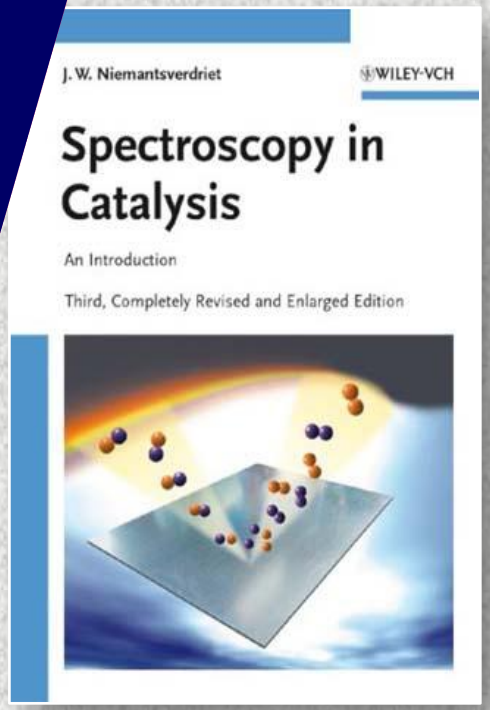
www.catalysiscourse.com

Characterization of solid catalysts

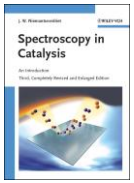
7. X-ray Absorption
XANES and EXAFS



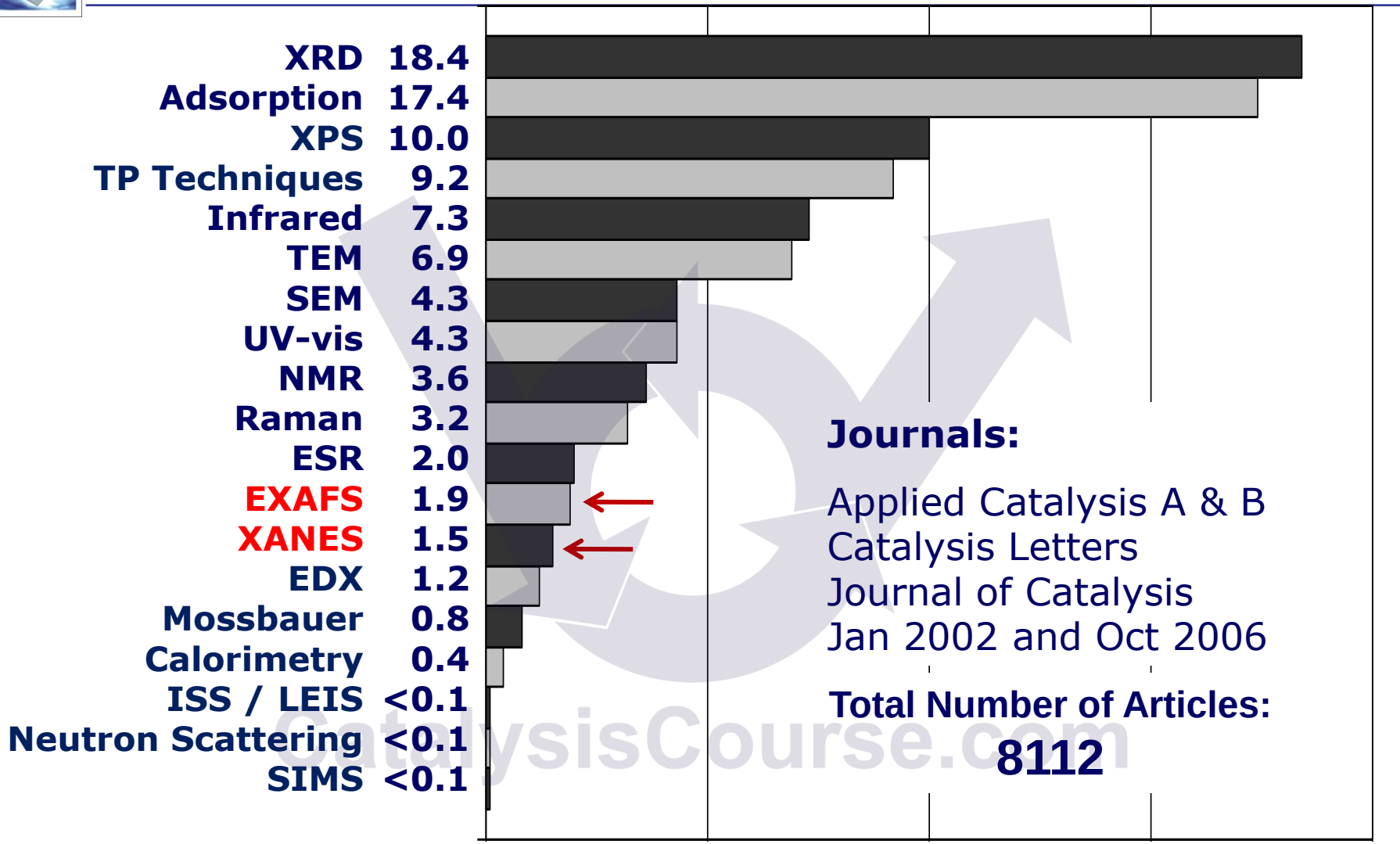
Prof dr J W (Hans) Niemantsverdriet
Schuit Institute of Catalysis

Technische Universiteit Eindhoven University of Technology

Where innovation starts



How often are techniques used

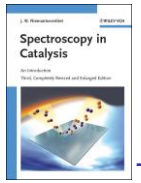


Journals:

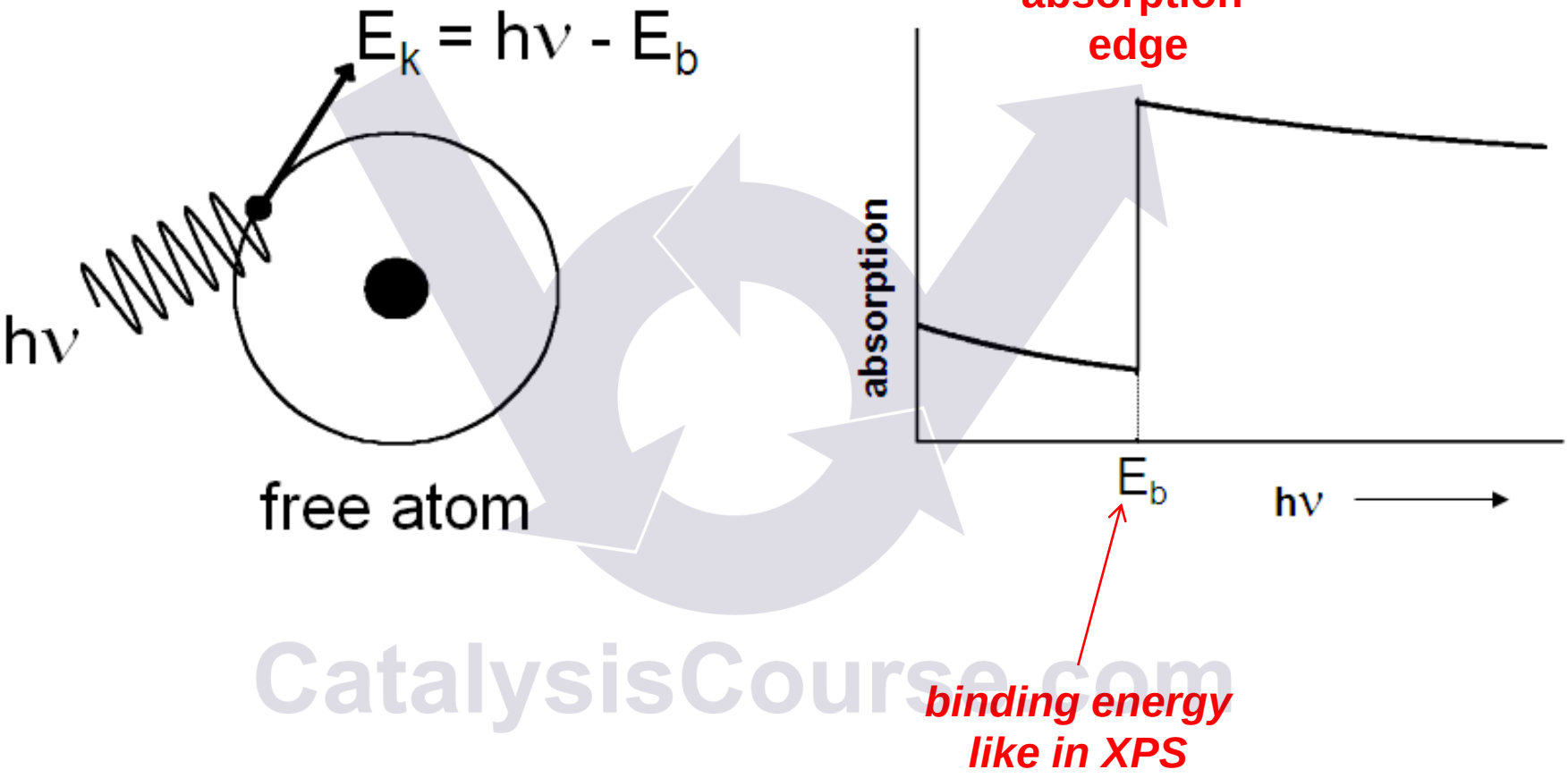
Applied Catalysis A & B
Catalysis Letters
Journal of Catalysis
Jan 2002 and Oct 2006

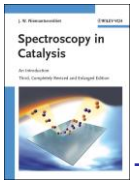
Total Number of Articles:

8112

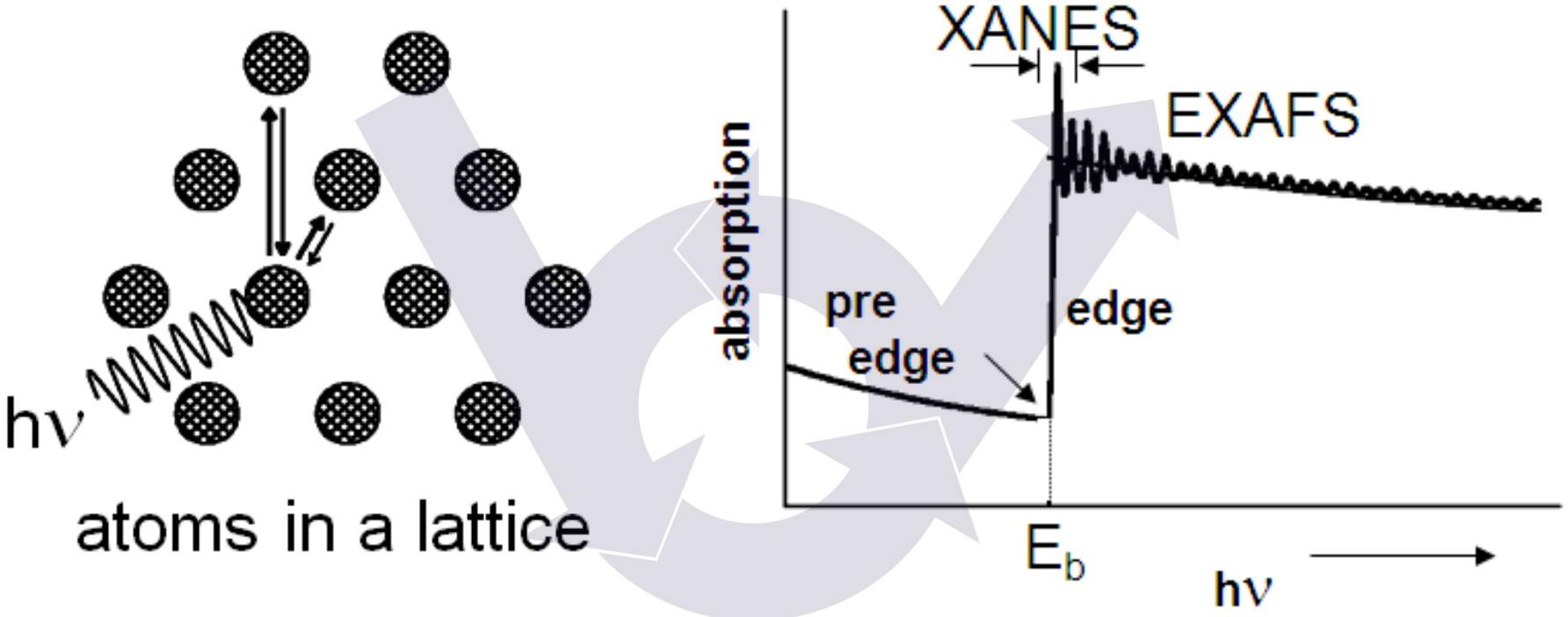


X-ray absorption in a free atom



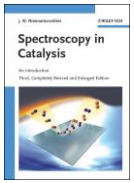


X-ray absorption by atoms in solids



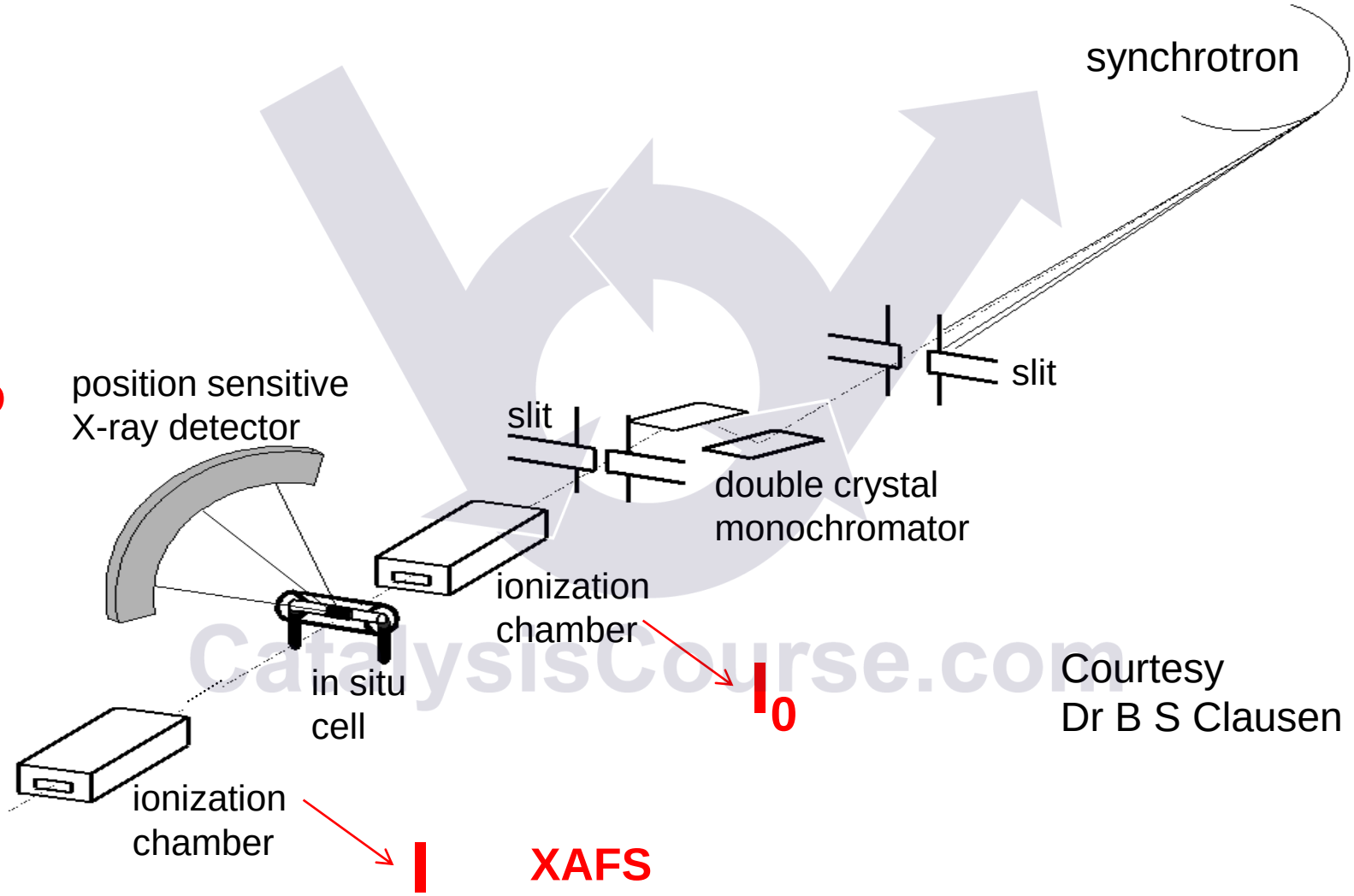
XANES: X-ray absorption near-edge structure

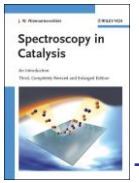
EXAFS: Extended X-ray absorption fine structure



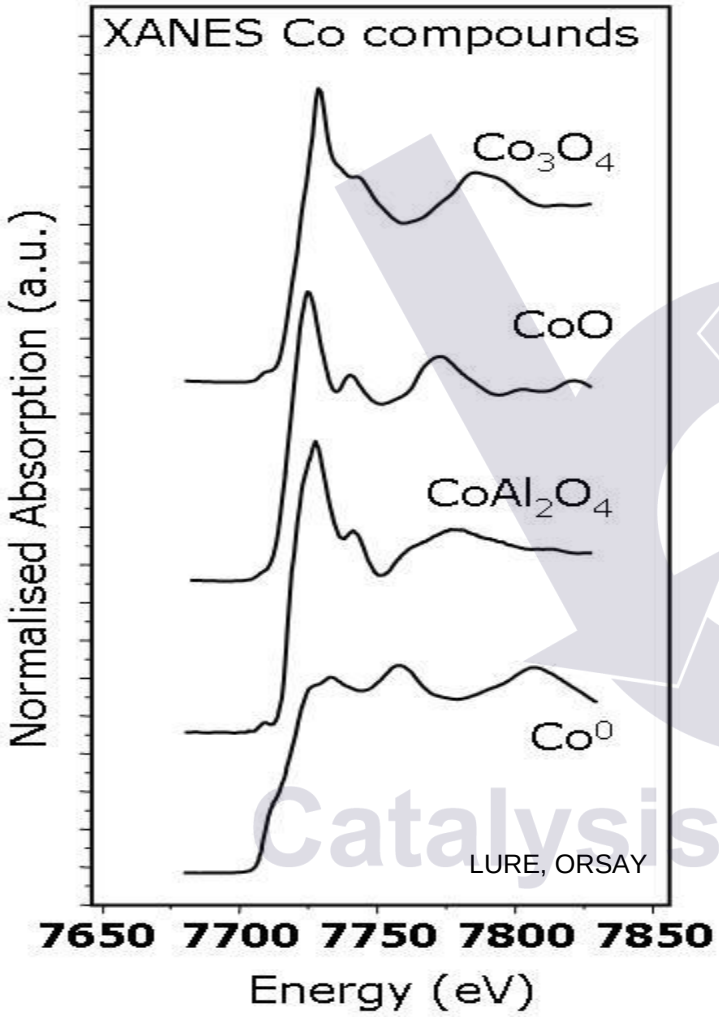
Synchrotron beamline

for XAFS and XRD





XANES of Cobalt Phases

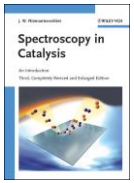


XANES:

- **phase identification**
- **oxidation state**
- **in situ measurement**
- **at synchrotron**
- **quantitation**

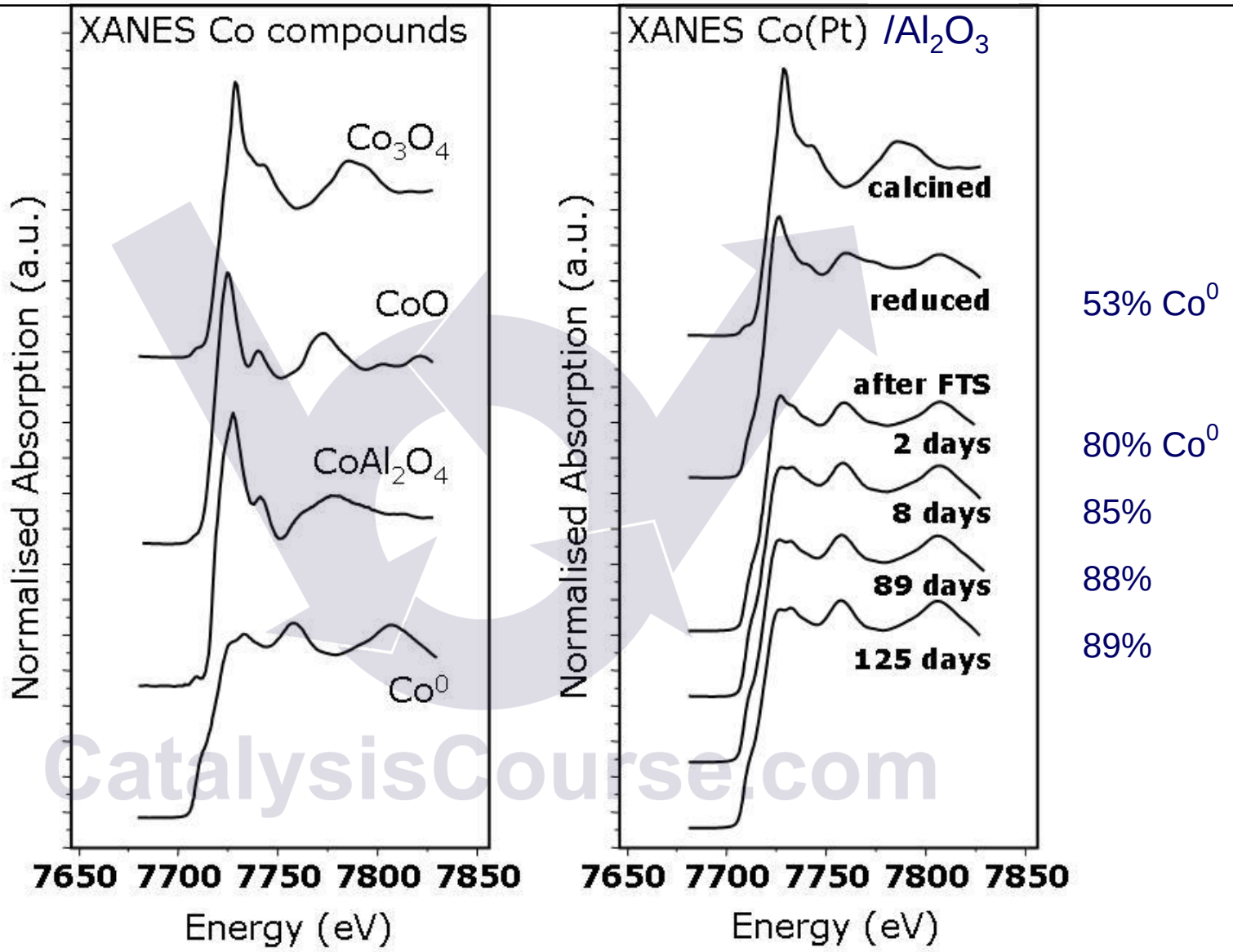
straightforward

Abdool Saib, Armando Borgna



XANES of Cobalt Fischer-Tropsch Catalyst

wax coated/protected catalysts from FT demonstration reactor



A.M. Saib, A. Borgna, J. van de Loosdrecht, P.J. van Berge, J.W. Niemantsverdriet
Appl. Catal. A: General 312 (2006) 12

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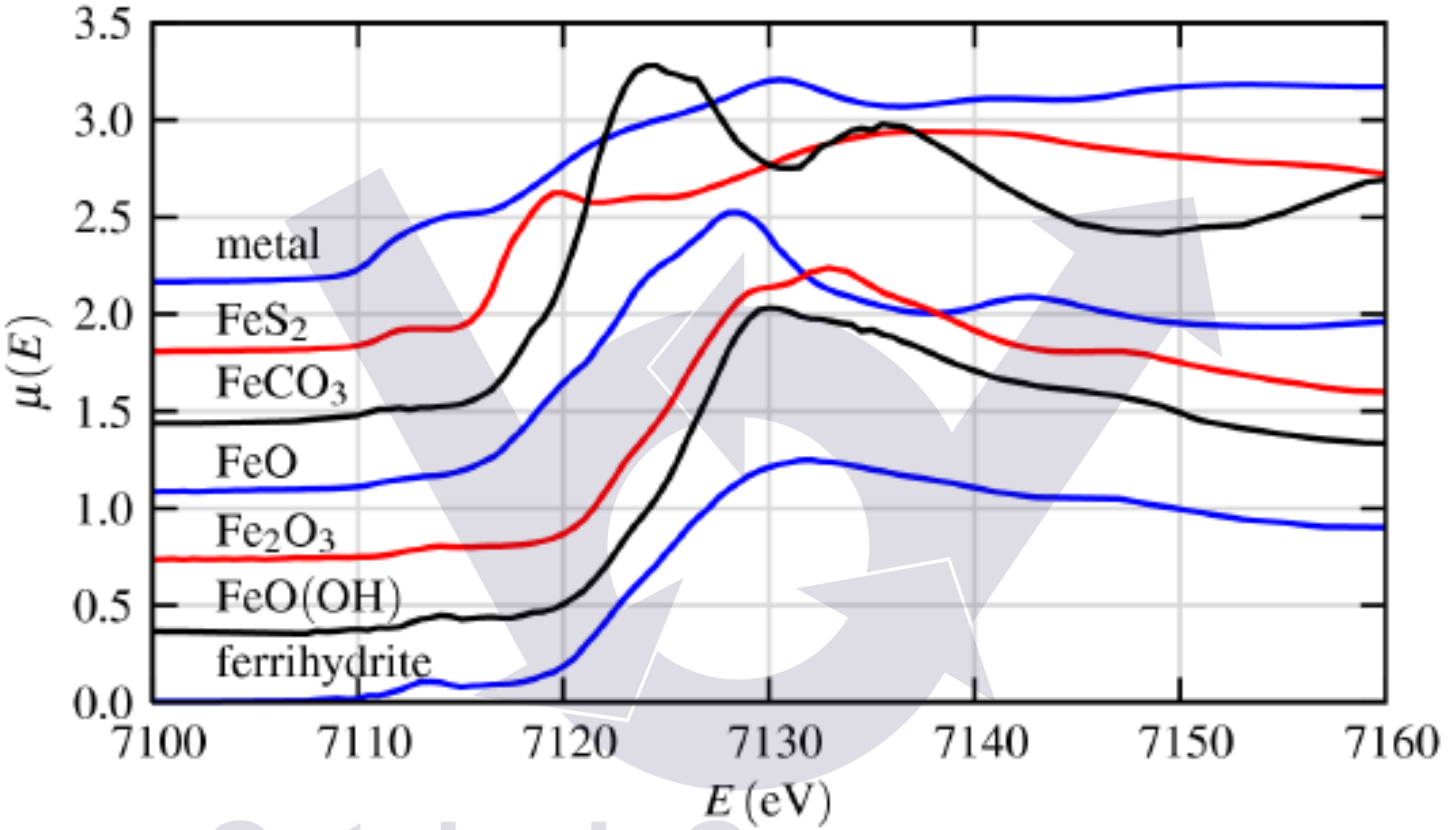
XANES Analysis: Oxidation State

The Normalized XANES from several Fe compounds:

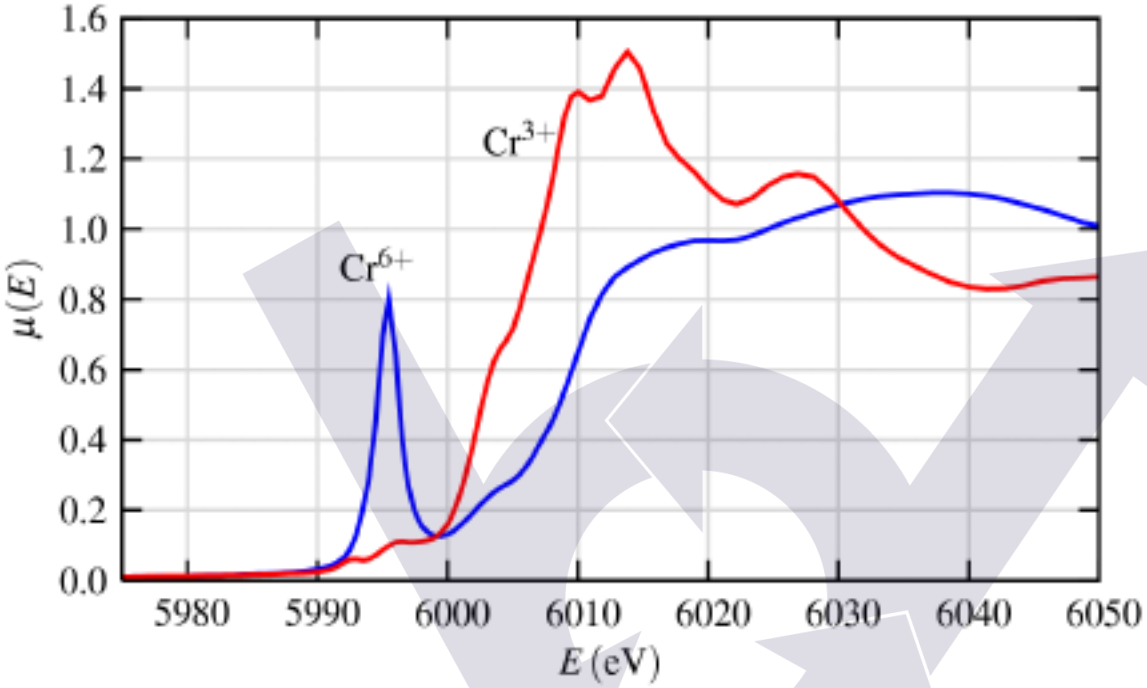


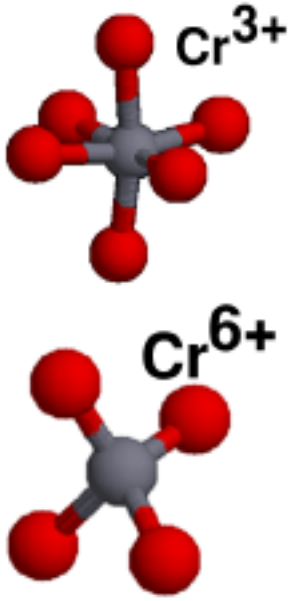
XANES can be used simply as a fingerprint of phases and oxidation state.

XANES Analysis can be as simple as making linear combinations of "known" spectra to get compositional fraction of these components.

From: Dr Matt Newville, Consortium for Advanced Radiation Sources, University of Chicago

XANES Analysis: Oxidation State and Coordination Chemistry





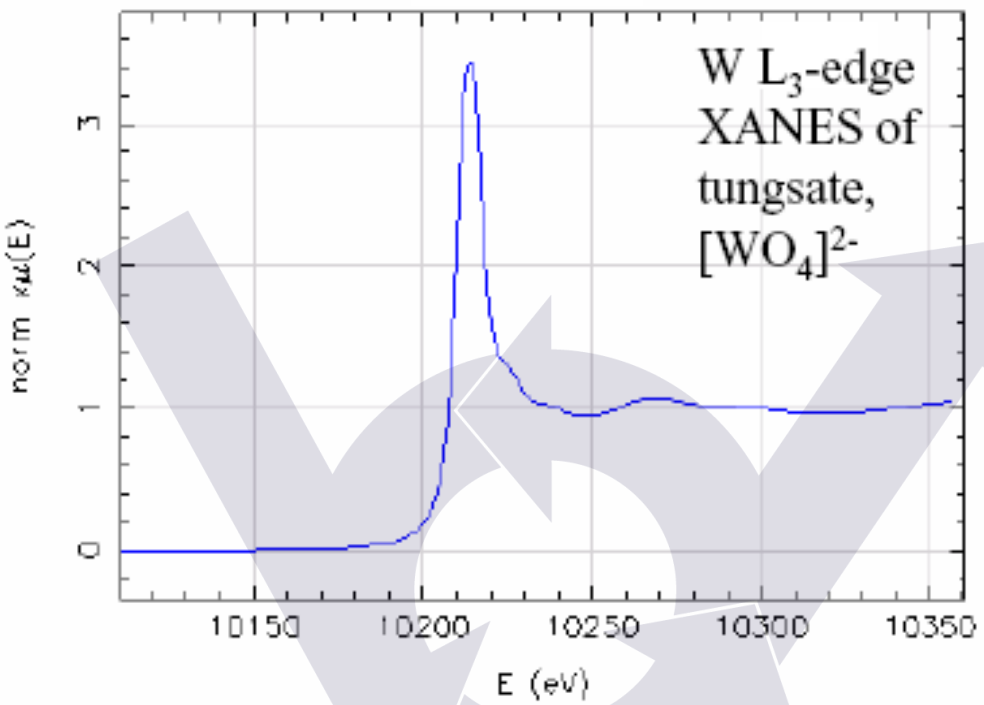
The XANES of Cr^{3+} and Cr^{6+} shows a dramatic dependence on oxidation state and coordination chemistry.

For ions with partially filled d shells, the p-d hybridization changes dramatically as *regular octahedra* distort, and is very large for *tetrahedral* coordination.

This gives a dramatic *pre-edge peak* – absorption to a localized electronic state.

From: Dr Matt Newville, Consortium for Advanced Radiation Sources, University of Chicago

"White line"

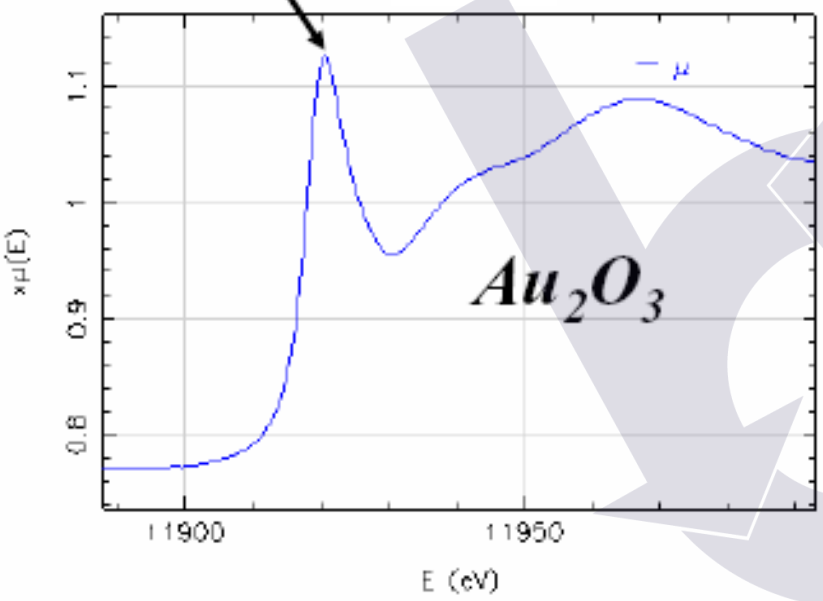


- In years past x-ray absorption spectra were taken with use of photographic plates.
- Absorption edges appeared as unexposed bands on the plate (developed in negative), or "white lines".
- Very prominent for L-edges of transition metals in high oxidation states.

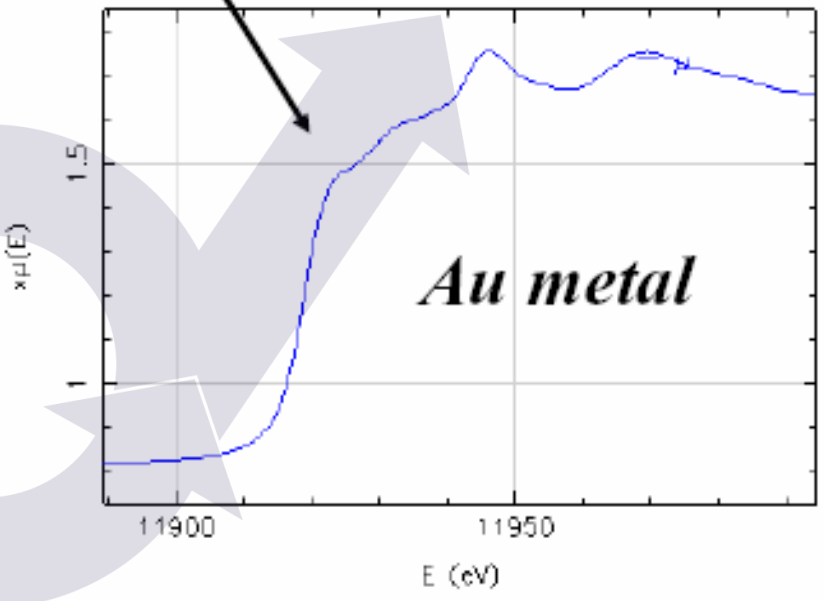
Metals & Oxides

Au L_3-edge XANES

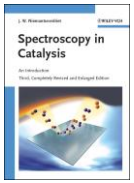
White line reflects holes in d-band



No white line



- Overall shape of spectrum also different.

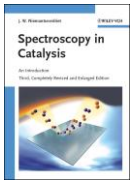


XANES:

- Oxidation state analysis
- Some structure information
- In situ!!!
- Analysis convenient (by fingerprinting)

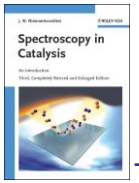
Very powerful in situ method

… but needs a synchrotron

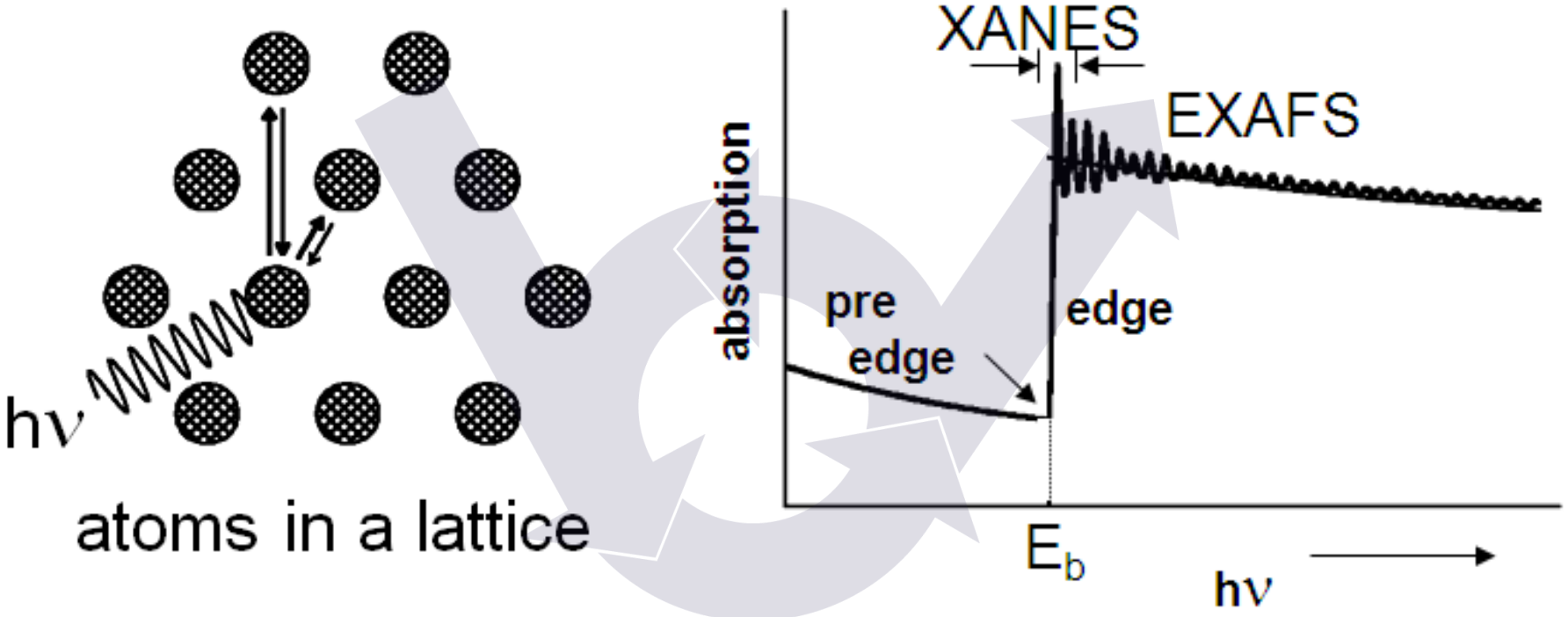


EXAFS

Extended X-ray Absorption Fine Structure



X-ray absorption by atoms in solids



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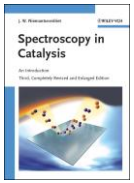
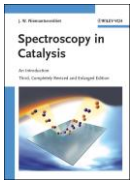


Information from EXAFS

EXAFS: $$\chi(k) = \sum_j A_j(k) \sin(2kr_j + \phi_j(k))$$

interatomic distances

$$k = \frac{2\pi}{h}\sqrt{2 m_e E_k} = \frac{2\pi}{h}\sqrt{2 m_e (h\nu - E_b)}$$



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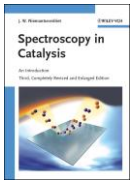
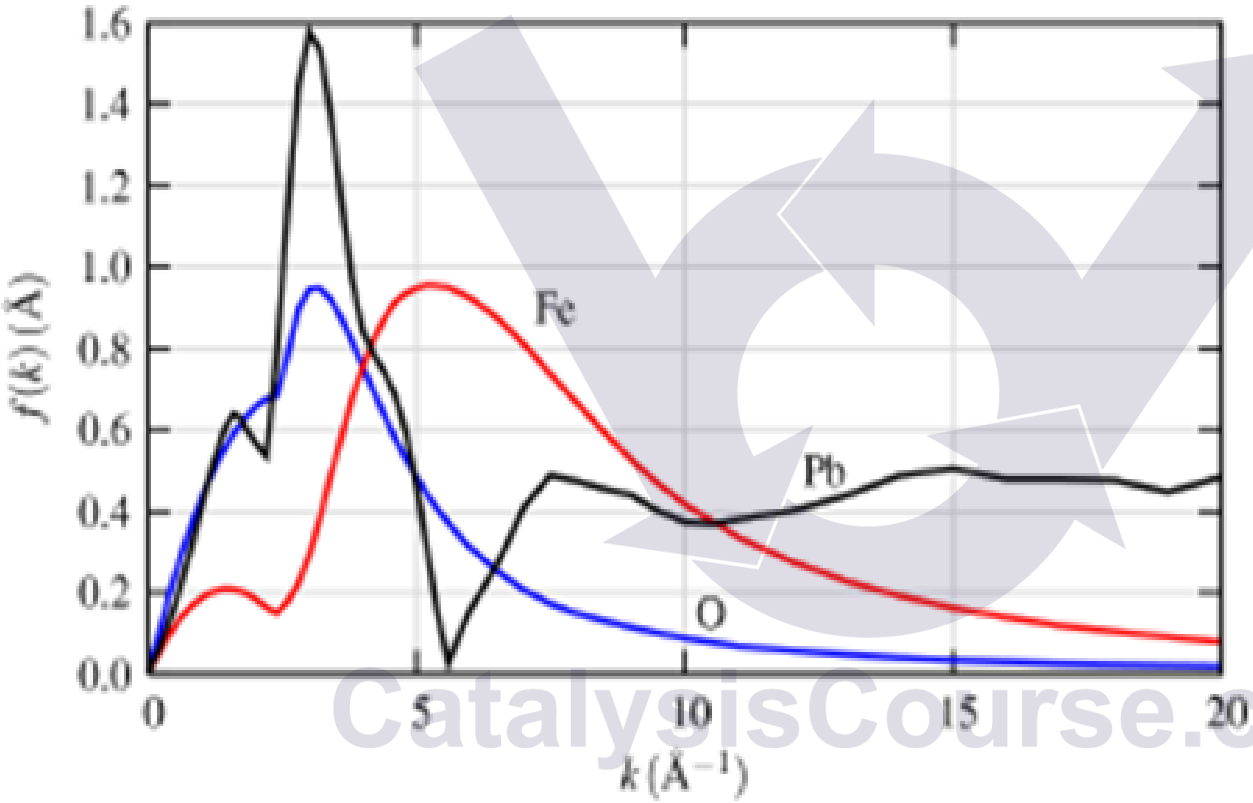
Amplitude: $$A_j(k) = N_j \frac{e^{-2r_j/\lambda(k)}}{k r_j^2} S_o^2(k) F_j(k) e^{-2k^2\sigma_j^2}$$

coordination numbers

backscattering factor
chemical sensitivity



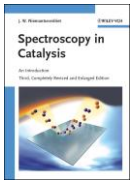
$$A_j(k) = N_j \frac{e^{-2r_j/\lambda(k)}}{k\,r_j^2} S_o^2(k) F_j(k) e^{-2k^2\sigma_j^2}$$



The backscattering factor F(k)

extends to higher energy k-values) for heavier elements

contains chemical information of the neighbours



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Amplitude: $$A_j(k) = N_j \frac{e^{-2r_j/\lambda(k)}}{k r_j^2} S_o^2(k) F_j(k) e^{-2k^2\sigma_j^2}$$

coordination numbers

backscattering factor
chemical sensitivity

Fourier Transform:

$$\theta_n(r) = \frac{1}{\sqrt{2\pi}} \int_{k_{min}}^{k_{max}} k^n \chi(k) e^{2ikr}\, dk$$

"radial distribution function"

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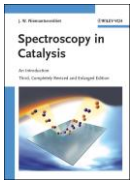
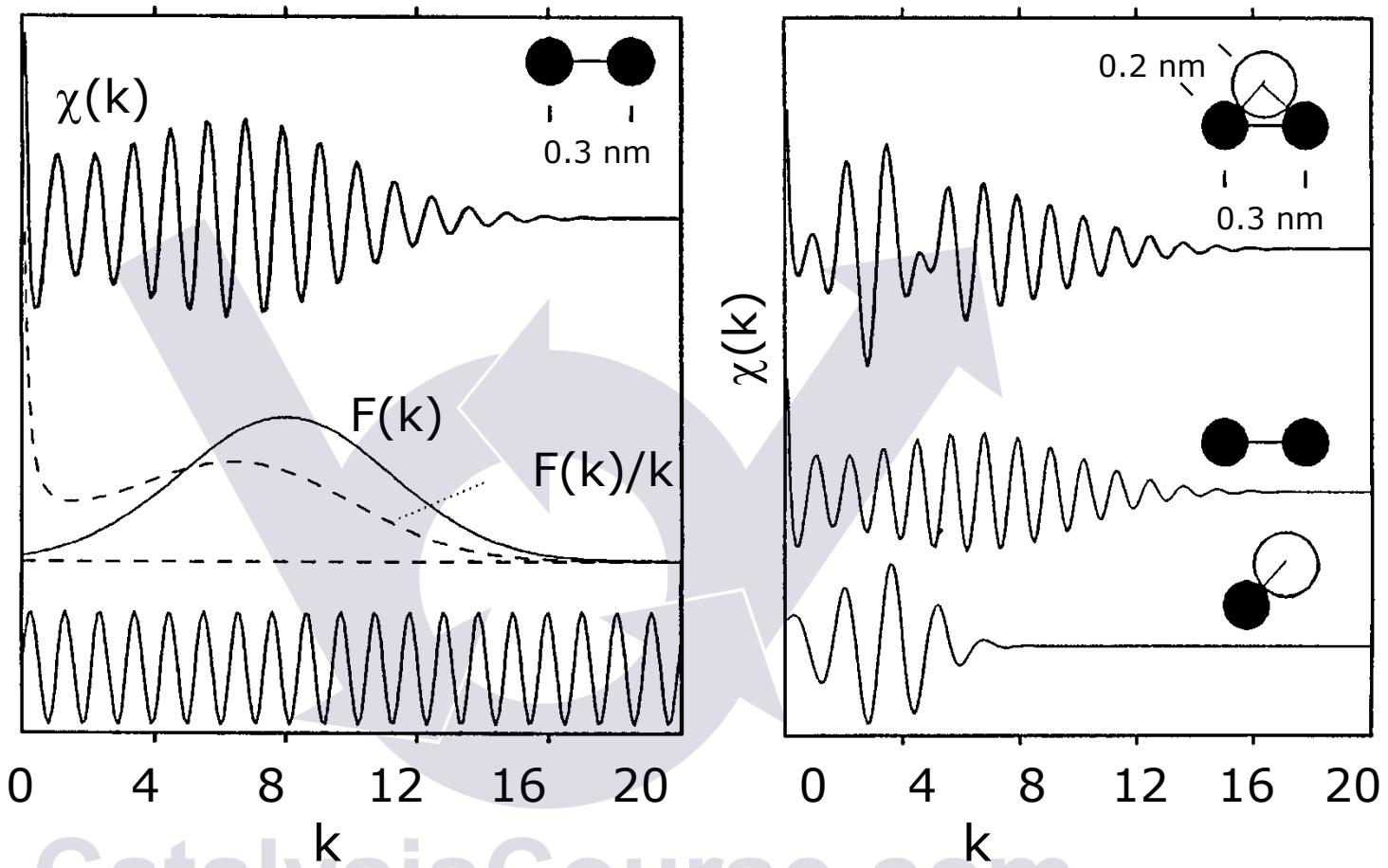
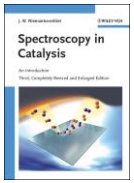


Simulated EXAFS of Cu_2 Dimer and Cu_2O Trimer



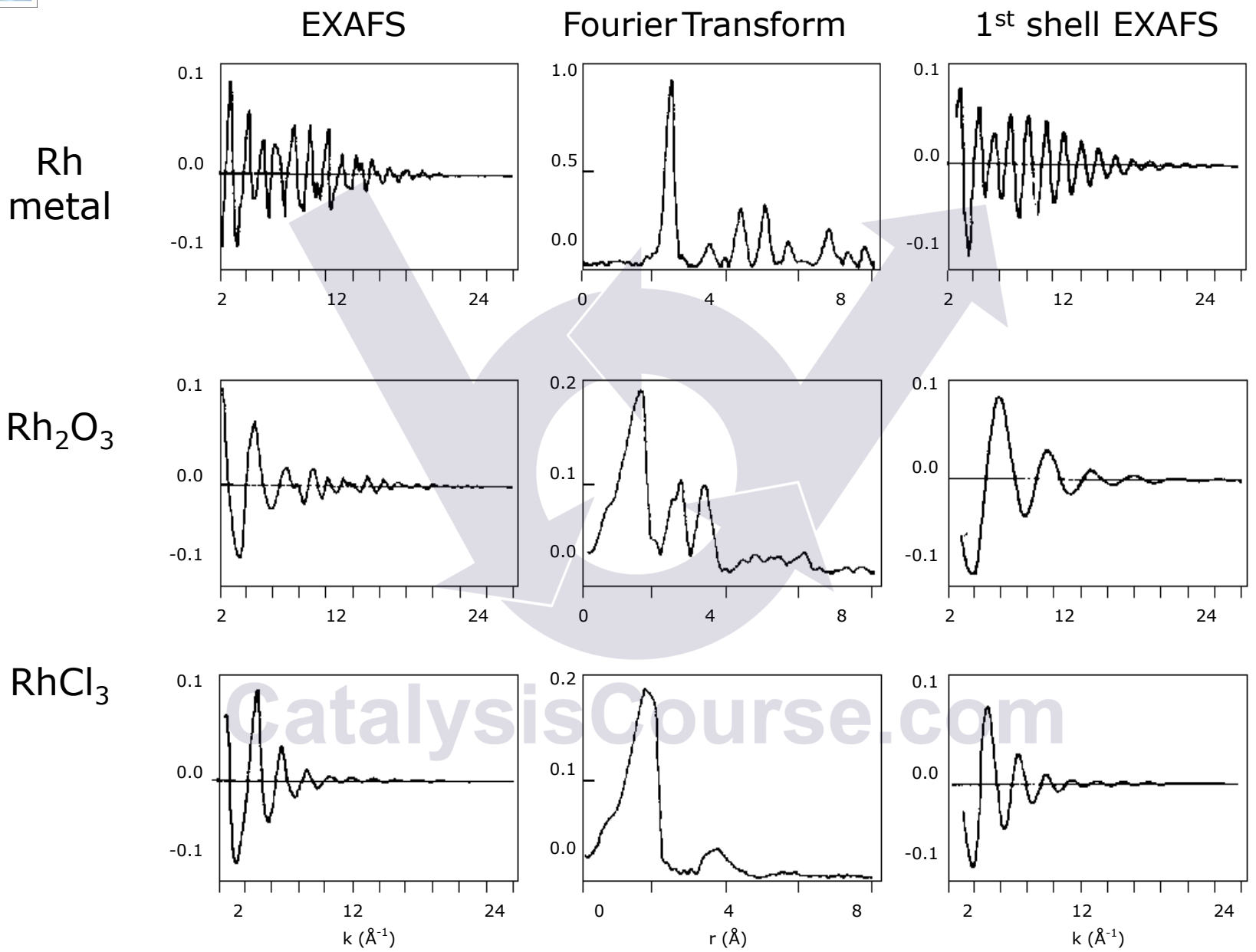
$$\chi(k) = \sum_j A_j(k) \sin(2kr_j + \phi_j(k))$$

$$A_j(k) = N_j \frac{e^{-2r_j/\lambda(k)}}{kr_j^2} S_o^2(k) F_j(k) e^{-2k^2\sigma_j^2}$$



EXAFS of Rhodium Compounds: Chemical Information

J.B.A.D. van Zon, D.C. Koningsberger, H.F.J. van 't Blik and D.E. Sayers, J. Chem. Phys. 82 (1985) 5742.



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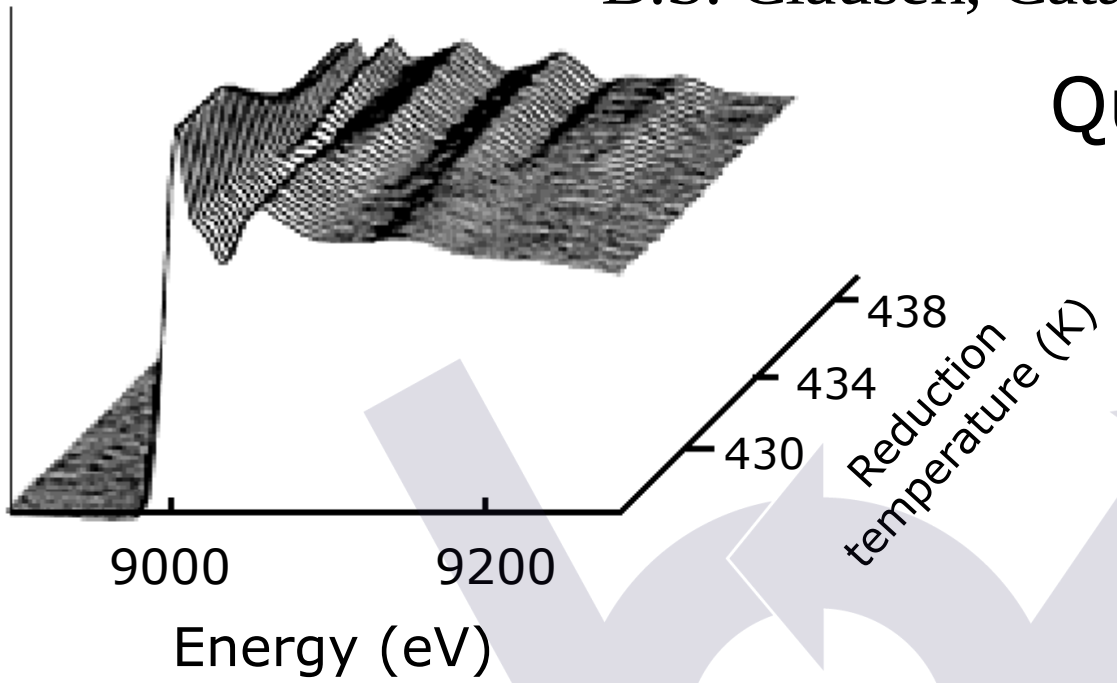
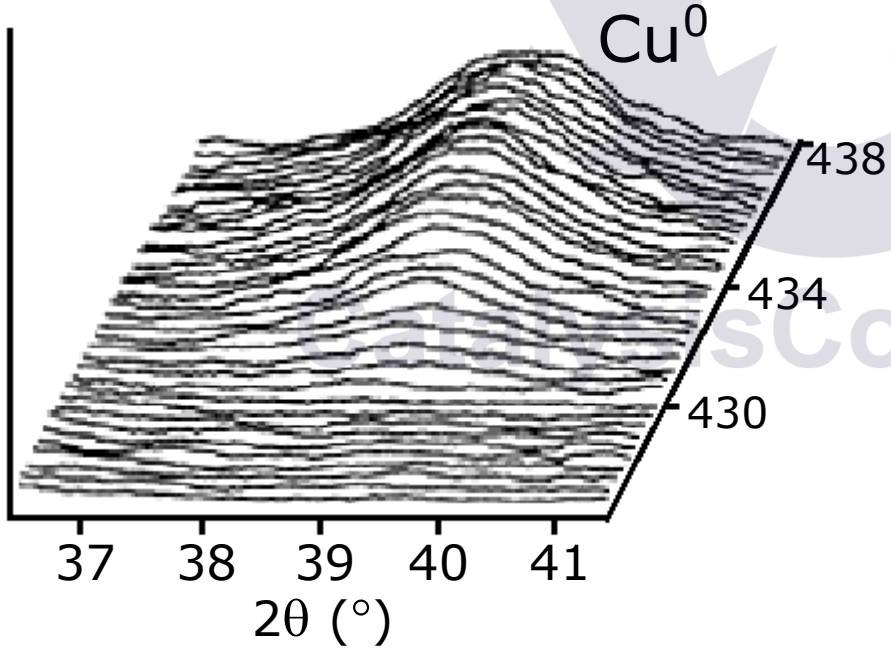
B.S. Clausen, Catal. Today, 39 (1998) 293

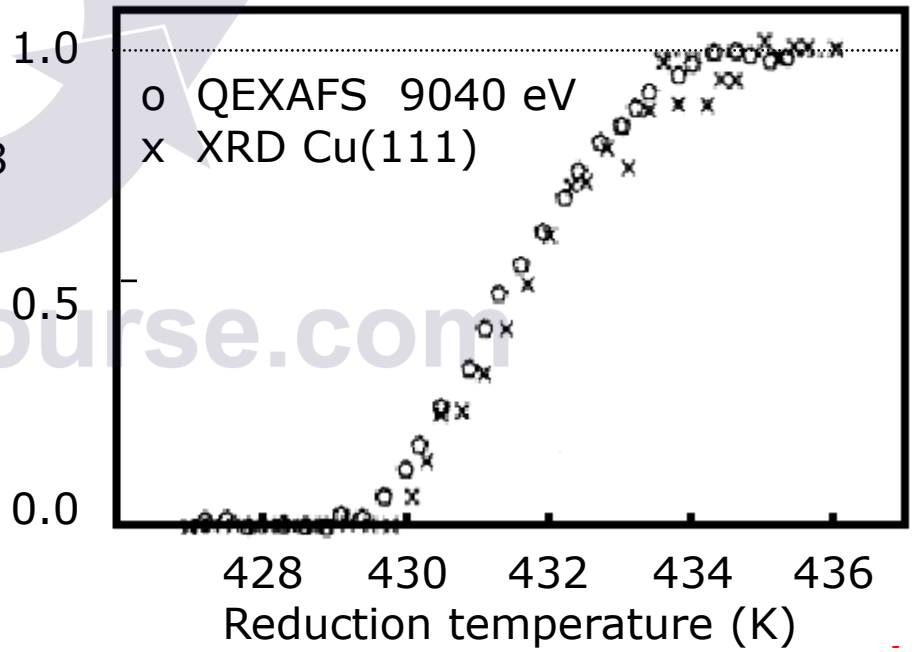
Quick EXAFS / XRD

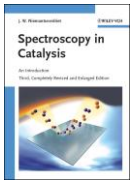
$Cu / ZnO / Al_2O_3$

reduction









EXAFS:

- Highly precise structure information
- Also on amorphous phases
- In situ studies
- Synchrotron needed
- Complicated analysis

Where To Go From Here

International XAFS Society:

http://ixs.iit.edu/

Books and Review Articles:

X-ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS, and XANES, in *Chemical Analysis* 92, D. C. Koningsberger and R. Prins, ed., John Wiley & Sons, 1988.

Basic Principles and Applications of EXAFS, Chapter 10 in *Handbook of Synchrotron Radiation*, pp 995–1014. E. A. Stern and S. M. Heald, E. E. Koch, ed., North-Holland, 1983

Tutorials and other Training Material:

http://gbxafs.iit.edu/training/tutorials.html Grant Bunker's tutorials

http://srs.dl.ac.uk/XRS/courses/ Tutorial from Daresbury Lab, UK

http://leonardo.phys.washington.edu/~ravel/course/ Bruce Ravel's Course on Advanced EXAFS Analysis.

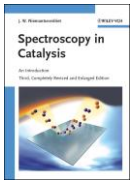
Software Resources:

http://www.esrf.fr/computing/scientific/exafs/

http://cars9.uchicago.edu/IXS-cgi/XAFS_Programs

http://leonardo.phys.washington.edu/feff

This tutorial and more links can be found at: http://cars.uchicago.edu/xafs/.



Comparison of X-ray diffraction and XAFS

XRD: information on crystalline structures

- Phase identification
- Particle size estimate from line broadening
- In situ studies
- Careful: only crystalline phases detected

EXAFS: local structure information

- Highly precise structure information
- Also on amorphous phases
- In situ studies
- Synchrotron needed
- Complicated analysis

XANES: chemical state information

- Oxidation state analysis
- Some structure information
- In situ!!!
- Analysis convenient (by fingerprinting)

Download the handout for this lecture from

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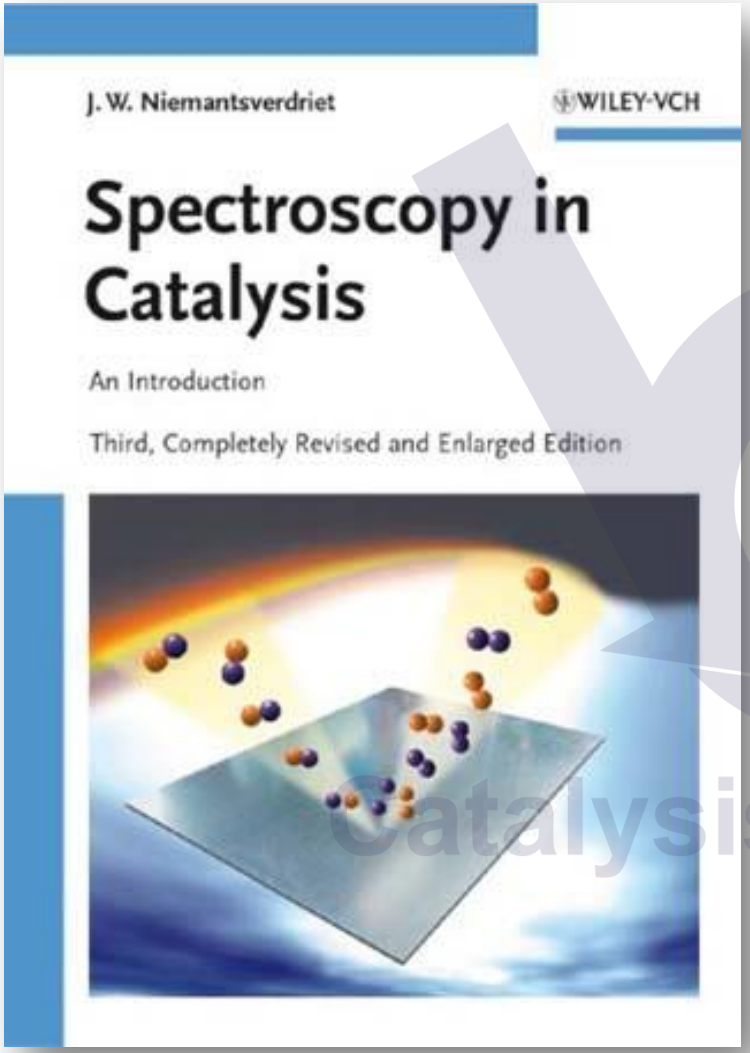


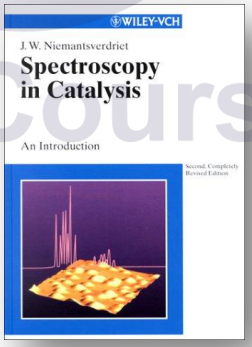
Read more about XRD, XANES and EXAFS

in Chapter 6 of

Spectroscopy in Catalysis: An Introduction, Third Edition

J. W. Niemantsverdriet

ISBN: 978-3-527-31651-9



Version 2000

gives many examples and references to the literature

Technische Universiteit Eindhoven University of Technology