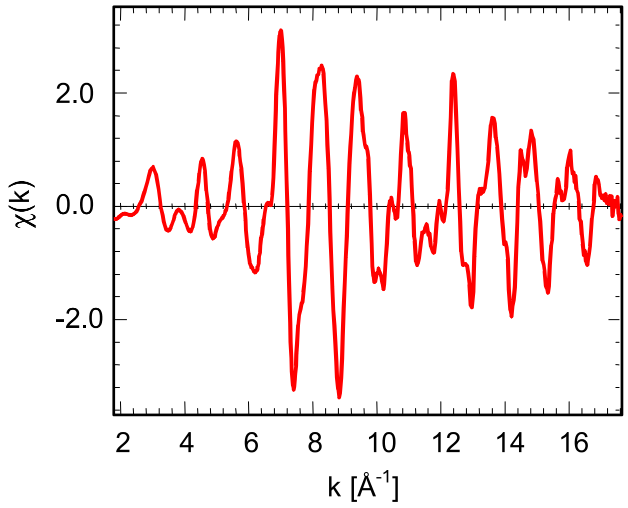




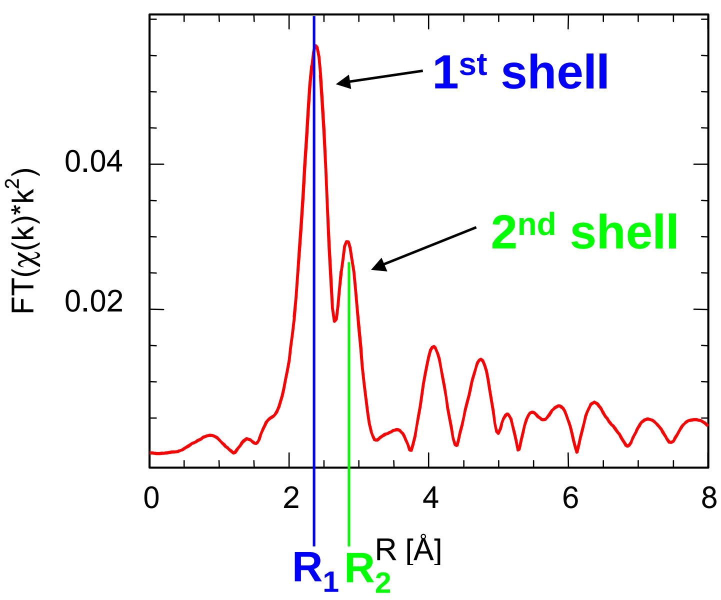
$$\mu d = \ln (I_0 / I_1)$$

XANES | EXAFS

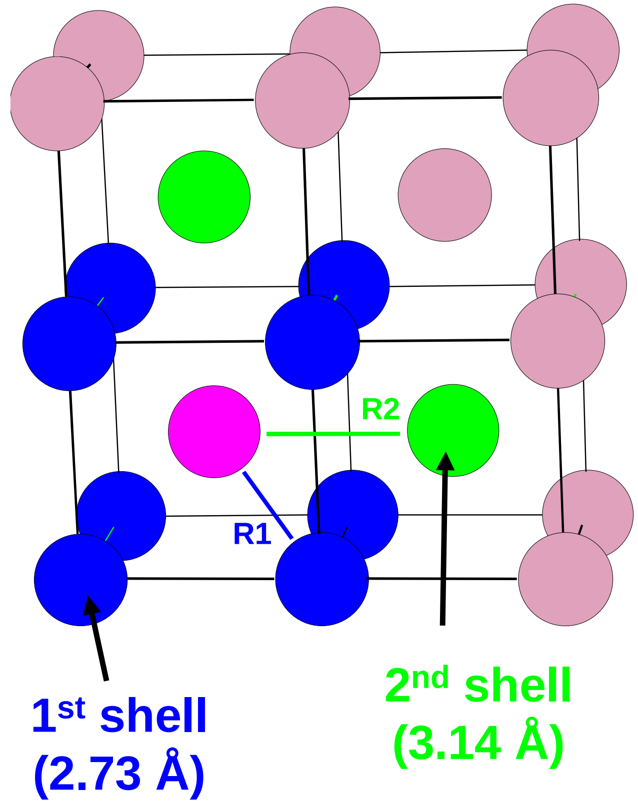
X-ray Absorption Spectroscopy - Structure



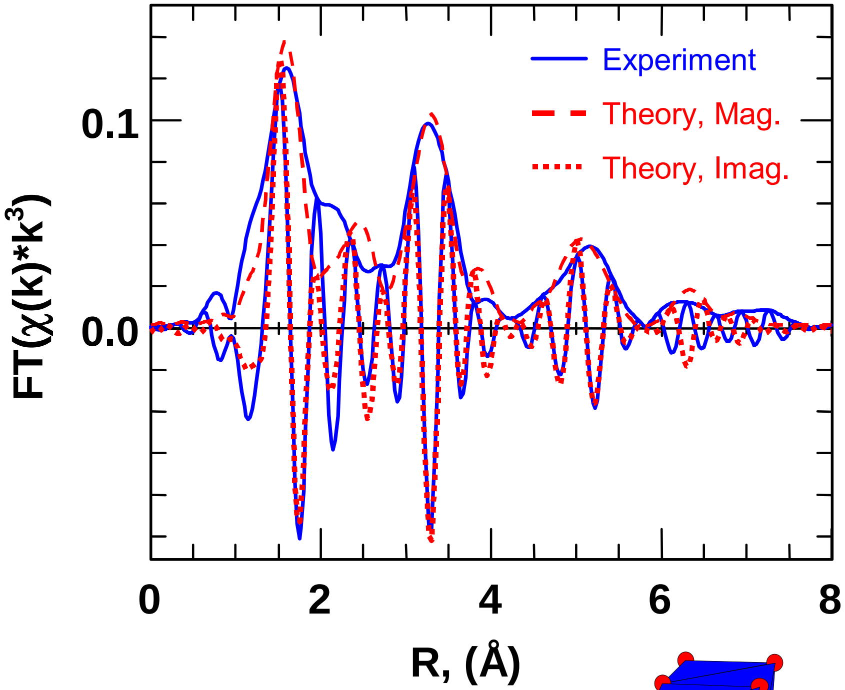
FT →

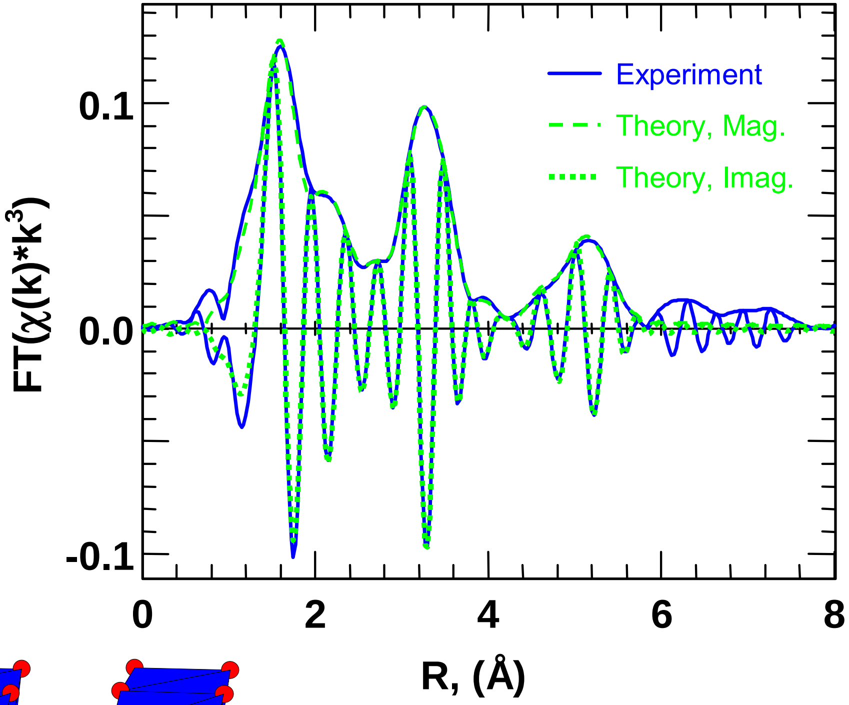


Mo Metal (bcc)

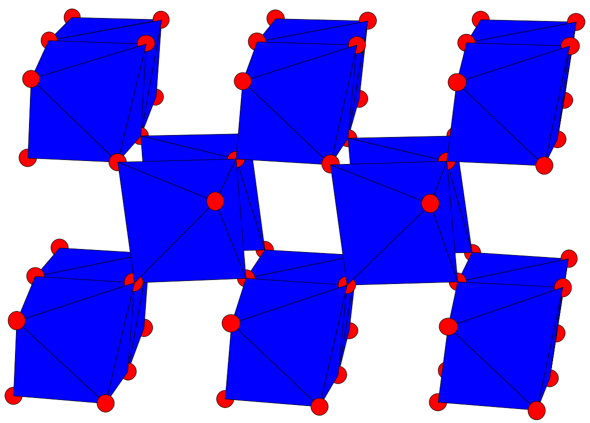


Short-range order from XAFS Data





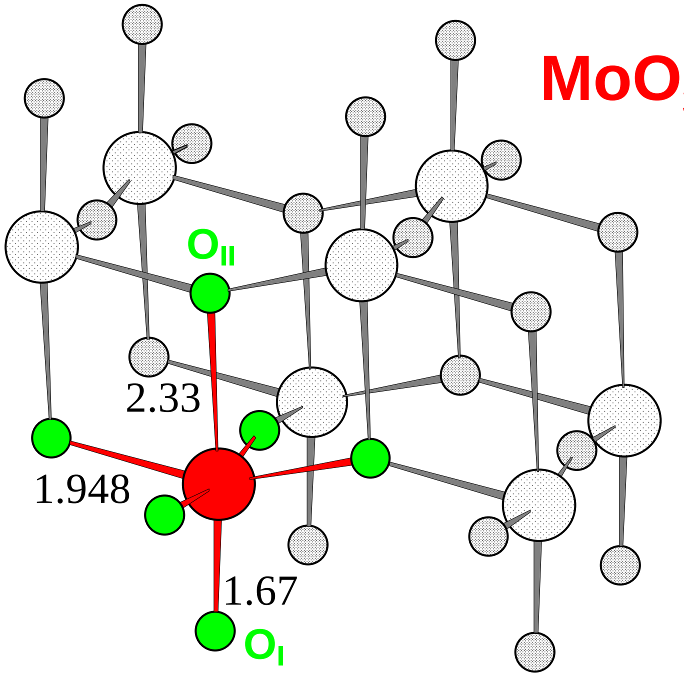
Tetragonal (P*42/mnm*)



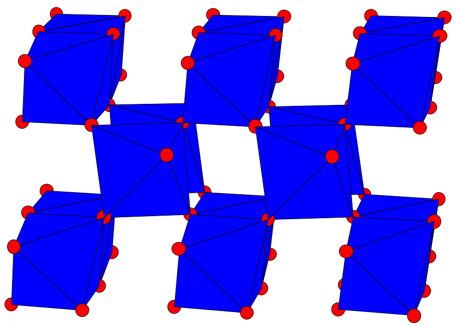
Monoklin (P*21/c*)

MoO_2

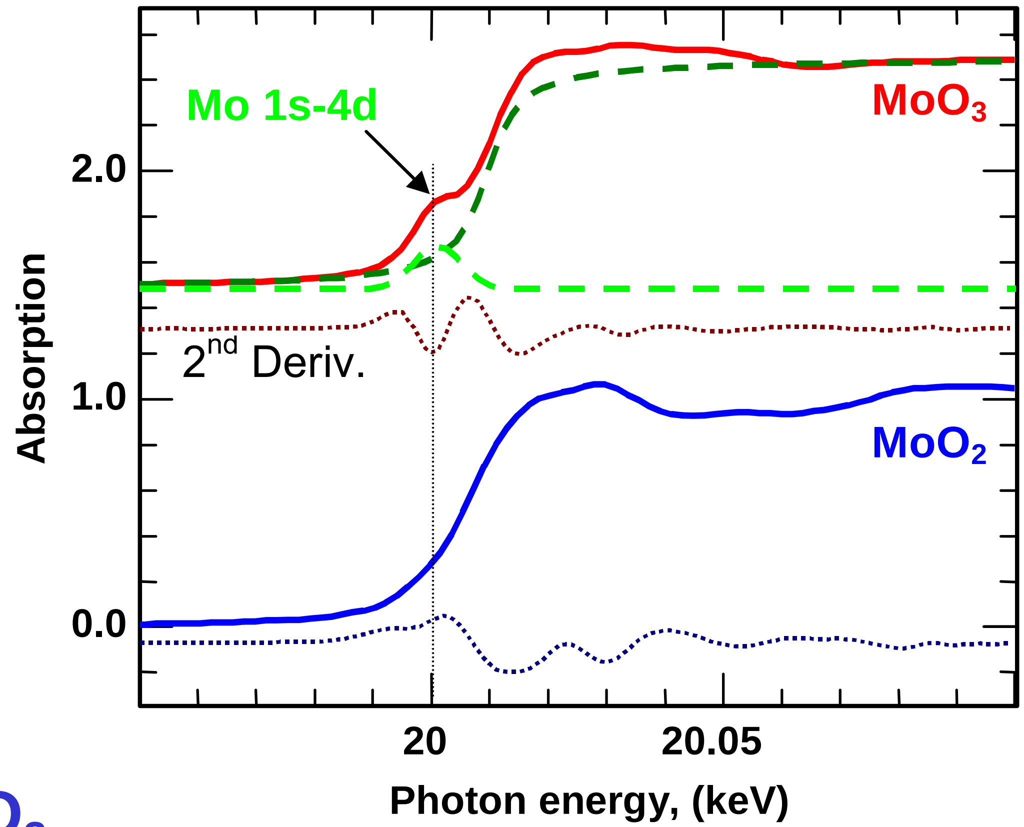
Coordination Geometry from Near-edge Structure



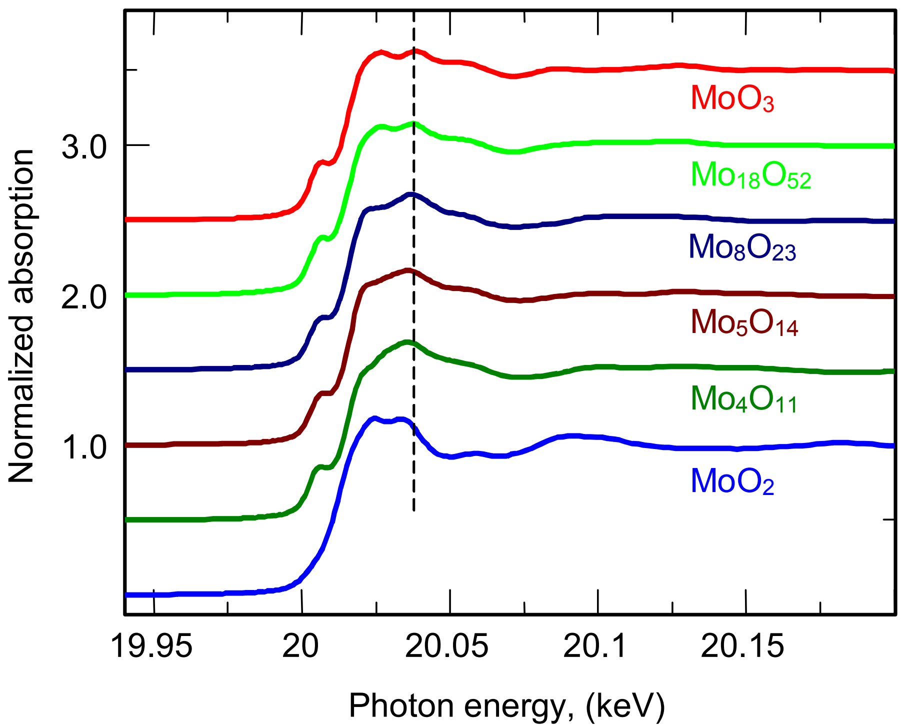
MoO_3

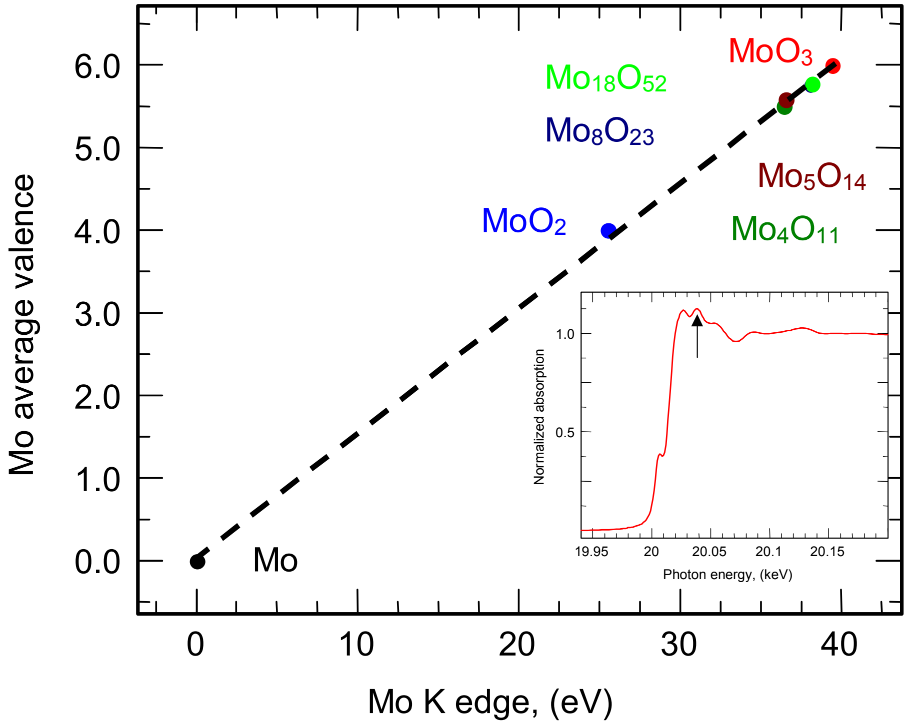


MoO_2

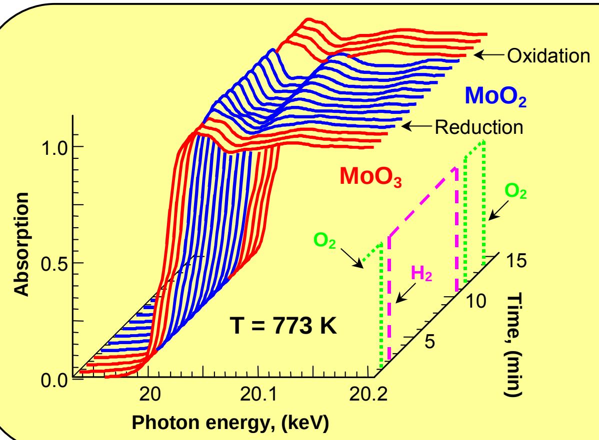


XAFS References – Near-edge Structure and Average Valence





Phase Analysis from XAFS Data (Factor Analysis)



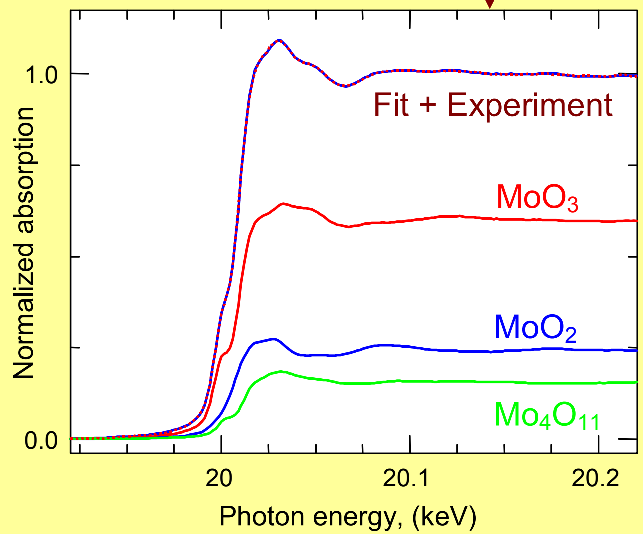
Faktoranalyse

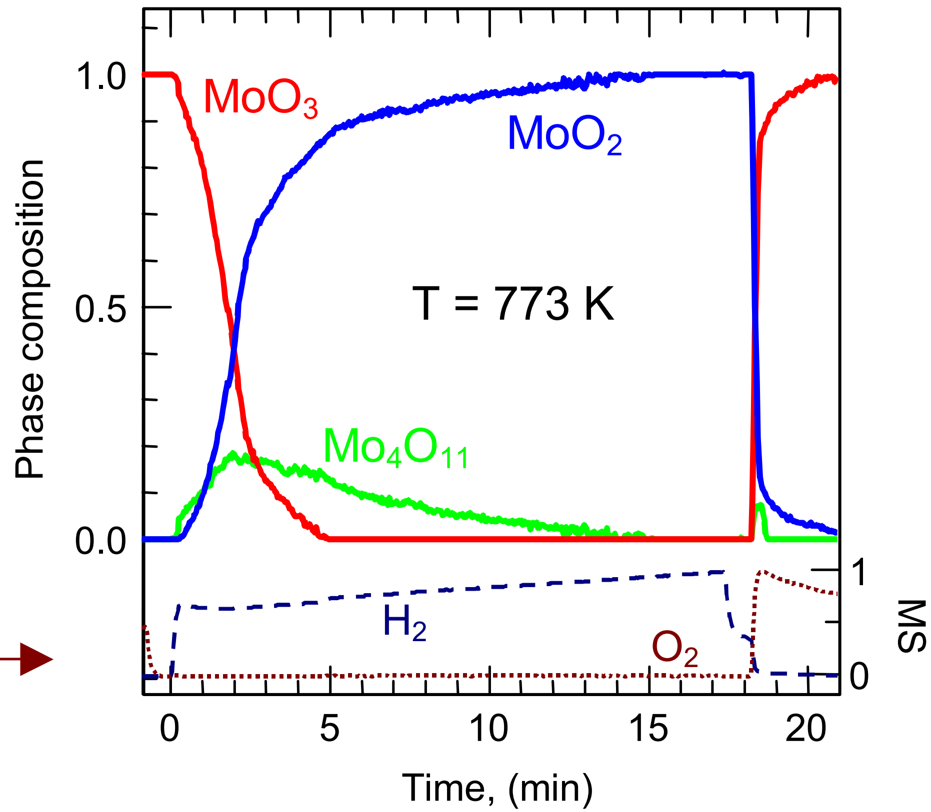
↓

MoO_3

MoO_2

Mo_4O_{11}

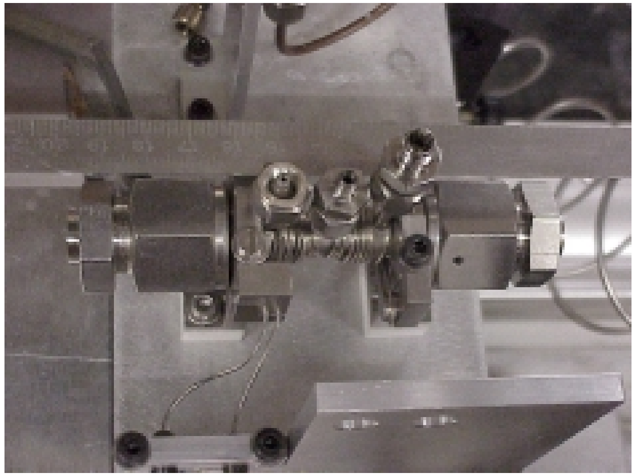


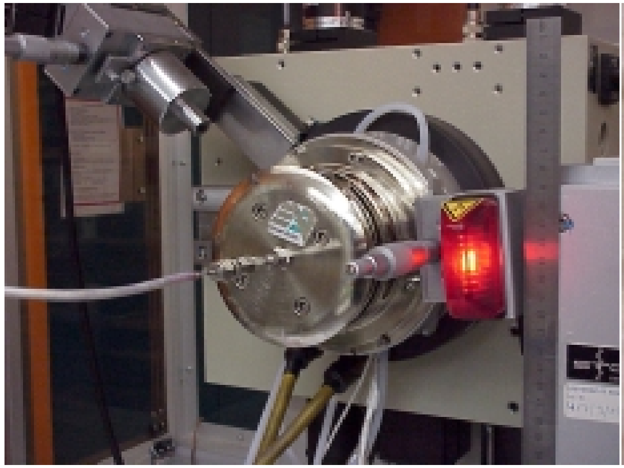


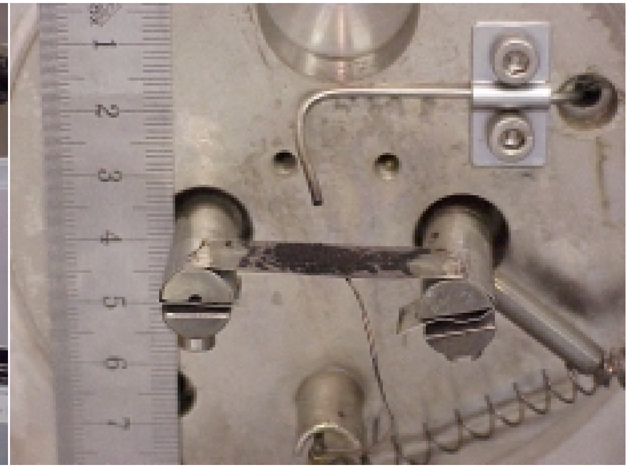
Example:

Molybdenum oxides

In situ XAS and XRD



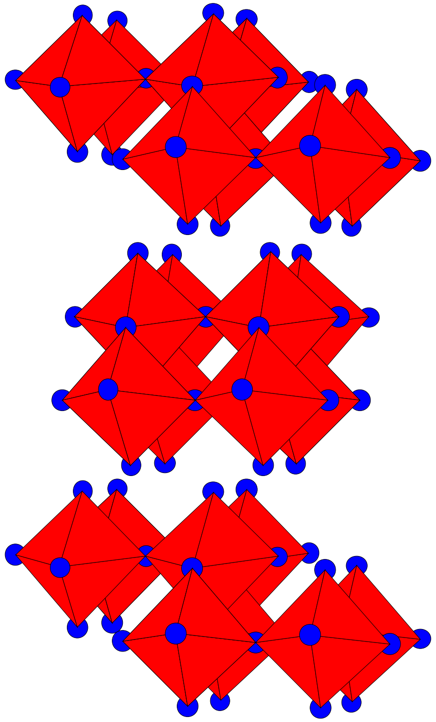




In situ XAS	**In situ Pulver-XRD**
DXAFS (ESRF, ID24), ~ 2 s/spec	STOE STADI P
QEXAFS (Hasylab, X1), ~ 4 min/spec	Bragg-Brentano (~ 7 min (10 °))
Pellet-Reactor in Transmission + MS	Bühler HDK S1 + MS
Elementspezifisch, Nahordnung, Mittlere Valenz, Phasen (amorph)	**Fernordnung, Kristallitgrößen, Verspannungen, Phasen (kristallin)**

Reduktion / Oxidation - Teilschritte des “Redox”-Mechanismus

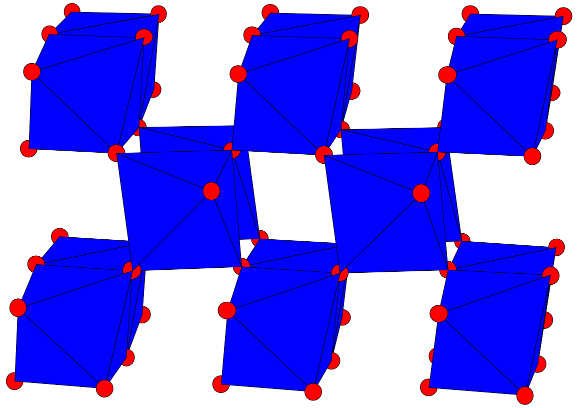
MoO_3



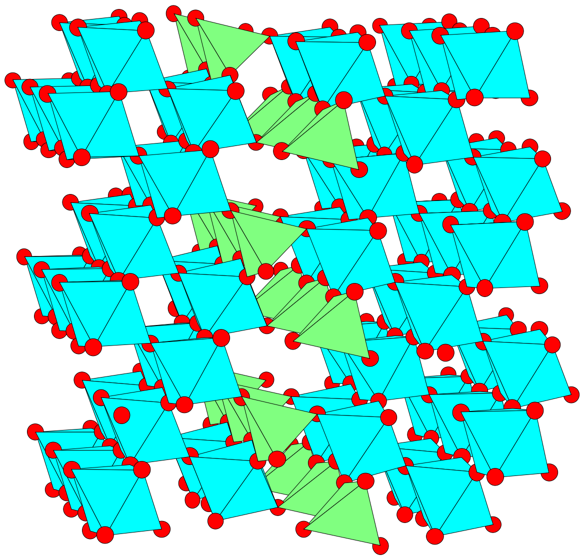
H_2, propene →

← O_2

MoO_2



Mo_4O_{11}

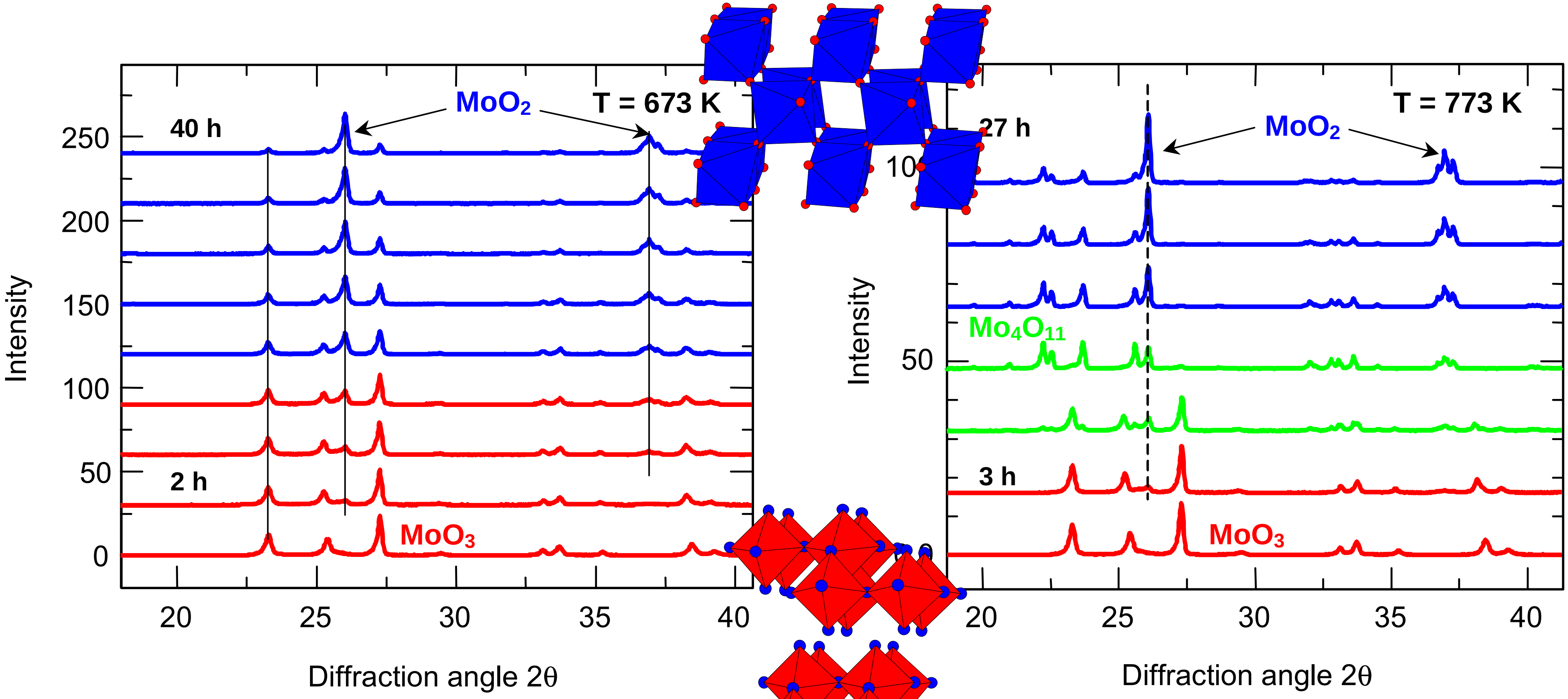


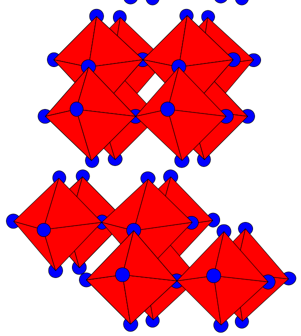
Mo_8O_{23}

Mo_9O_{26}

$Mo_{18}O_{52}$

Reduktion von MoO_3 in 5 % H_2 – In situ XRD

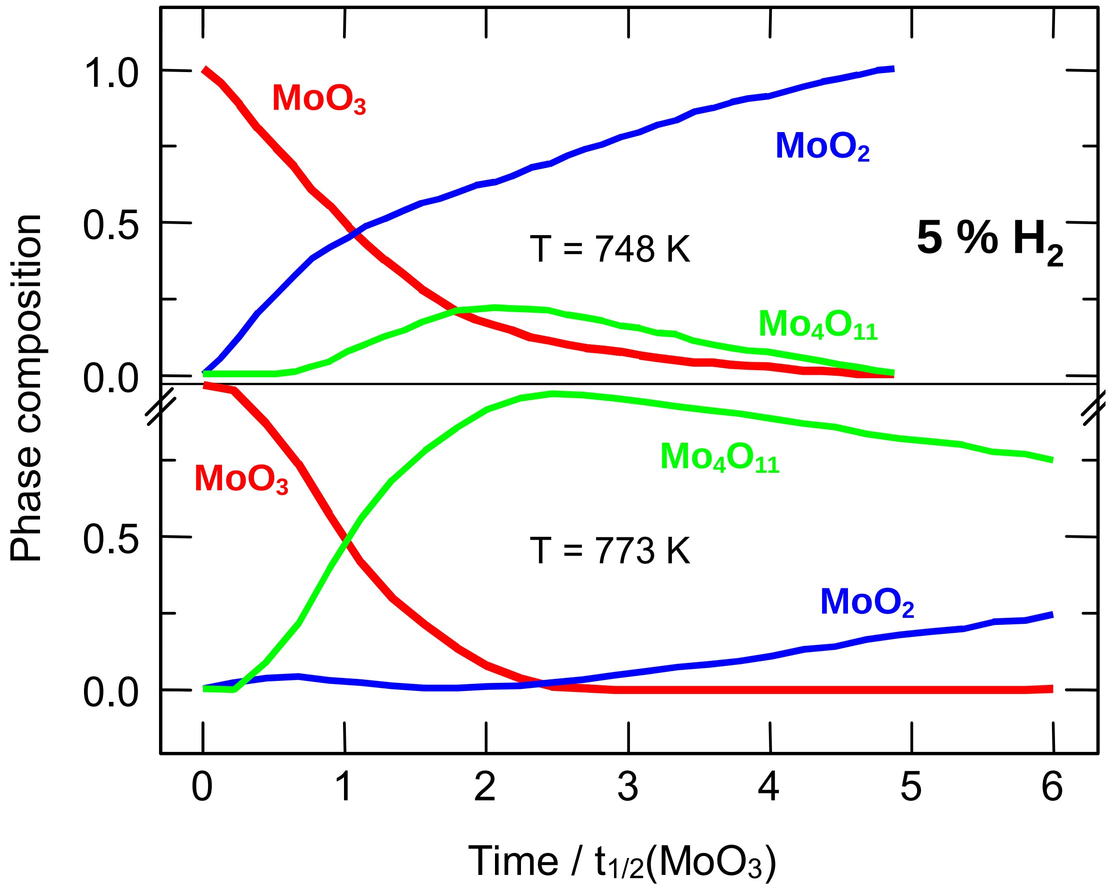




Keine Bildung von Mo_4O_{11} bei T < 700 K

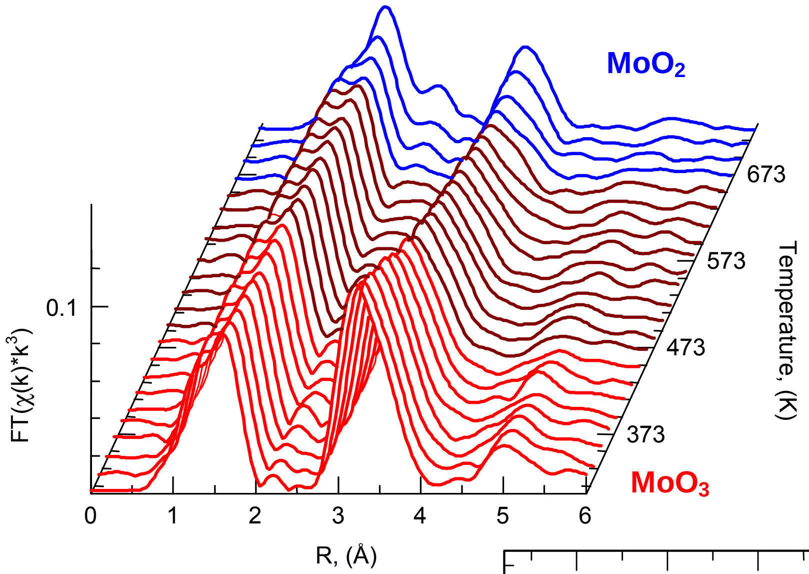
Bei T > 700 K Mo_4O_{11} kein Zwischenprodukt

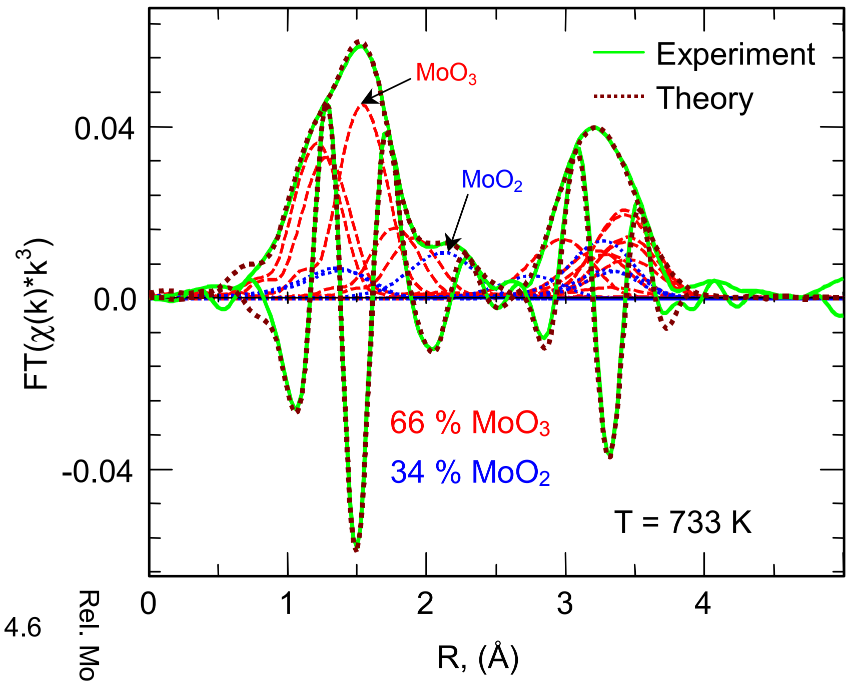
Bildung von Mo_4O_{11} aus MoO_3 und MoO_2

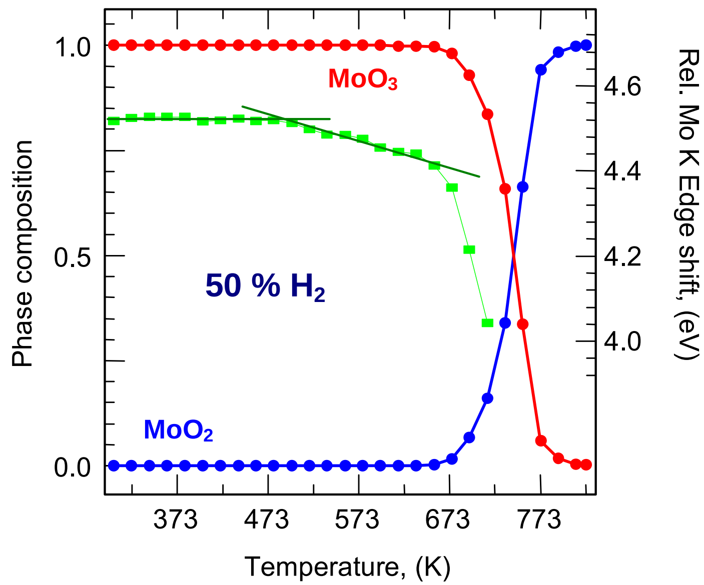


Keine Bildung von Mo_4O_{11} bei T < 700 K

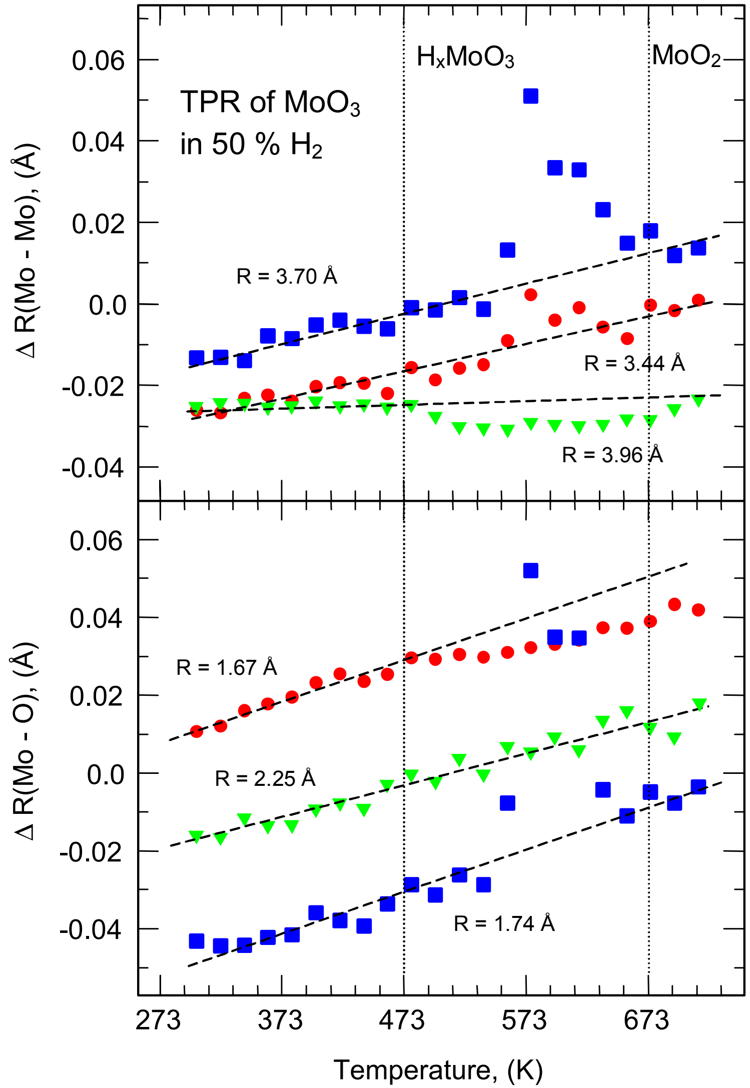
Change in FT(χ(k)) and Mo K edge position during TPR of MoO_3 with H_2 prior to MoO_2 formation

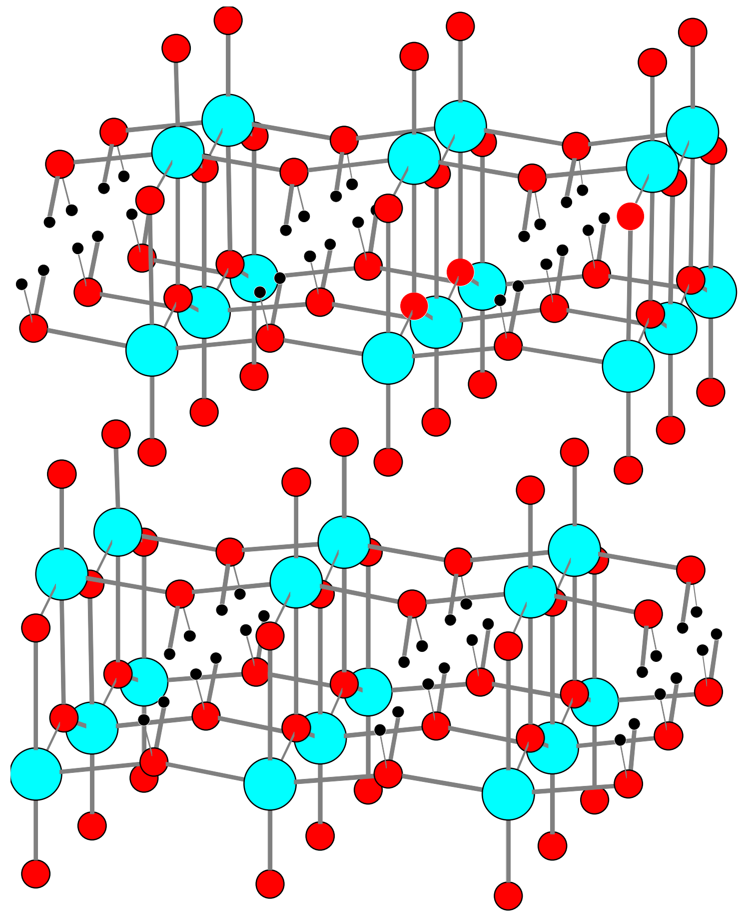






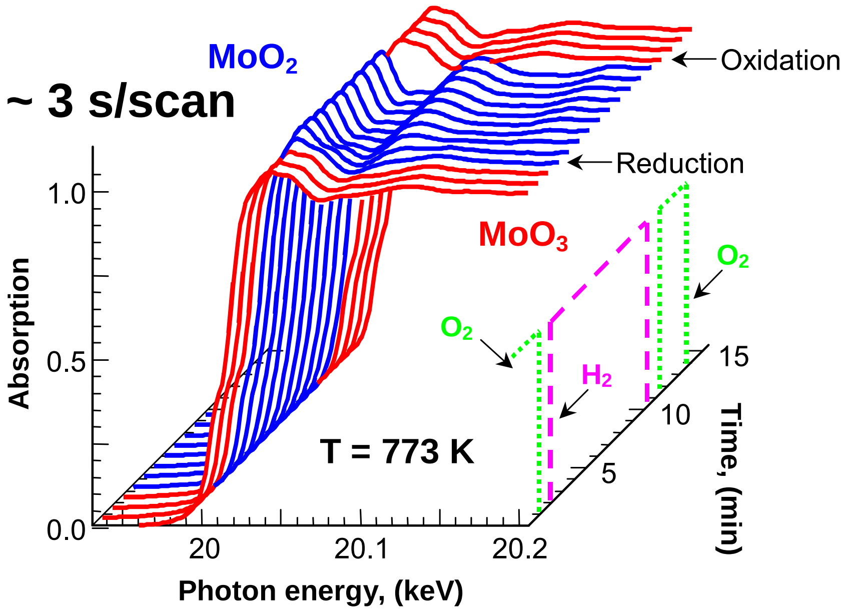
Local structural changes indicate formation of H_xMoO_3 (x ~ 0.07)

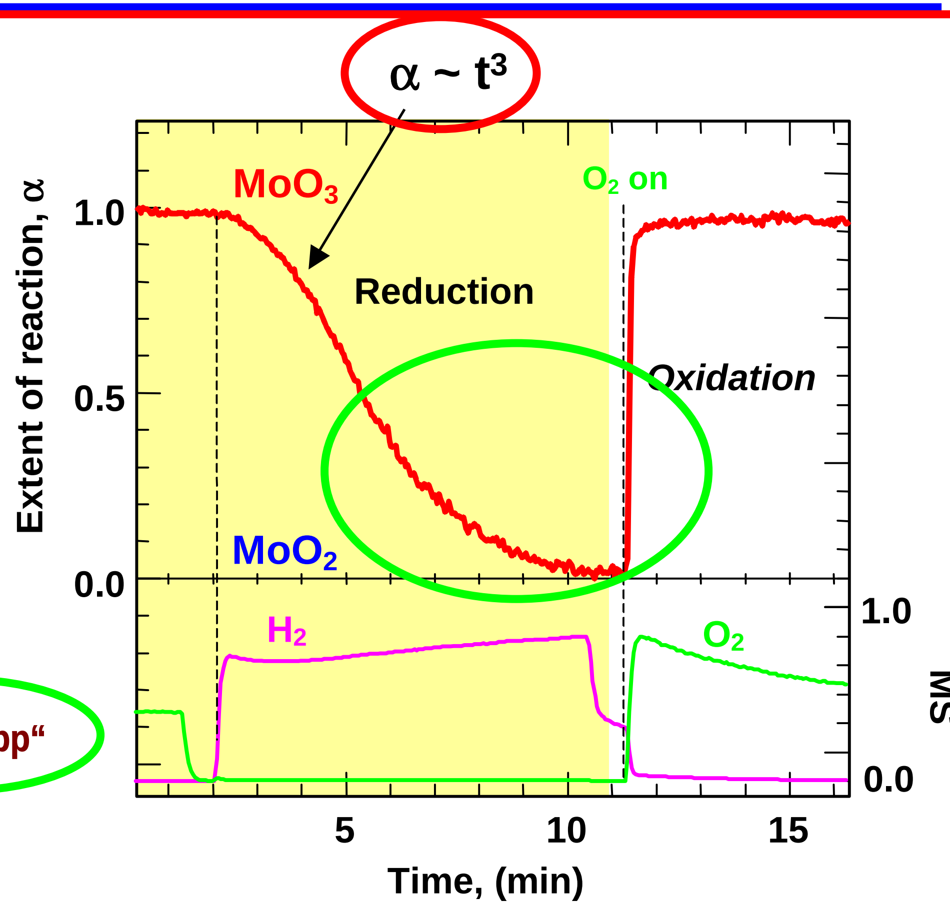


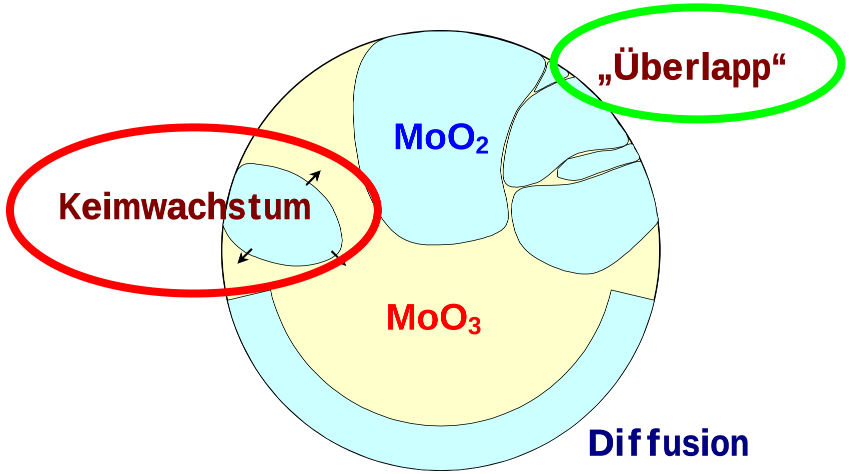


$H_{0.34}MoO_3$ (*Cmcm*)

Kinetics of the Reduction of MoO_3 in H_2

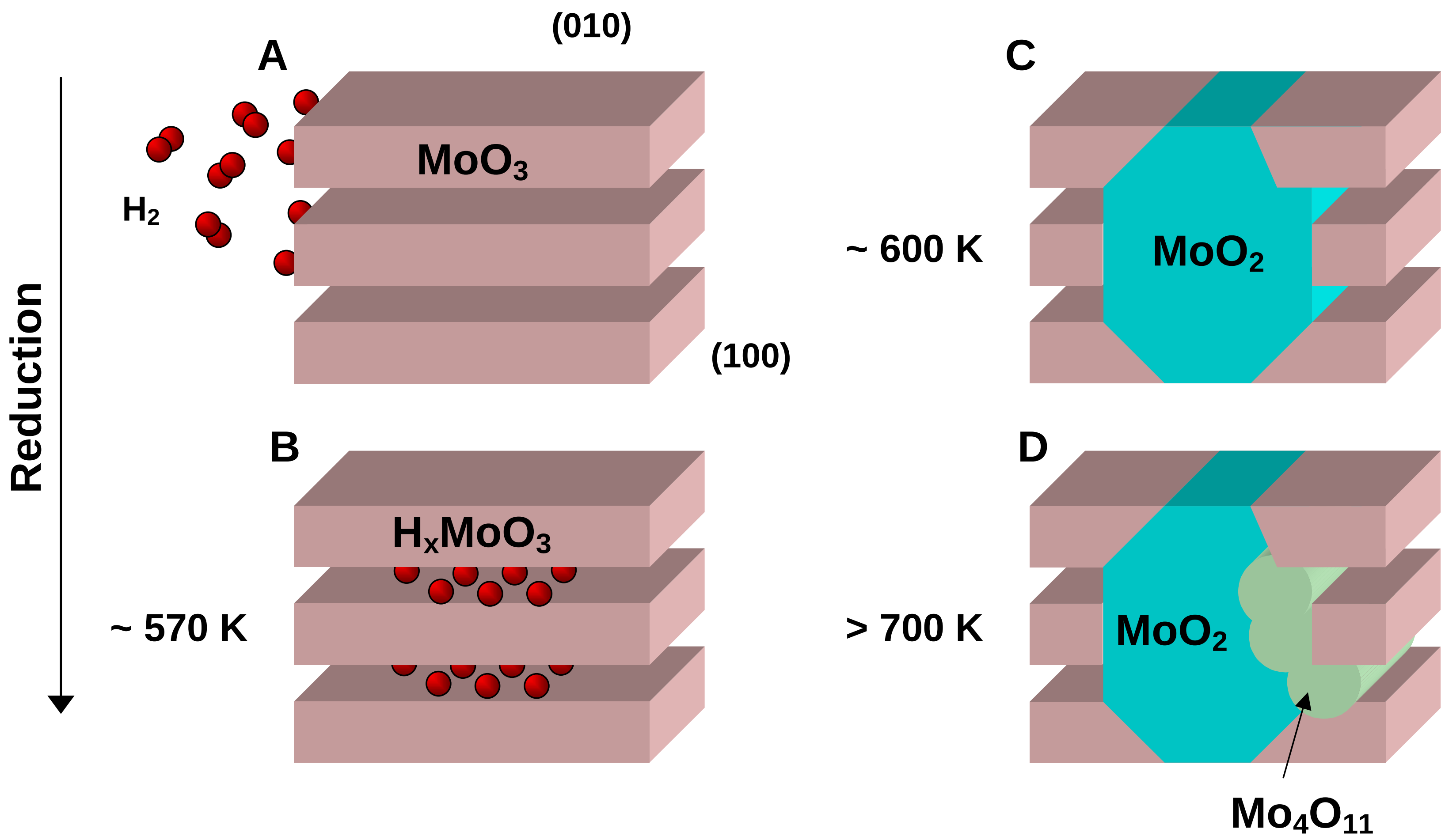






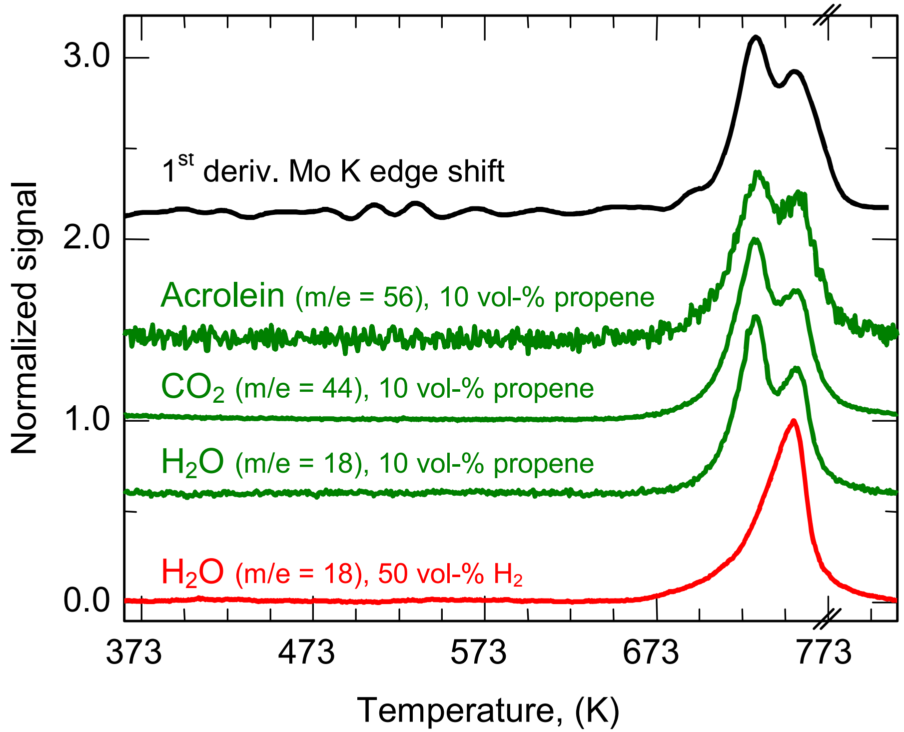
nucleation growth kinetics

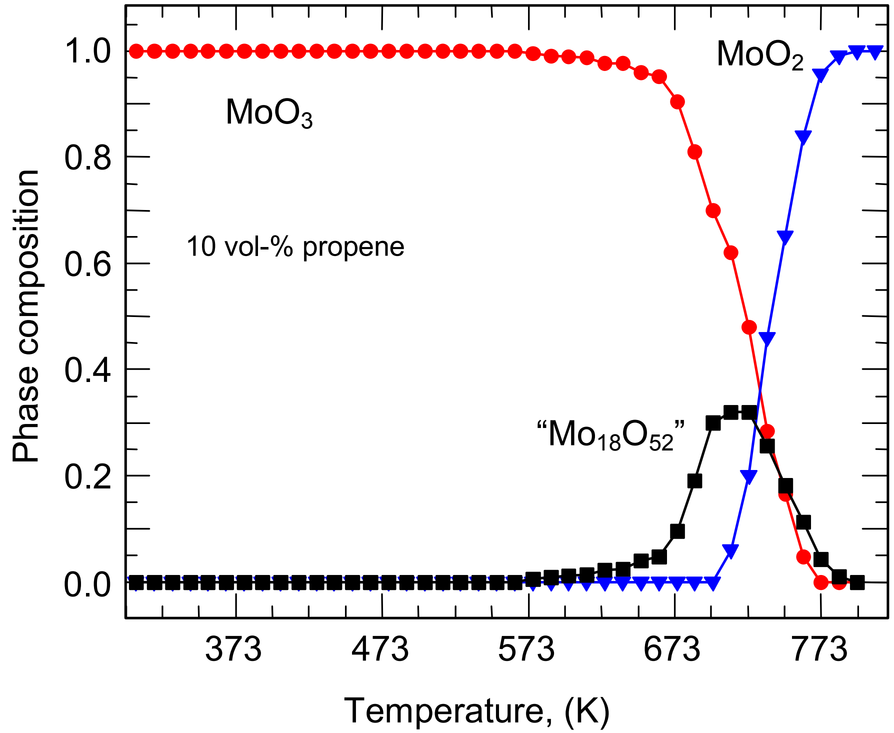
Schematischer Mechanismus der Reduktion von MoO_3 in H_2



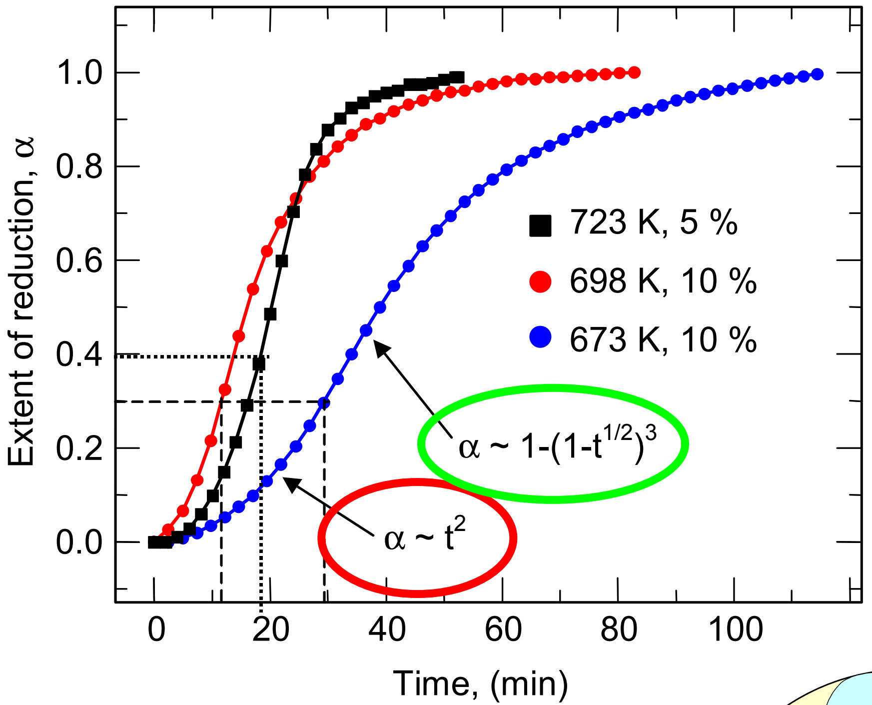
Bildung von "$Mo_{18}O_{52}$" bei der Reduktion von MoO_3 in Propen

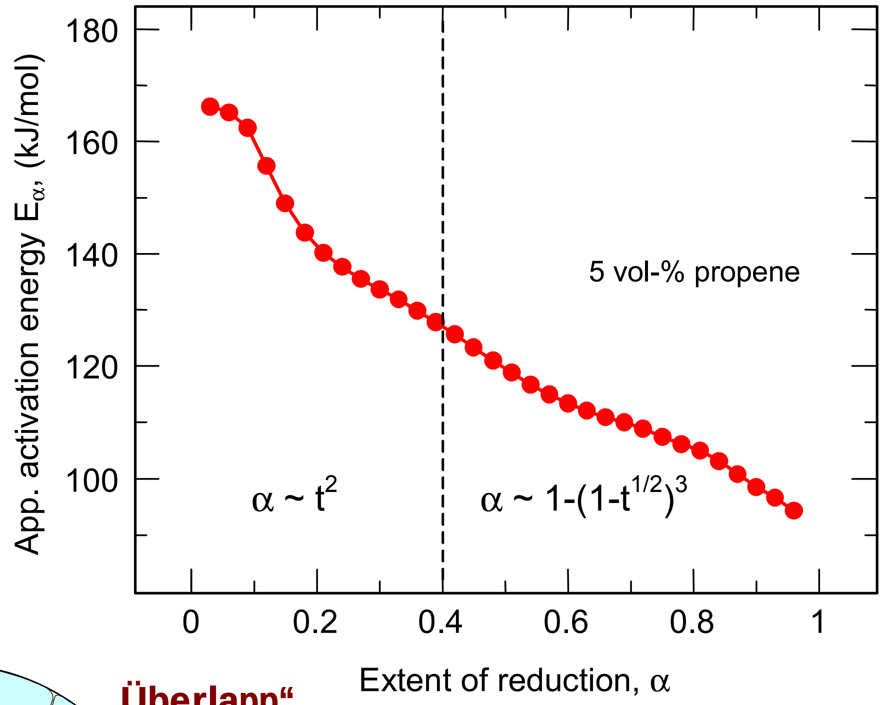
$$4\ C_3H_6 + 22\ MoO_3 \rightarrow 2\ C_3H_4O + 6\ CO_2 + 8\ H_2O + 22\ MoO_2$$

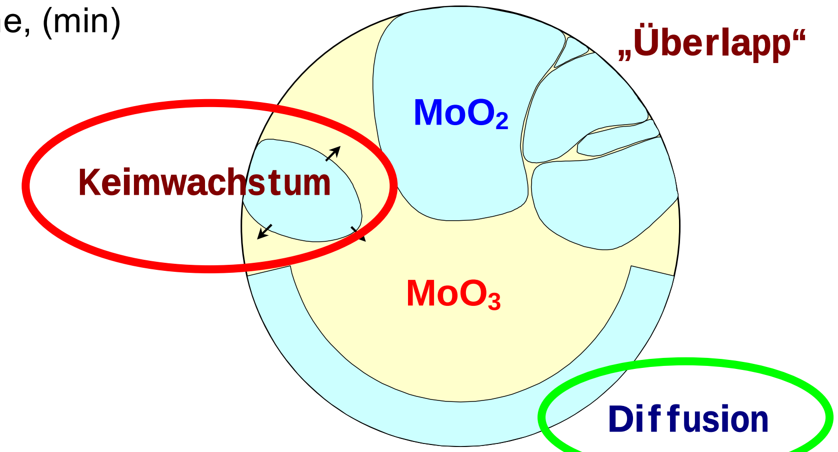




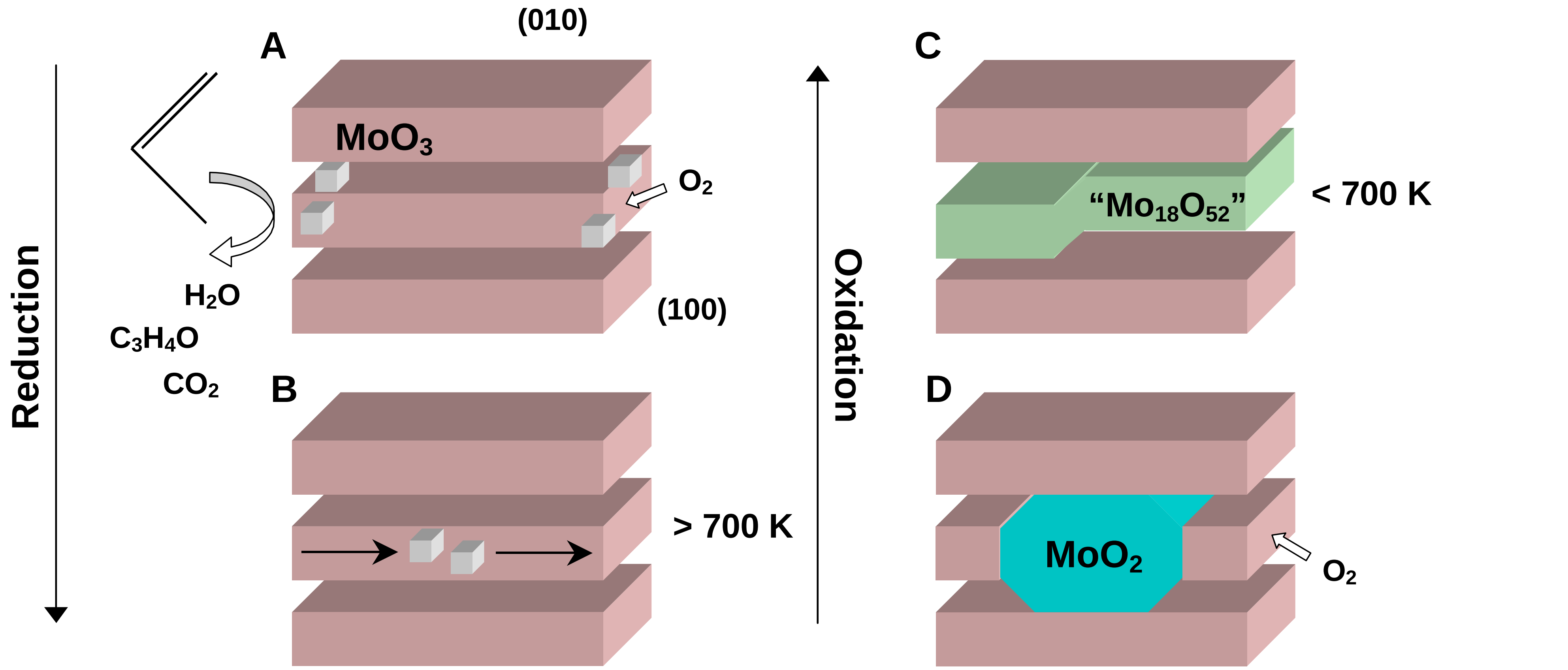
Kinetics of the Reduction of MoO_3 in Propene





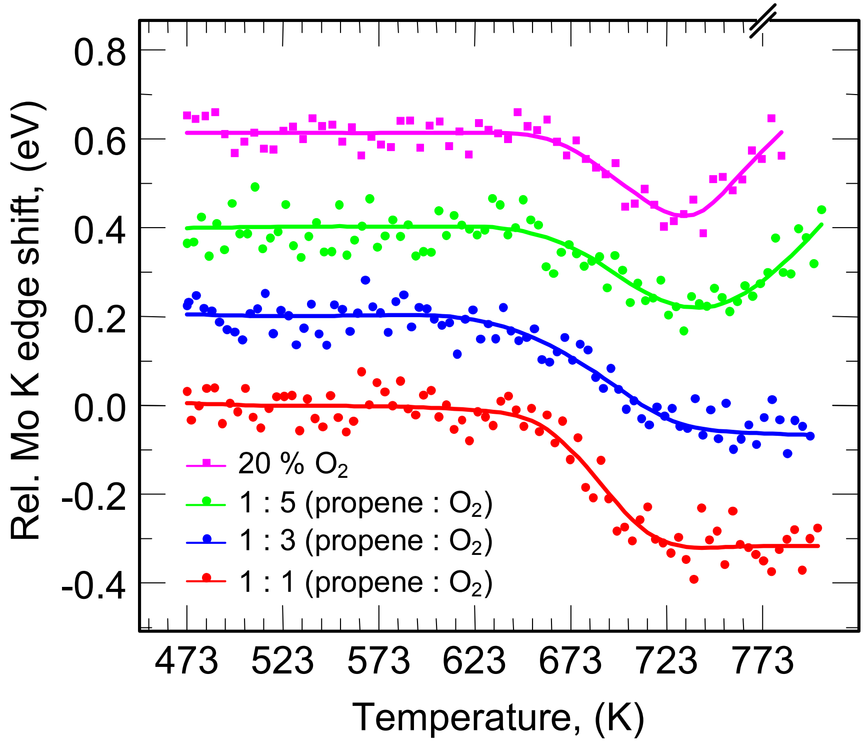


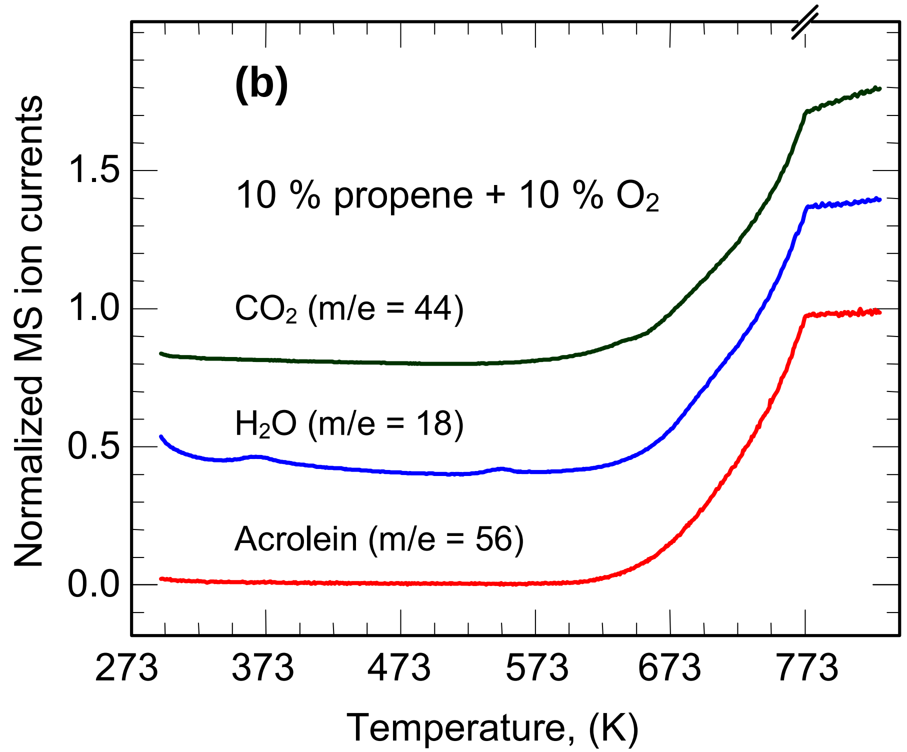
Schematischer Mechanismus der Reduktion von MoO_3 in Propen



Mittlere Valenz von MoO_3 unter Reaktionsbedingungen

$$4\ C_3H_6 + 11\ O_2 \xrightarrow{MoO_3} 2\ C_3H_4O + 6\ CO_2 + 8\ H_2O$$



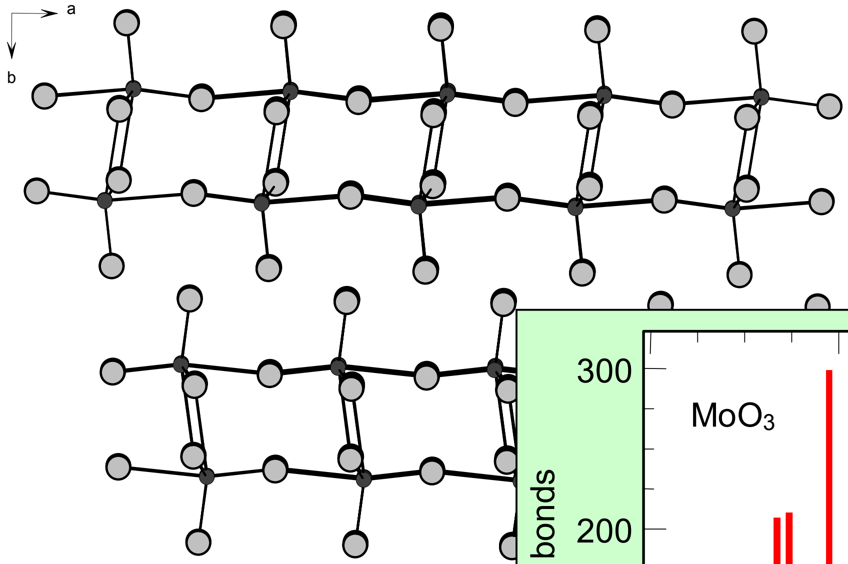


0.3 eV ~ 5.94

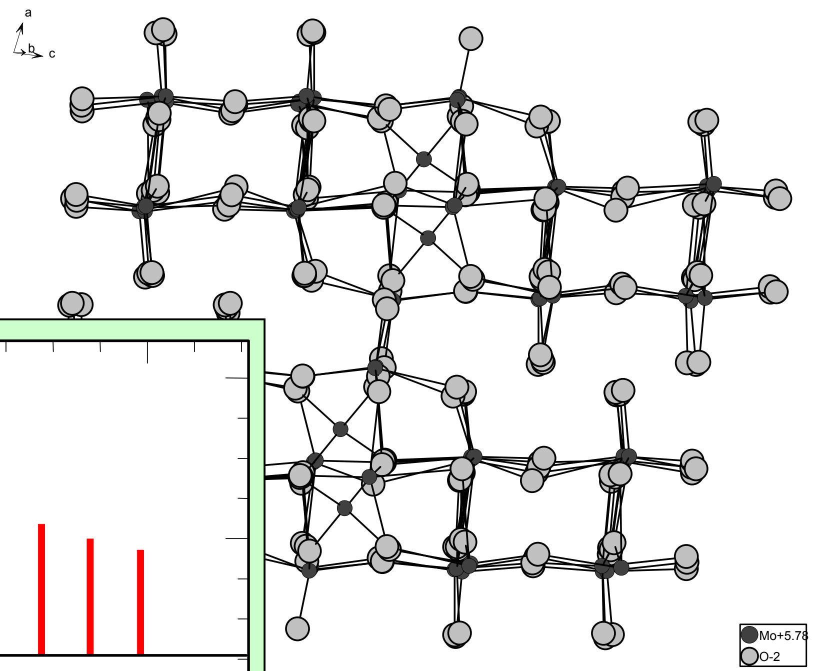
Reduktion von MoO_3 in H_2, He, Propen und Propen + O_2 bei ~ 620 K

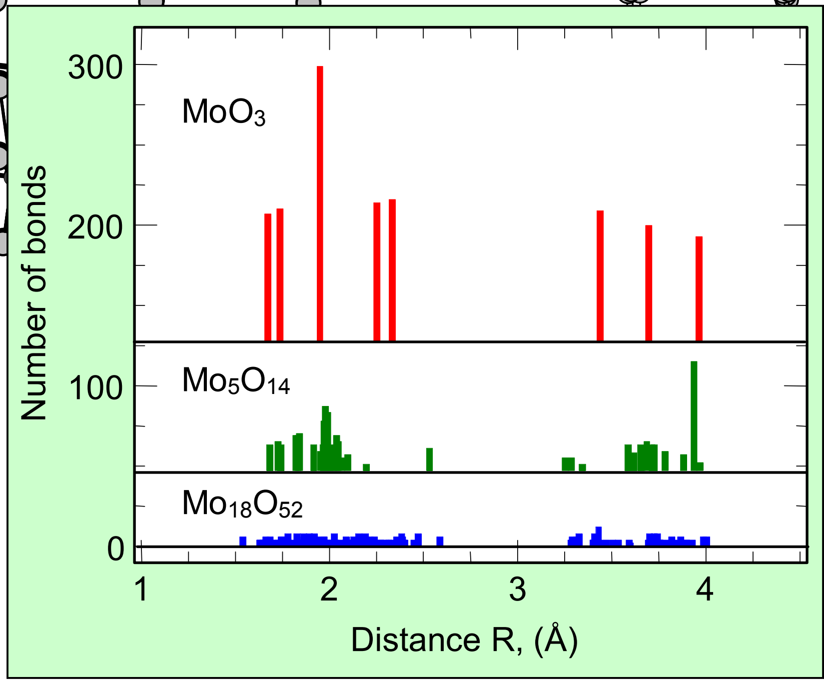
Vergleich der Strukturen von MoO_3 und $Mo_{18}O_{52}$

MoO_3

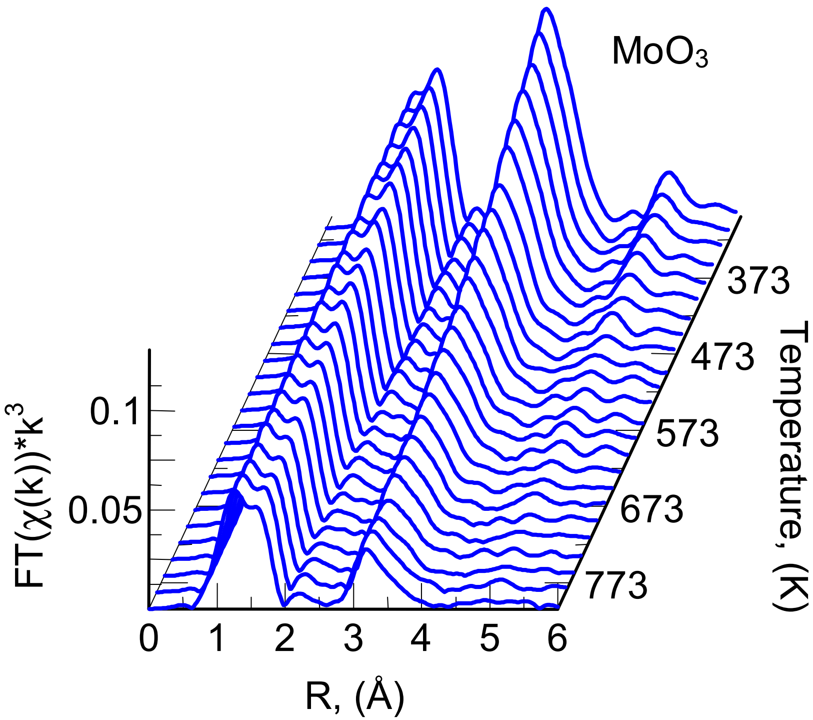


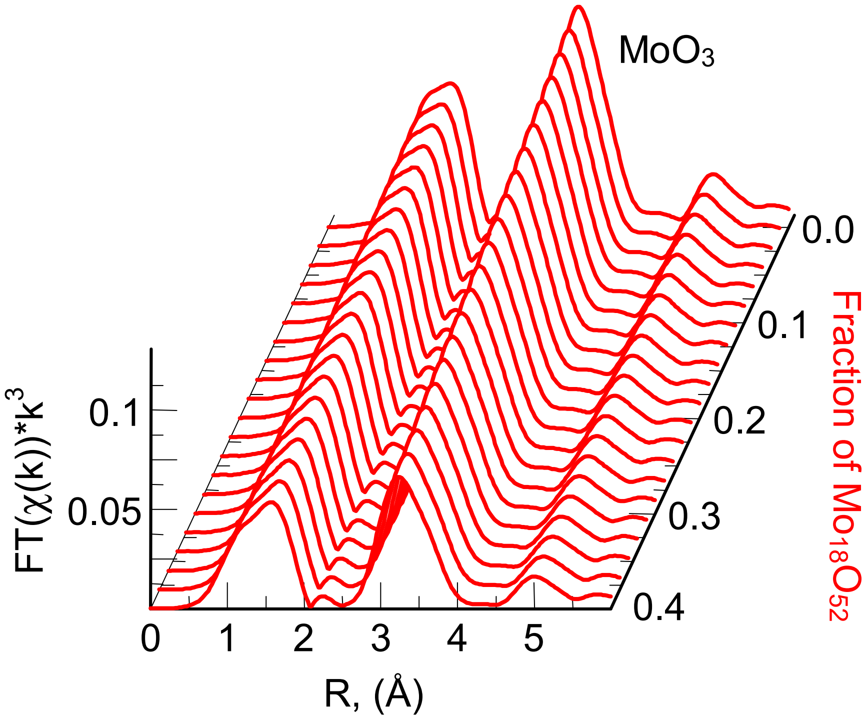
$Mo_{18}O_{52}$





RDF von MoO_3 als Funktion von T oder $c(Mo_{18}O_{52})$

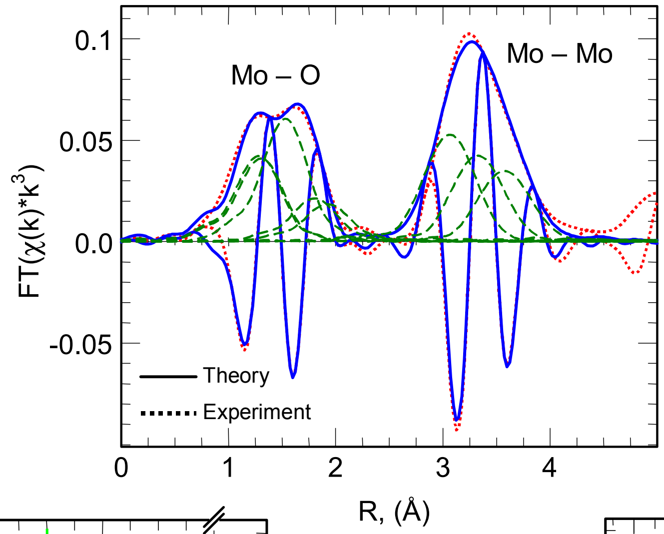


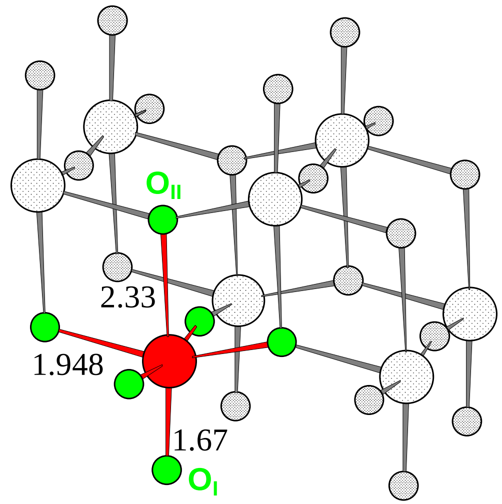


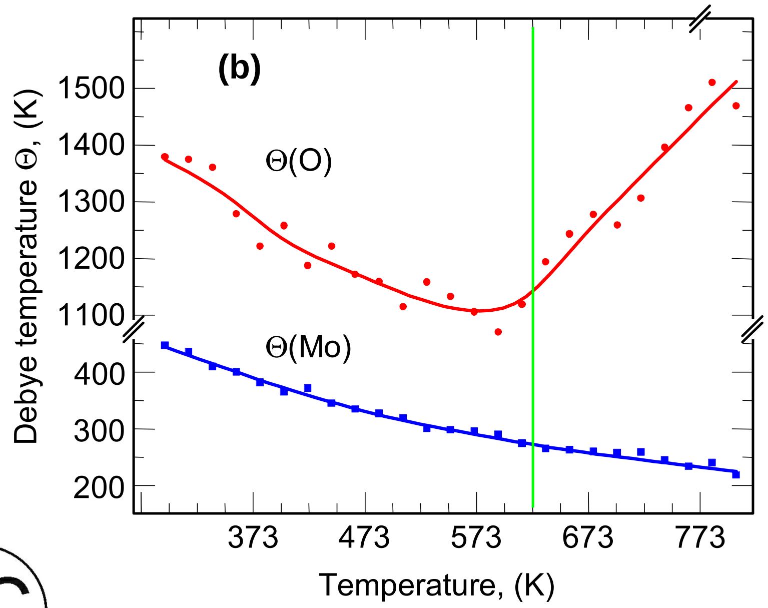
0.3 eV ~ 5.94 ~ 25% $Mo_{18}O_{52}$

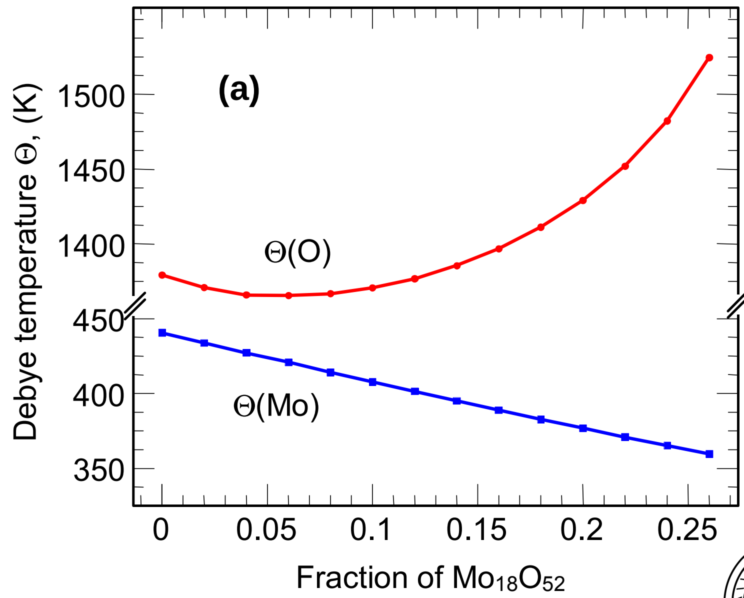
Bildung von „$Mo_{18}O_{52}$“ Defekten unter Reaktionsbedingungen

XAFS Verfeinerung von MoO_3 Struktur an experimentelle Daten

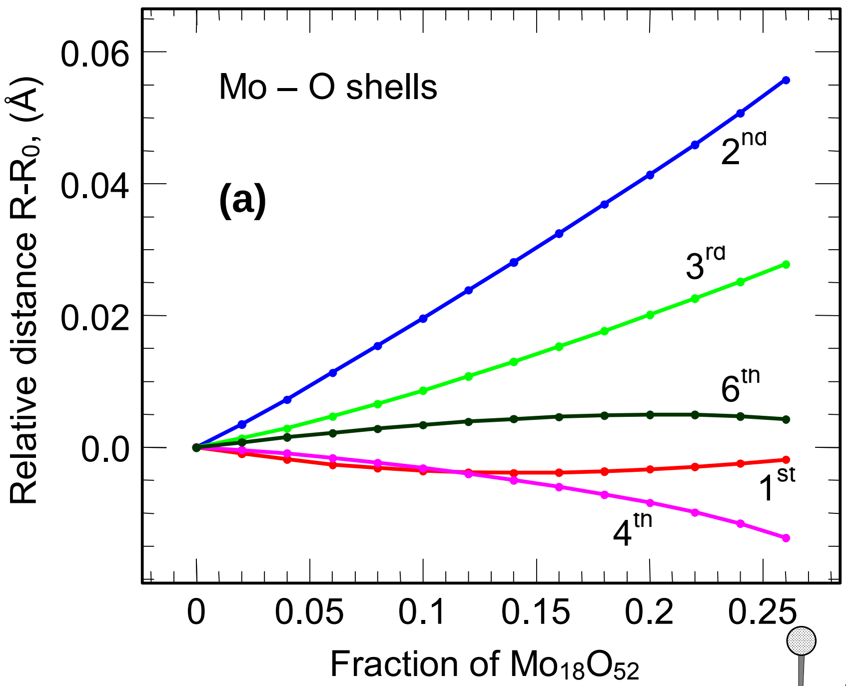


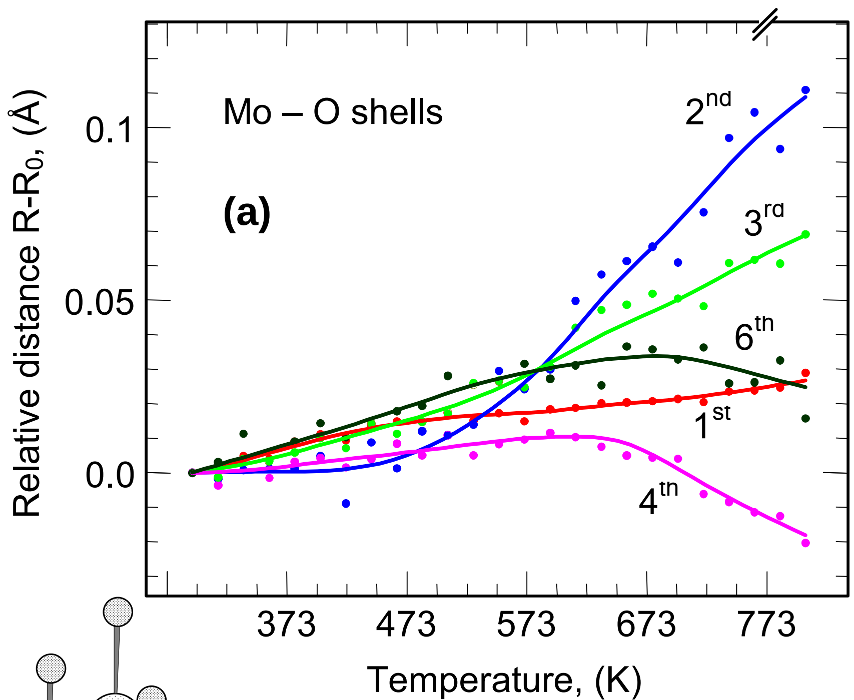


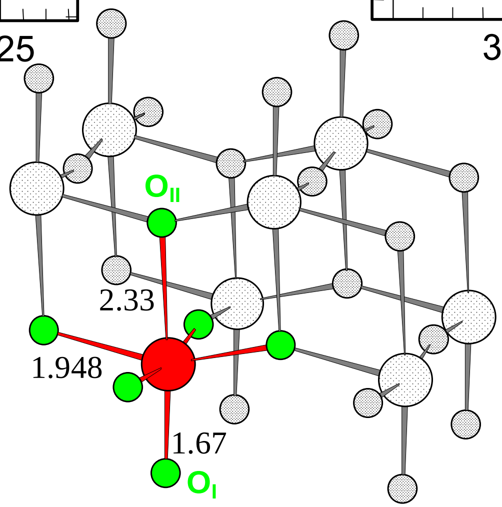




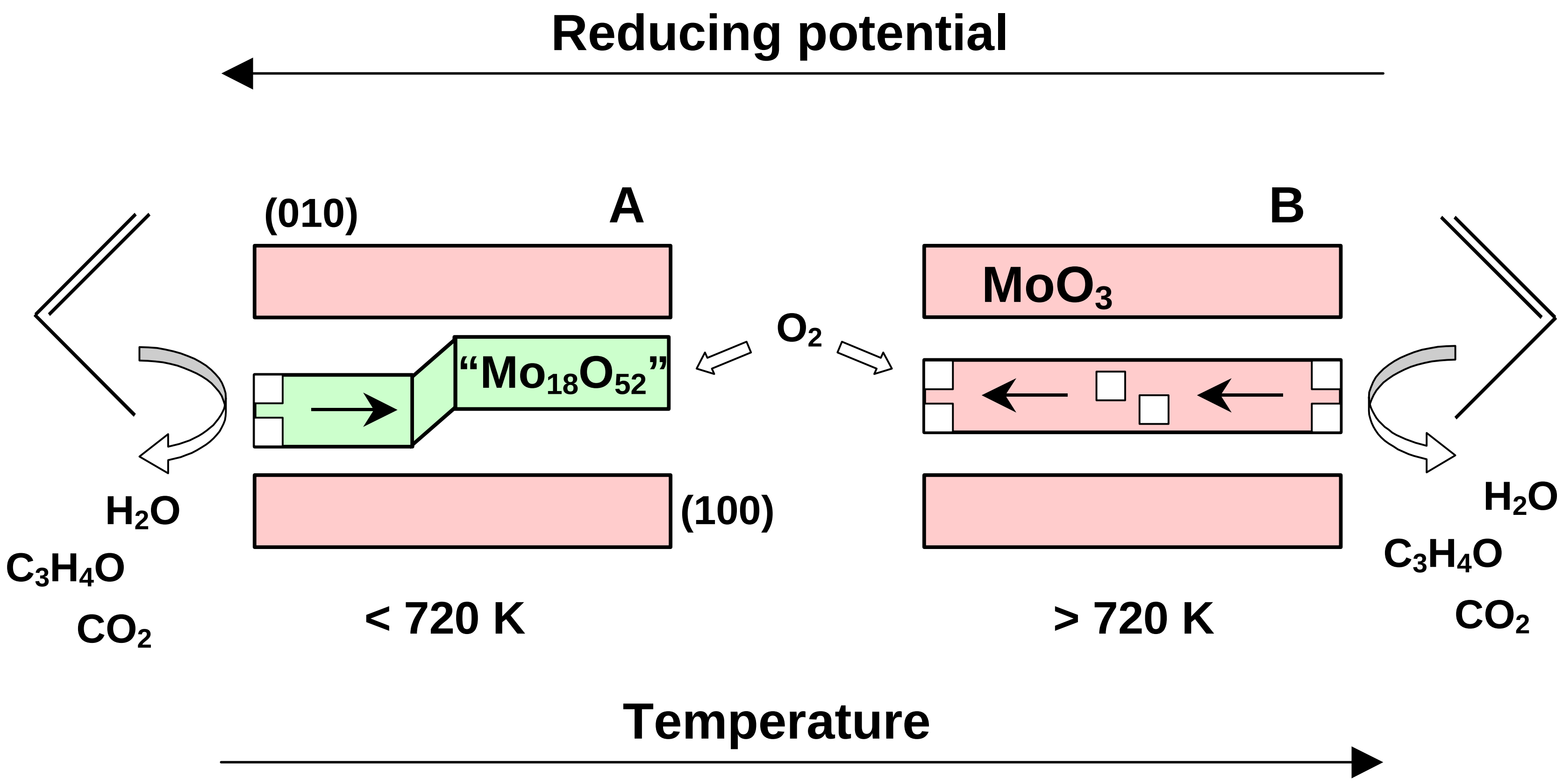
Bildung von „$Mo_{18}O_{52}$“ Defekten unter Reaktionsbedingungen







Bildung von „$Mo_{18}O_{52}$“ Defekten unter Reaktionsbedingungen



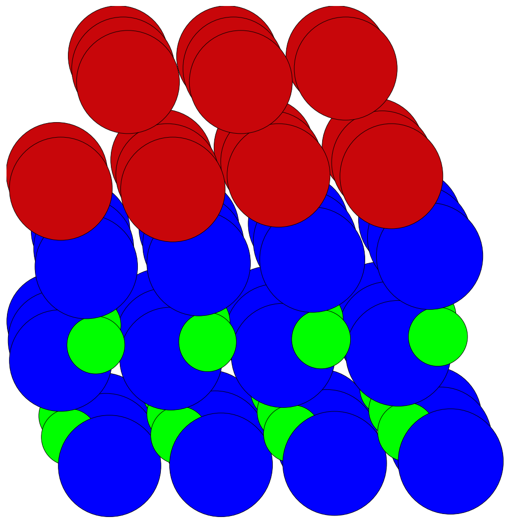
Example:

Supported Cu clusters

Cu/ZnO Catalysts for Methanol Synthesis and Steam Reforming

Methanol synthesis

$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$



Methanol steam reforming

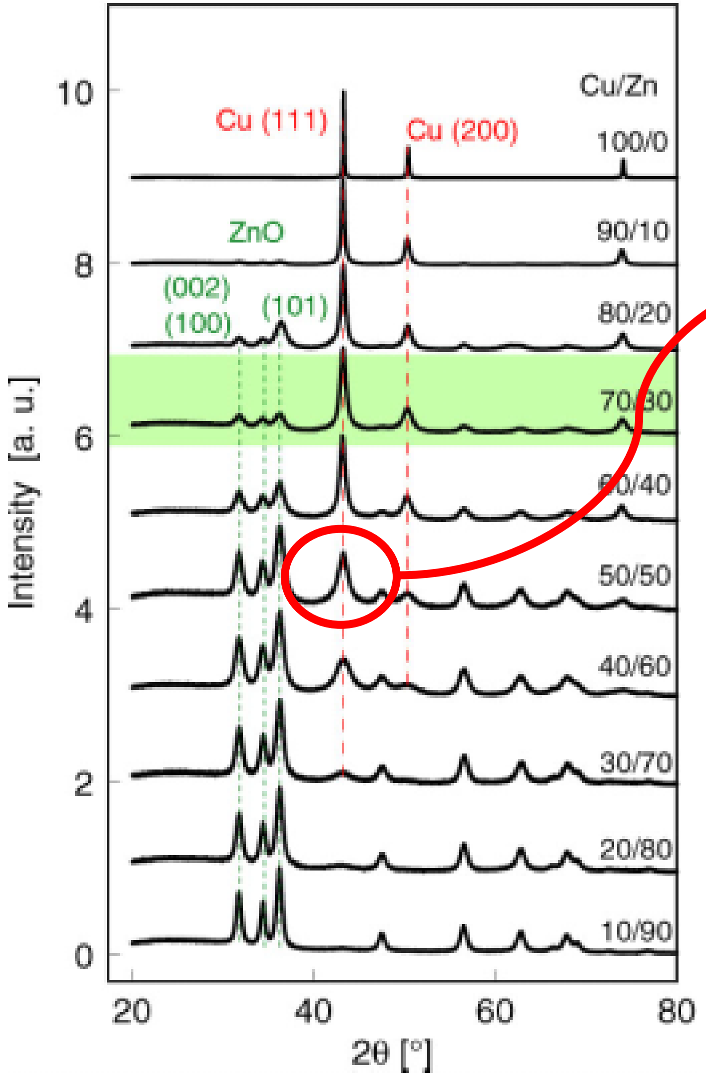
$CH_3OH + H_2O \rightarrow CO_2 + 3H_2$

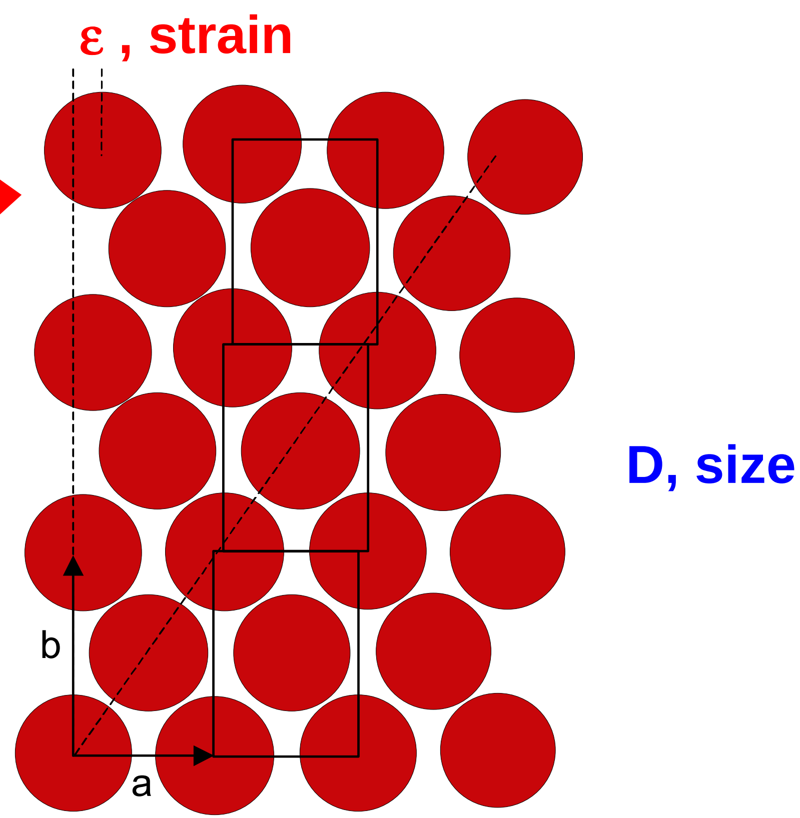
Preparation

Co-precipitation from Cu/Zn nitrate and soda solution. Calcined at 600 K 3 h in air (Cu/Zn 100/0, 90/10, 80/20, 70/30, …, 0/100).

Temperature programmed reduction at 523 K in 2 vol-% H_2

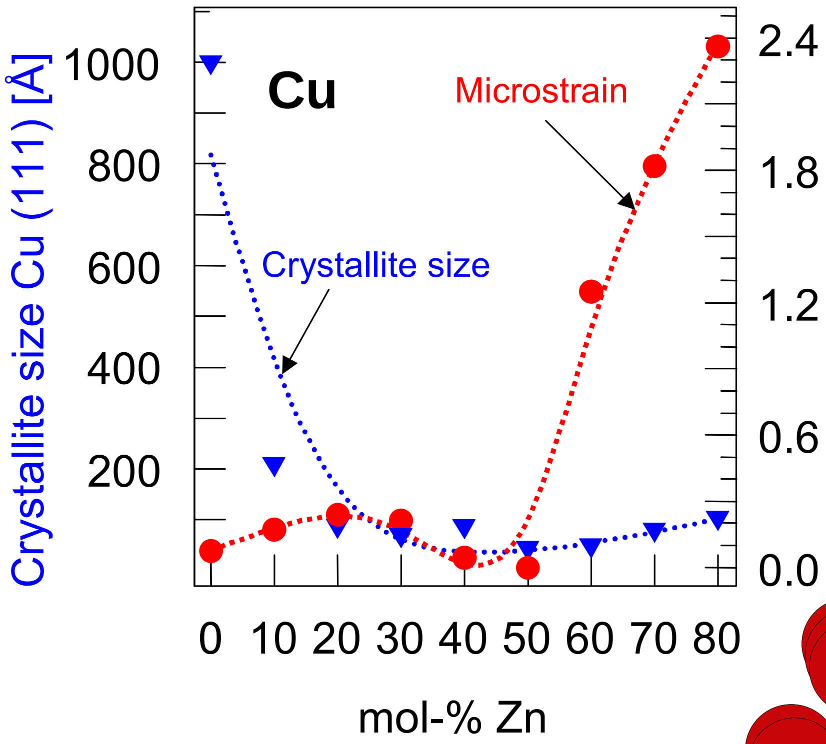
Micro Structural Bulk Properties of Cu/ZnO Catalysts

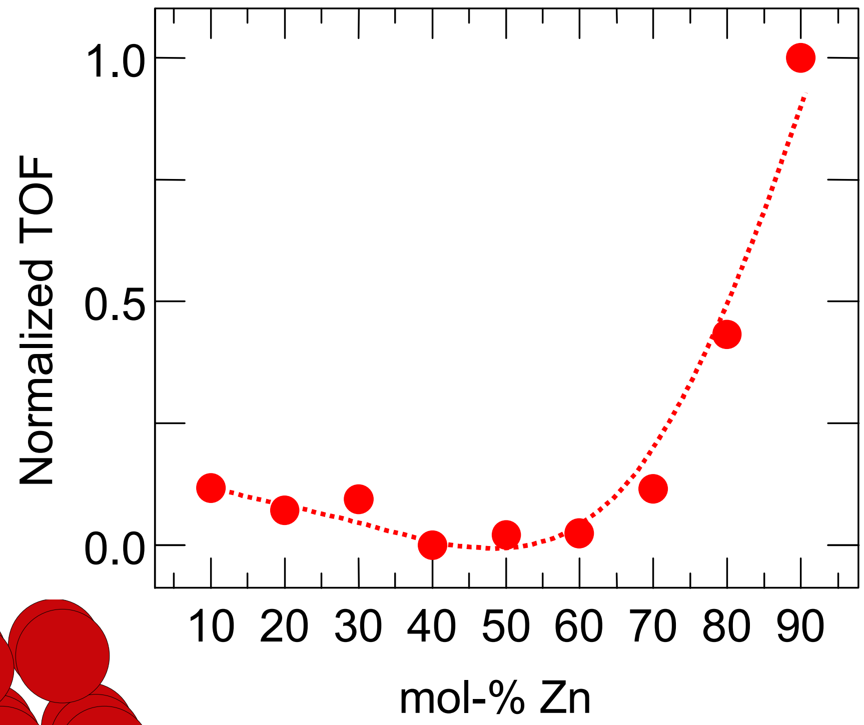


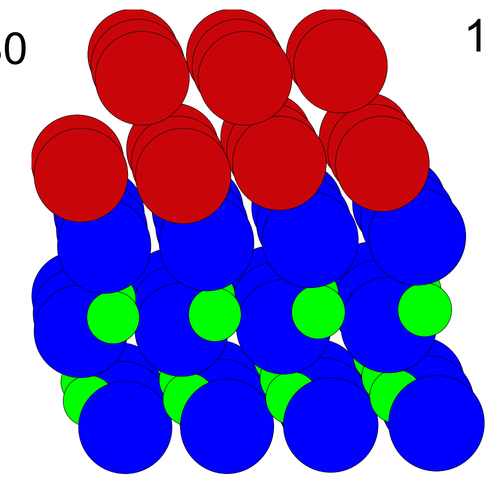


Cu-Cluster

Increase in Micro Strain in Cu Clusters Correlates to Increased Methanol Synthesis Activity



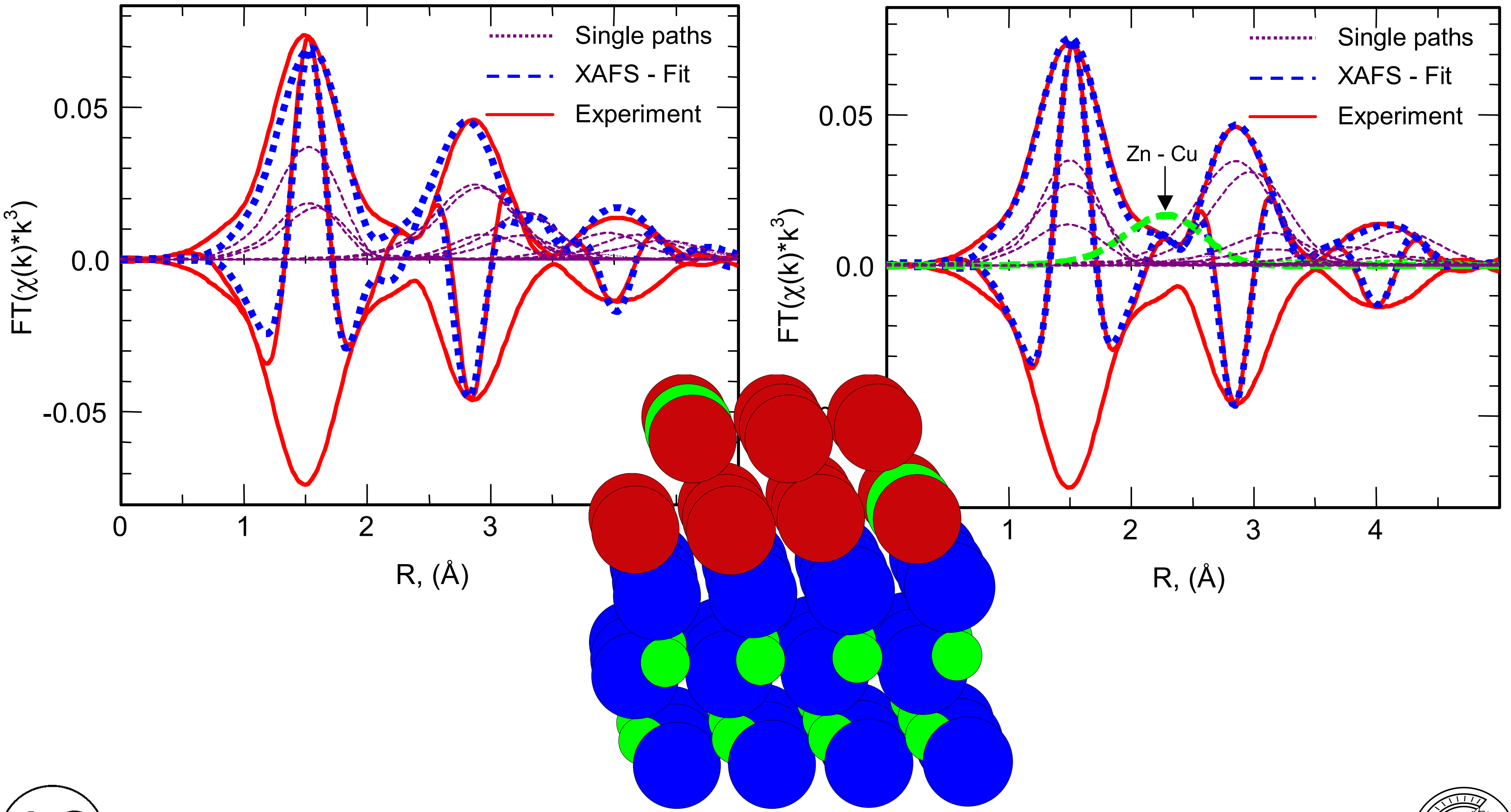




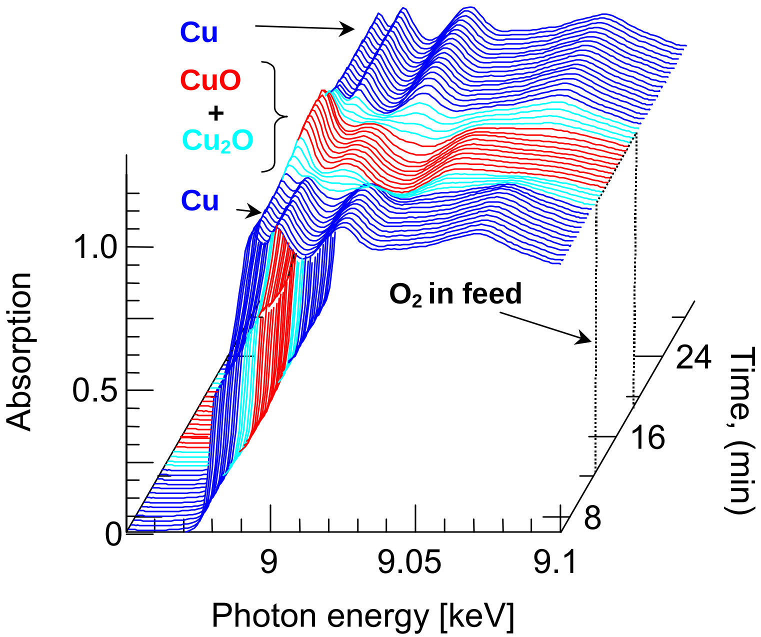
Methanol synthesis

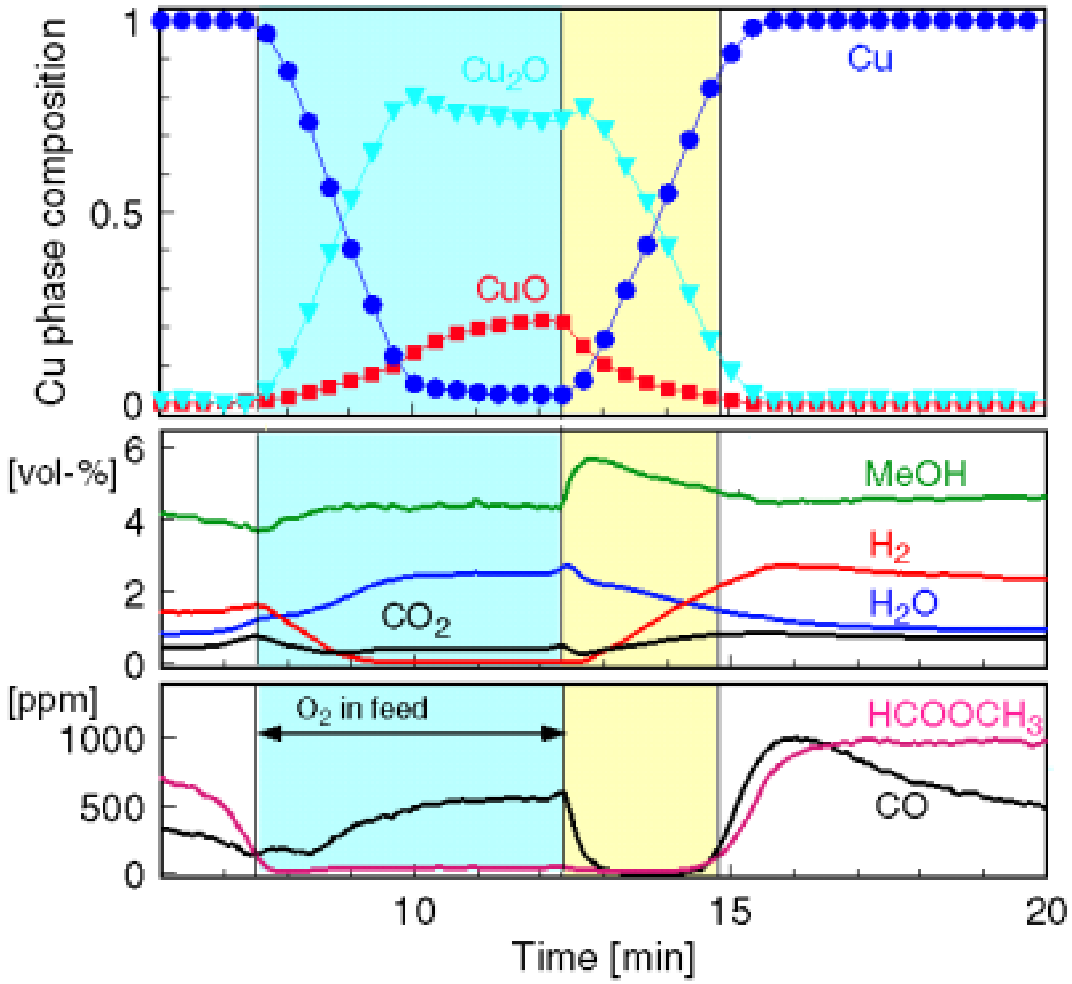
$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$

“Real” Structure of Cu/ZnO Catalysts – Zn in Cu Clusters



Reversible Oxidation - Reduction of Cu/ZnO





“Real” Structure of Cu/ZnO Catalyst – Increase in Micro Strain