

Introduction to X-ray Absorption Spectroscopy: an element sensitive method for local spatial and electronic structure

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Reading:

Proceedings of the HERCULES (Higher European Research Course for Users of Large Experimental Systems),
Neutron and synchrotron radiation for condensed matter studies. Vol. 1. Theory, instruments and methods.
J.Baruchel, J.-L.Hodeau, M.S.Lehmann, J.-R.Regnard, C.Schlenker (eds.), Springer-Verlag, Berlin, 1994

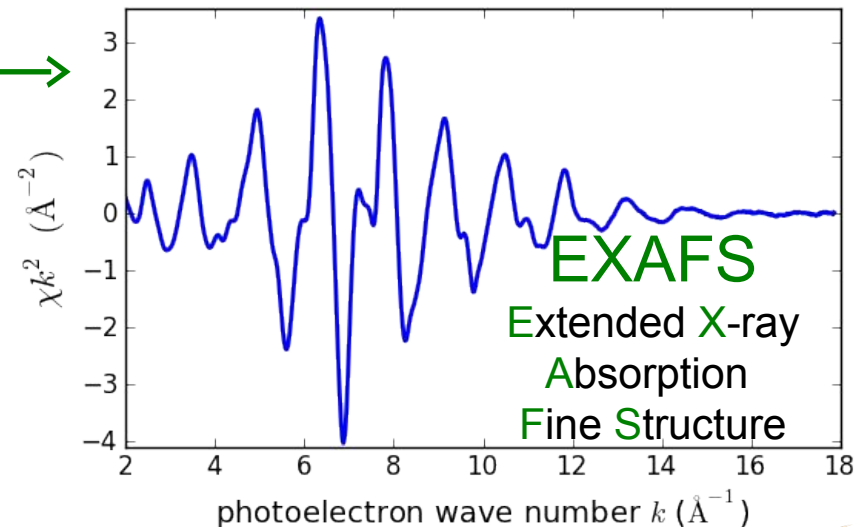
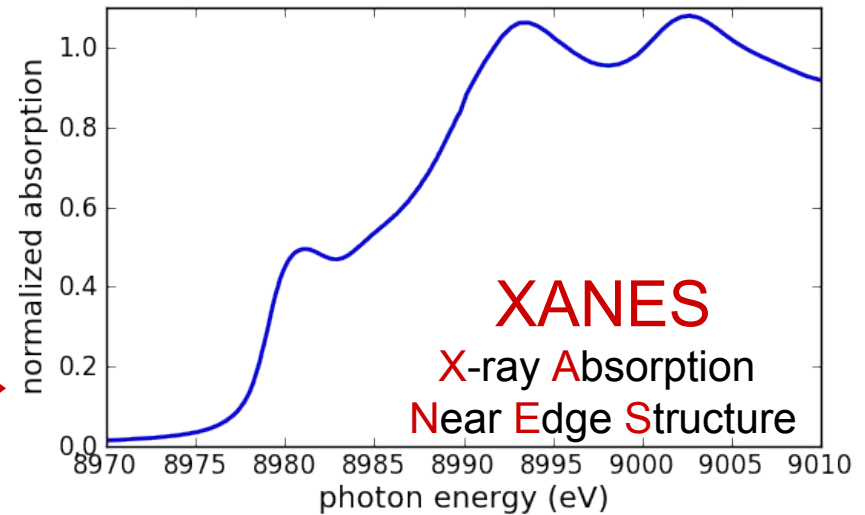
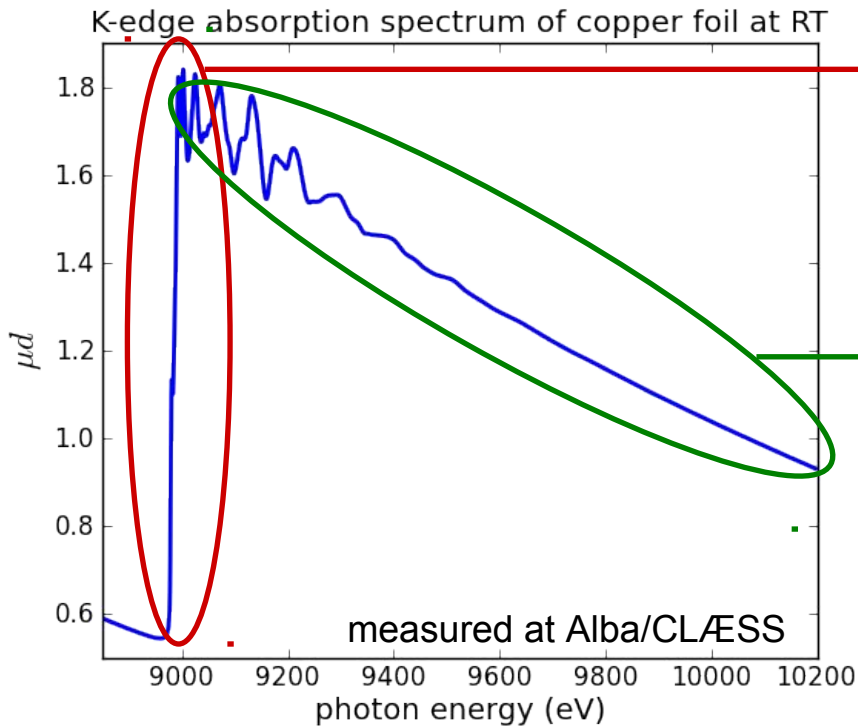
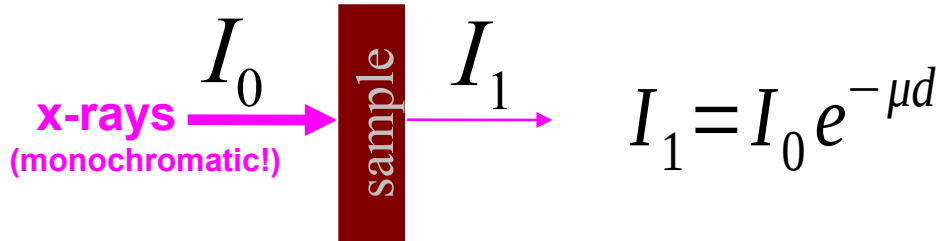
Outlook

Main intentions:

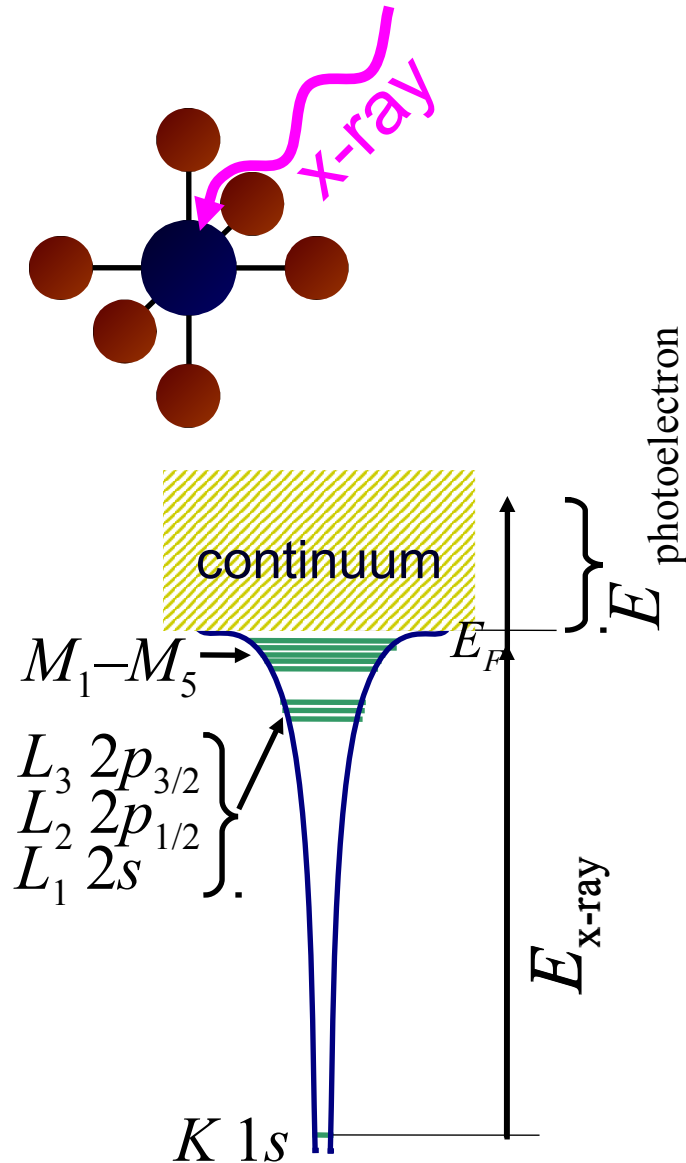
- To show that XAFS needs good ab initio calculations
 - Give an example of quantitative EXAFS study
 - **To show what is possible *without* ab initio calculations**
-
- Basic definitions and qualitative picture of XAFS (slide 3)
 - Qualitative picture of XAFS (slide 4)
 - The EXAFS formula and the need for amplitudes and phases (slides 5–7)
 - XAFS at various T (slide 8)
 - Experimental XAS setup (slides 9–10)
 - An example of EXAFS study (slides 11–14)
 - Using XANES without ab initio calculations (slides 15–17)
 - Using EXAFS without ab initio calculations (slides 18–19)

X-ray Absorption Spectra

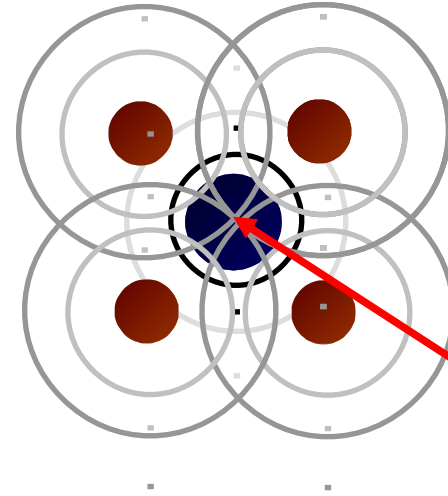
transmission experiment



Qualitative Picture of XAFS

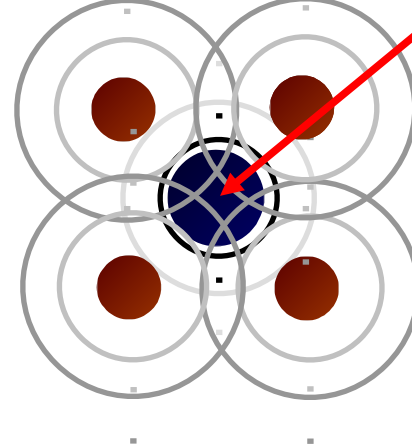


constructive interference –
absorption maximum



Here is where
the interference
is important!

destructive interference –
absorption minimum



Theoretical Description

In the MS theory, the expression for μ can be factored in terms of an atomic background μ_0 and the oscillatory part χ

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

In the photoelectron momentum space,

$$k = [2m/\hbar^2(E - E_F)]^{1/2},$$

the χ function is parameterized as:

$$\chi(k) = S_0^2 \sum_j N_j \frac{|f_j(k)|}{kR_j^2} \sin(2kR_j + \phi_j(k)) e^{-2R_j/\lambda(k)} e^{-2\sigma_j^2 k^2}$$

For each coordination shell j :

R_j , N_j , σ_j^2 are the sought distance, coord. number and variance of distance

$f_j(k) = |f_j(k)|e^{i\phi_j(k)}$ is the scattering amplitude (calculated),

λ is the electron free path (calculated),

S_0^2 accounts for many-electron excitations.

The present theory cannot give reliable μ_0 .

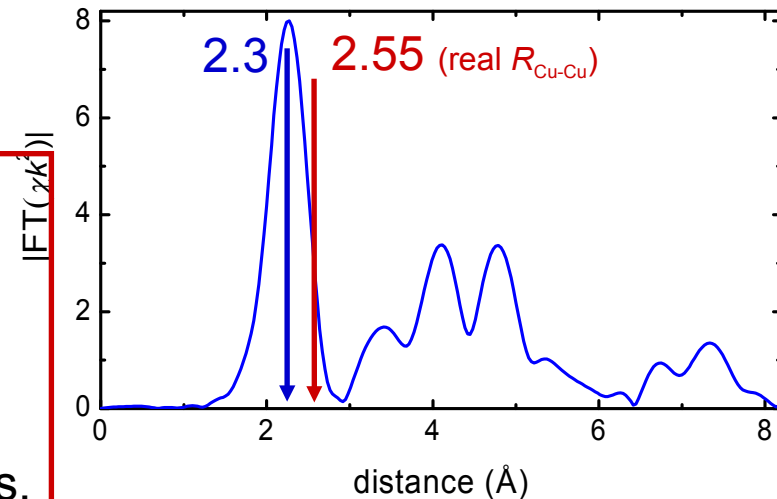
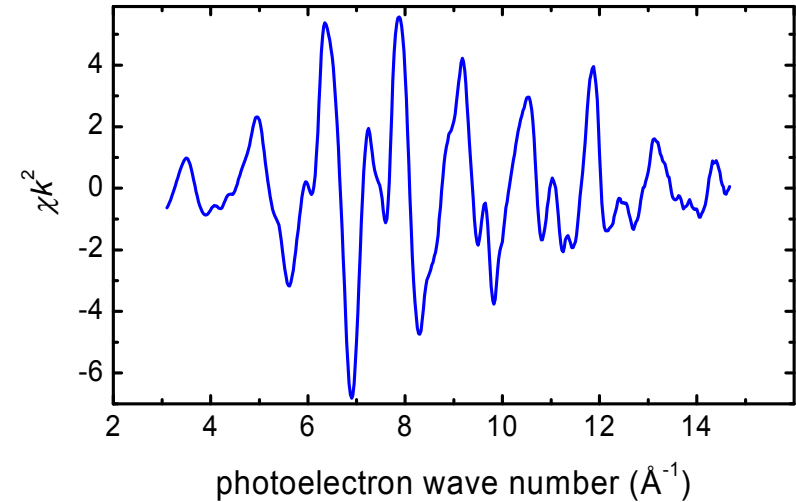
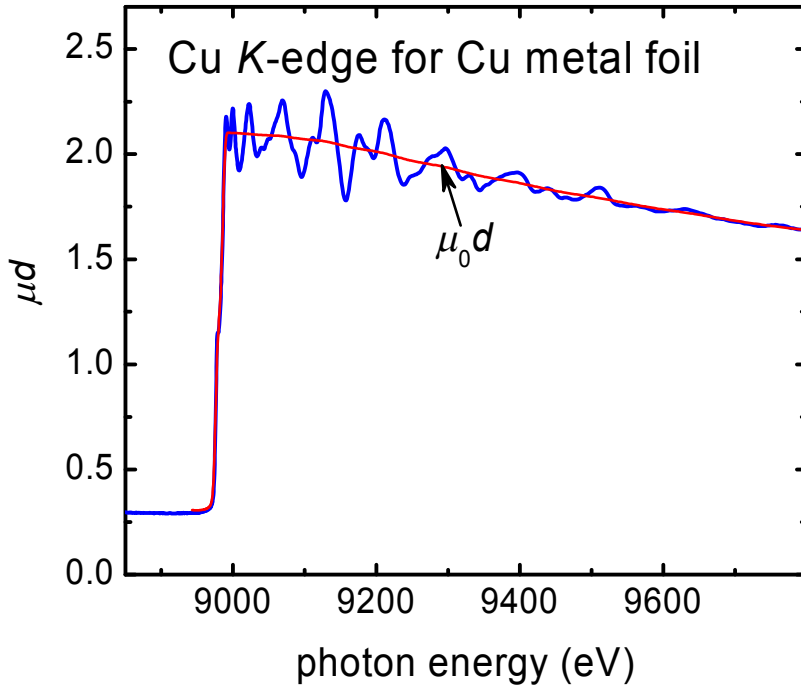
- For XANES region this is a problem, because μ_0 there is a rapidly changing function with features comparable with χ .
- In EXAFS region μ_0 is a smooth function and can be constructed empirically.

Thus, XANES spectra are mostly *interpreted*, not analyzed.
EXAFS spectra can be analyzed quantitatively.

See more in the
“*Theory*” lecture

Importance of EXAFS phases

$$\mu = \mu_0(1 + \chi), \quad \chi(k) = S_0^2 \sum_j N_j \frac{|f_j(k)|}{kR_j^2} \sin(2kR_j + \phi_j(k)) e^{-2R_j/\lambda(k)} e^{-2\sigma^2 k^2}$$



Unpleasant thing about EXAFS:
 FT positions are shifted towards small distances.
 More unpleasant: Each FT peak has its own shift.
 Because of the phase shifts, extracting the
 structural information from EXAFS requires
 curve fitting with assumed (calculated) phase shifts.

EXAFS amplitudes and phases

<http://feffproject.org/>

The FEFF9 code

Home » Codes » The FEFF9 code

Search

Overview Documentation Download Order Troubleshooting XAFS Data Analysis

The screenshot displays the FEFF9 code interface with several windows open. The main window shows a 3D molecular model of a complex structure. Other windows include a terminal window with command-line input, a plot of EXAFS amplitude, and a table of calculated parameters.

FEFF 9.5.1
Core hole lifetime set to 7.5779381351716 -w
Thomson's Backscattering Coefficient (Bethe)
Ti K2 O42 O42 O42 O42 O42
Calculating potentials ...
Electron configuration set to feff7 recipe
Free atom potential and density for atom type 1
Free atom potential and density for atom type 2
Free atom potential and density for atom type 3
Initial state energy
Overlapped potential and density for unique potential 0
Overlapped potential and density for unique potential 1
Overlapped potential and density for unique potential 2
Overlapped potential and density for unique potential 3
Calculating potentials ...
Coefficients for radial and spherical parameters
gth, mweight, hthr, mweight, hthr, fupright
0 1.875421e-05 1.48664e-05 1.10000e+00
0.00000e+00 0.00000e+00 0.00000e+00

EXAFS 1 20.0
RPATH 6.5709 LDOS
Module Options
SCF
MIX 1.0
EXCHANGE
COREHOLE Final State Rule 1
Print Level 1 1

Atoms Data Editor

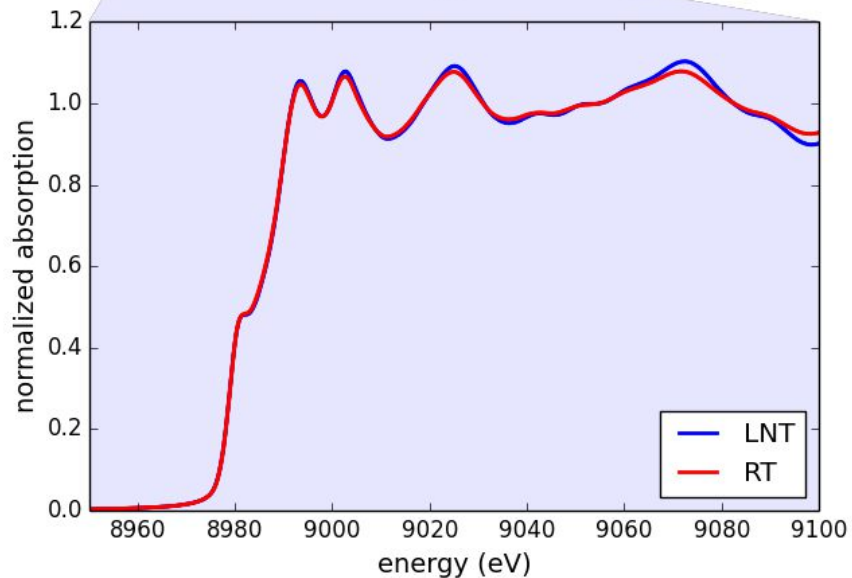
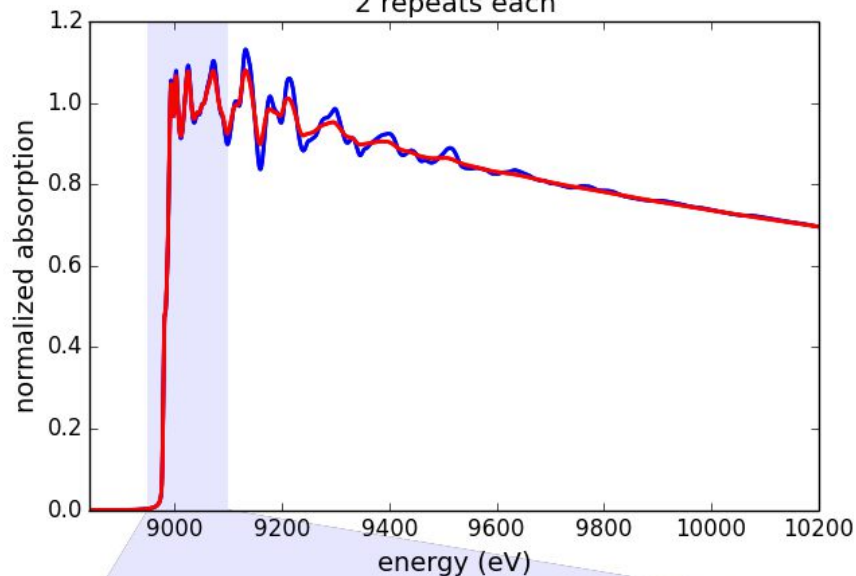
Atom	Z	Type	Atom1	Atom2	Weight	Length
0	30	Ti	0	0	0.0001	
1	8	O	1	1	4	
2	8	O	1	1	48	
3	8	O	1	1	16	

Atoms

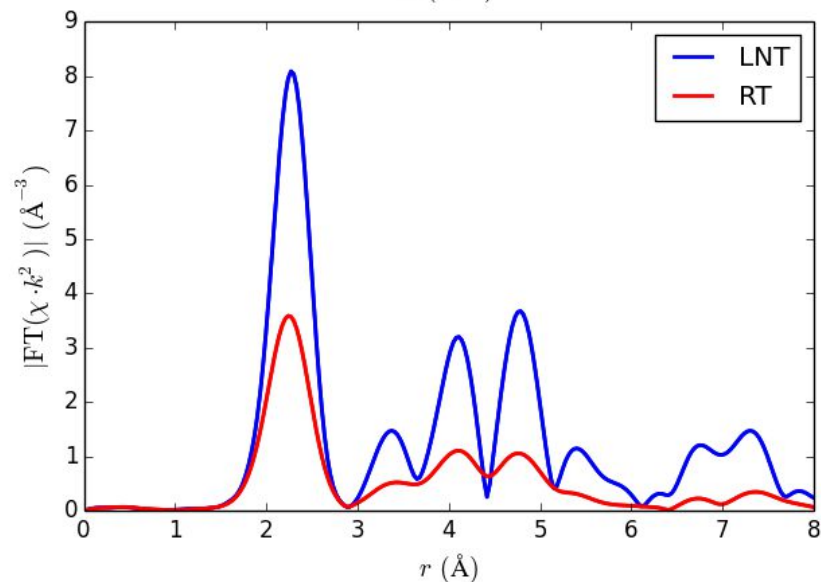
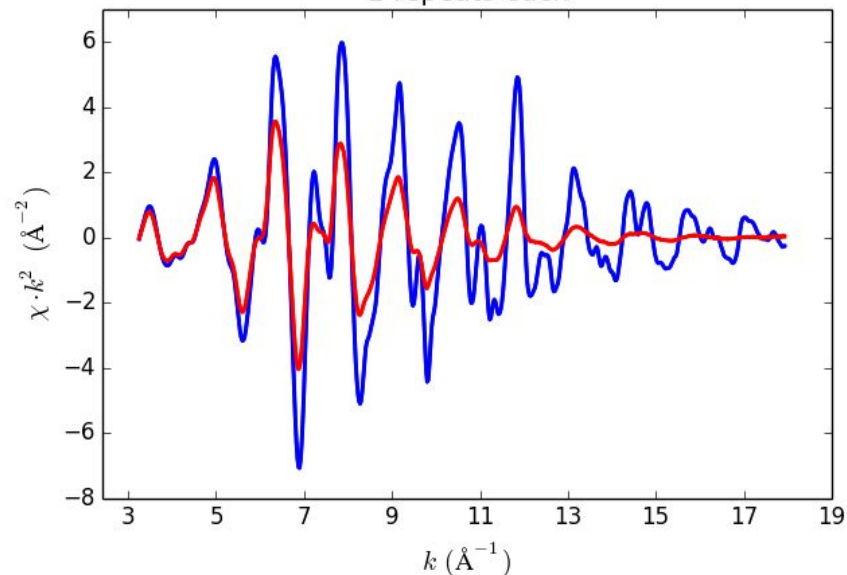
Atom	Z	Type	Atom1	Atom2	Weight	Length
0	30	Ti	0	0	0.00000	0
-0.19	1.967	1.077	2.02	2.41101	2	
0.99	1.967	-1.077	2.02	2.41101	2	
0.747	-2.09	1.137	2.04	2.50279	3	
-0.747	-2.09	-1.137	2.04	2.50279	3	
1.639	0.82	1.638	2.05	2.50496	5	
-1.639	0.82	-1.638	2.05	2.50496	5	
-2.407	-0.441	0.317	2.05	2.51621	7	
2.407	-0.441	-0.317	2.05	2.51621	7	
-0.713	-0.333	2.433	2.01	2.56875	9	
0.713	-0.333	-2.433	2.01	2.56875	9	
3.274	-0.352	0.484	3.13	3.32841	11	
-3.274	-0.352	-0.484	3.13	3.32841	11	
2.439	0.548	1.639	3.13	3.33363	13	
-2.439	0.548	-1.639	3.13	3.33363	13	
0.634	-2.388	2.337	3.12	3.36969	15	
-0.634	-2.388	-2.337	3.12	3.36969	15	
-0.434	-1.352	3.981	3.12	3.57417	17	
0.434	-1.352	-3.981	3.12	3.57417	17	
-2.333	-3.877	0.358	2.06	4.13454	19	
2.333	-3.877	-0.358	2.06	4.13454	19	
3.706	0.636	2.351	2.05	4.54879	21	
-3.706	0.636	-2.351	2.05	4.54879	21	

XAS spectra at various T

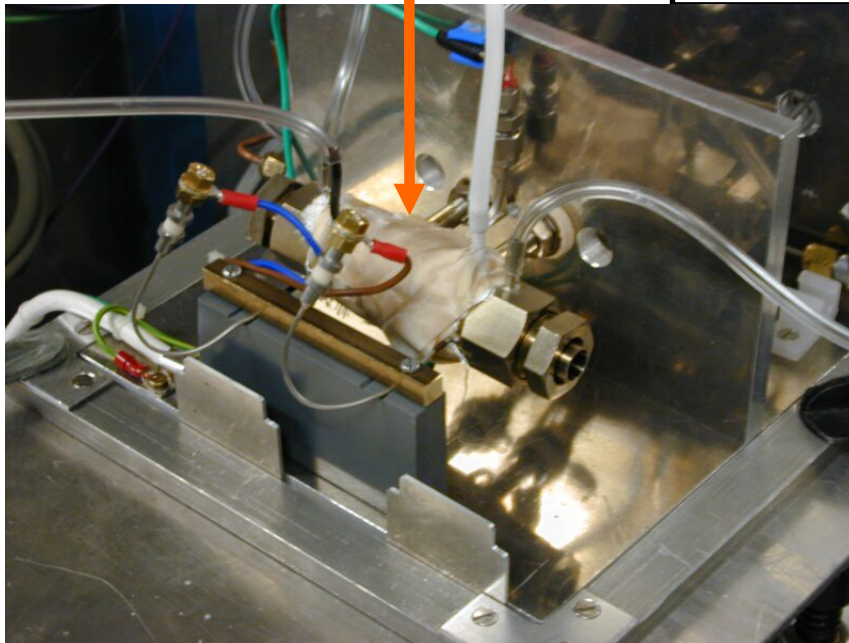
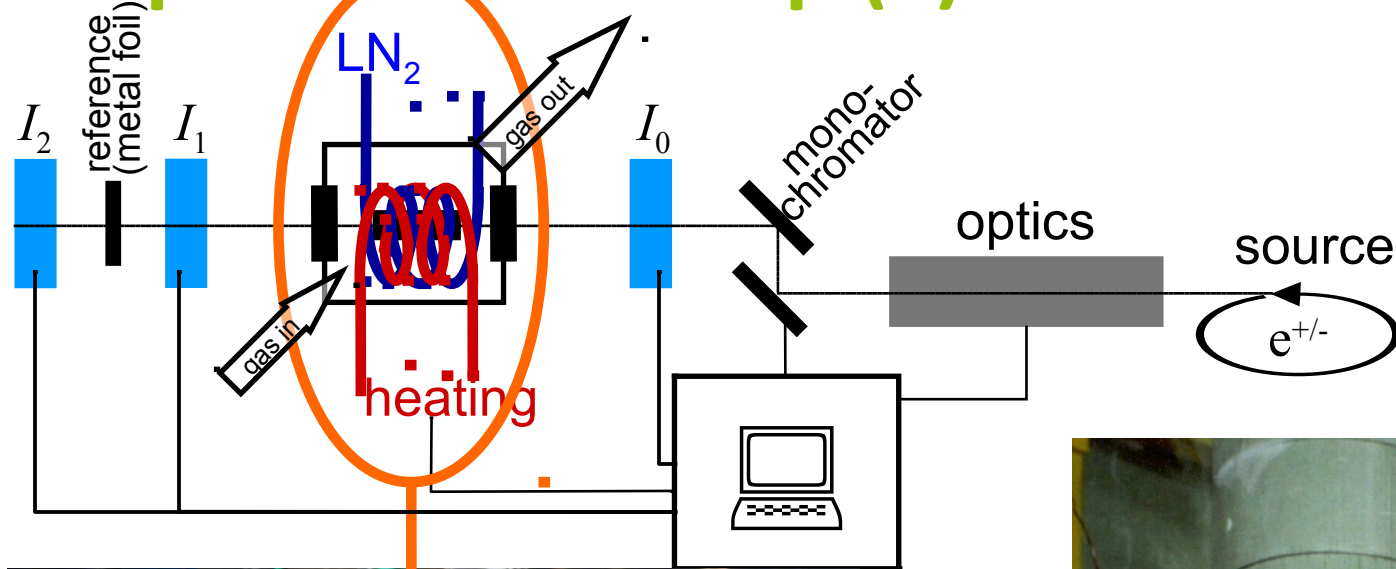
Absorption spectrum of copper foil at RT and LNT,
2 repeats each



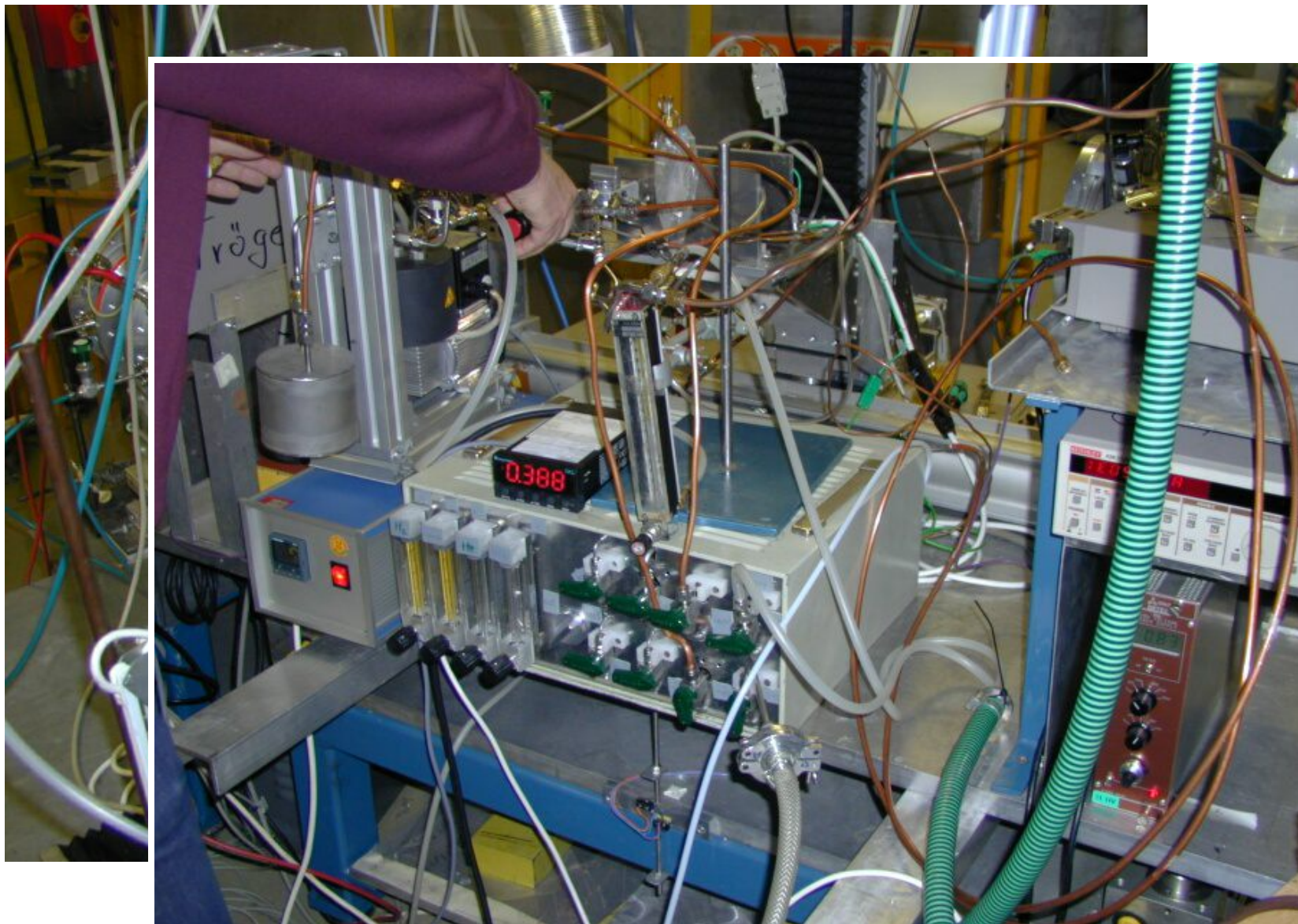
EXAFS spectrum of copper foil at RT and LNT,
2 repeats each



Experimental Setup (a)



Experimental Setup (b)



Example: Application of EXAFS to Pd,Pt/C Catalysts (a)

Supported noble metal catalysts are used in a number of commercial chemical processes (Pd,Pt/C → toluene and benzene hydrogenation).

Pd,Pt/C catalyst

- **Support:** graphite-like carbon (sibunit)
- **Preparation:** mild oxidative treatment of the support followed by ion exchange with Pd or Pt amine complexes
- **Characterization:** XPS, TPR, catalytic studies
- **Outcome:** highly dispersed metal clusters with ~1.1 wt% of Pd and ~0.9 wt% of Pt

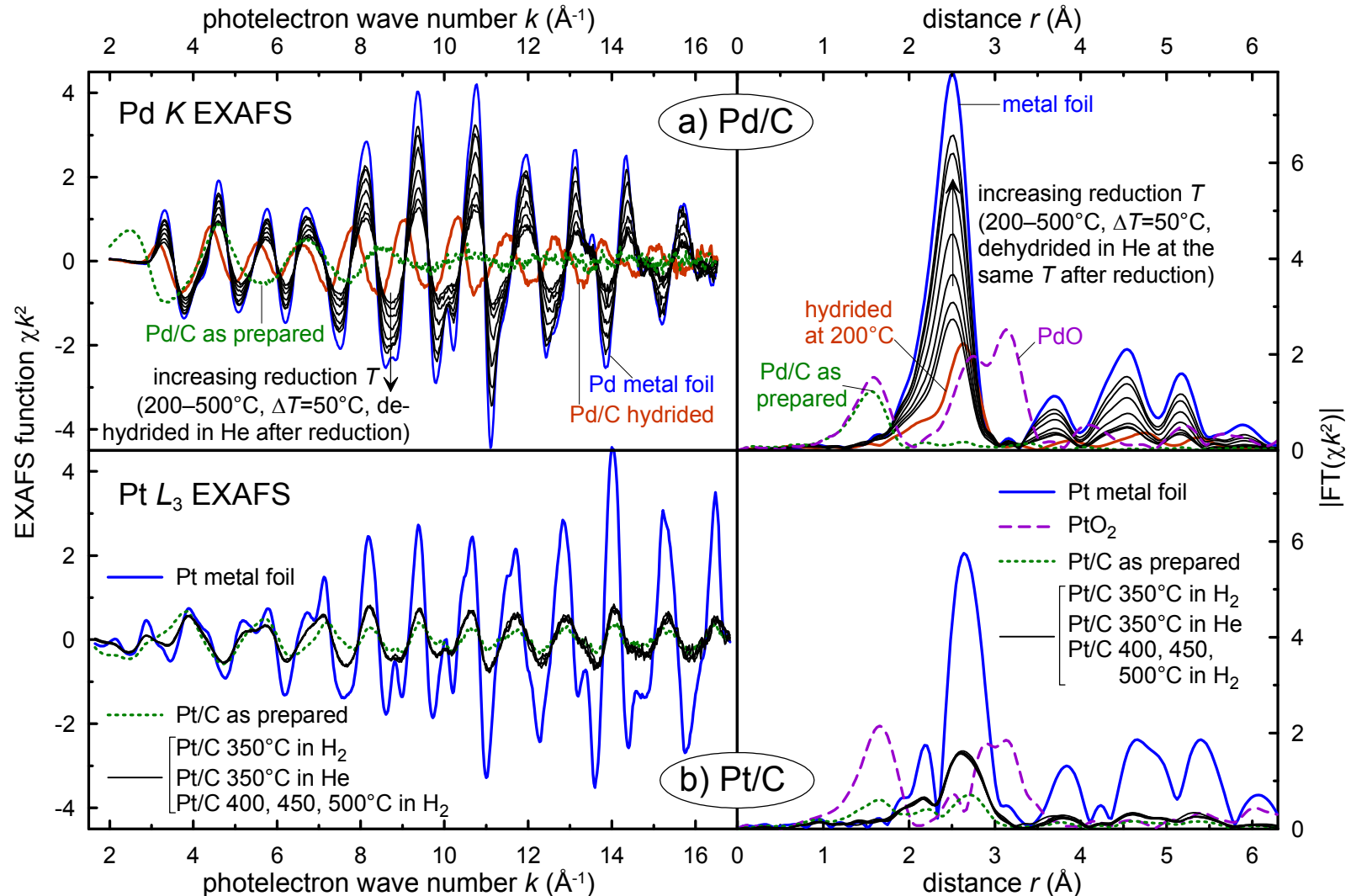
XAFS measurements

- X1 beamline at Hasylab/DESY with a Si 311 double crystal monochromator, transmission mode
- Samples: non-pressed powders

Example: Application of EXAFS to Pd,Pt/C Catalysts (b)

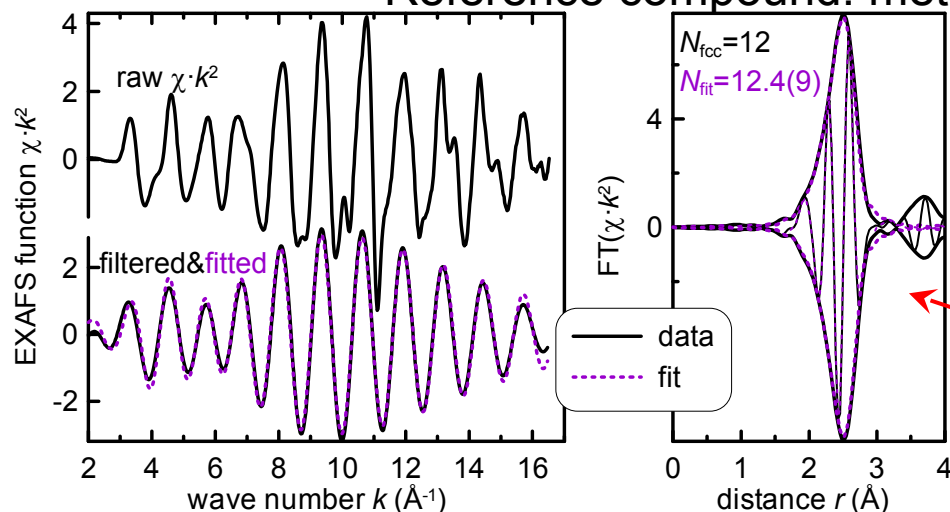
Reduction treatment: in 5% H_2 /He atmosphere, stepwise with $\Delta T=50^\circ\text{C}$.

Measurements at LN_2 temperature in order not to have interference of two effects: (i) due to different temperature vibrations and (ii) due to different particle sizes.



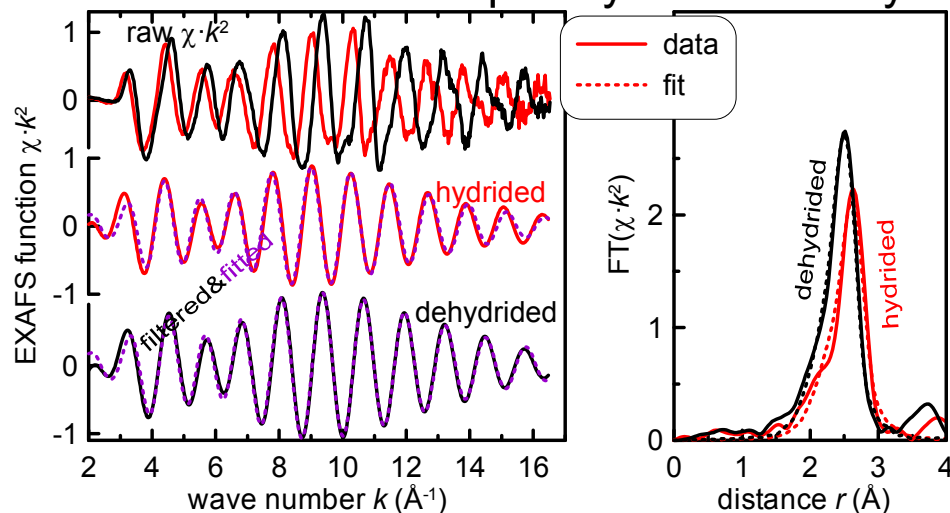
Example: Application of EXAFS to Pd,Pt/C Catalysts (c)

Reference compound: metallic Pd foil

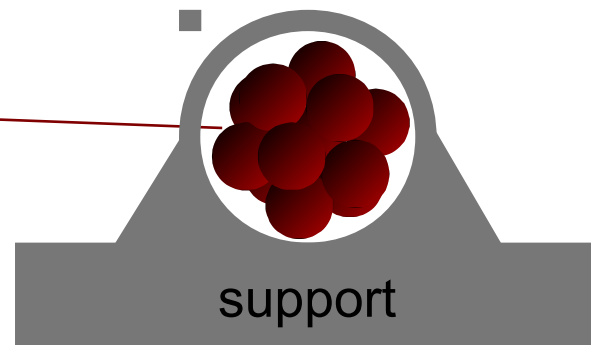
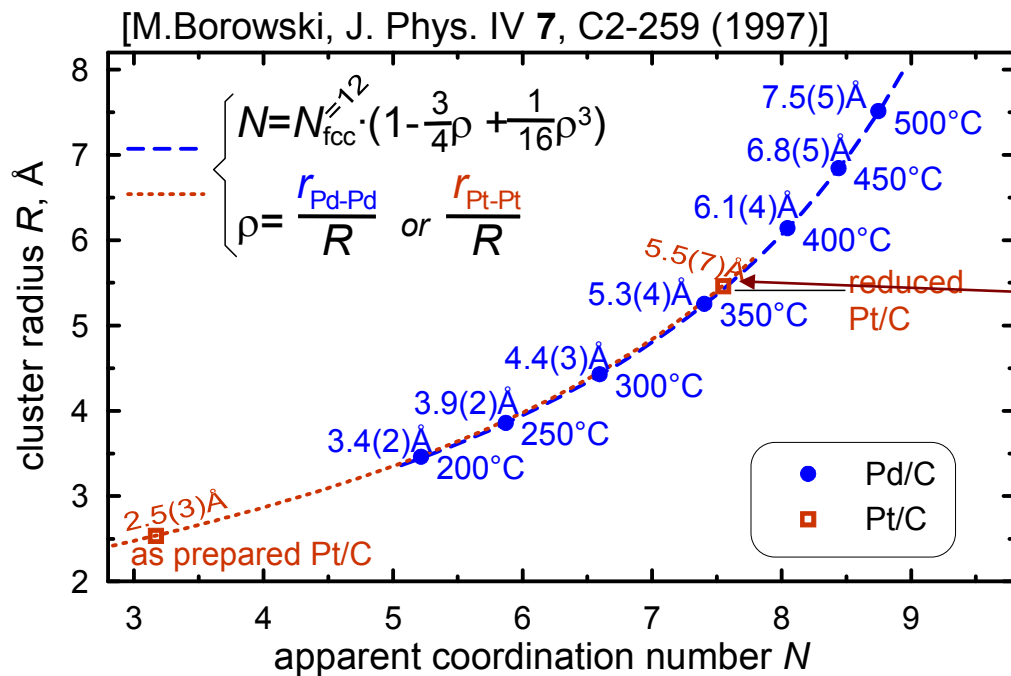


Checking your amplitudes and phases with reference spectra must be always the first step in every EXAFS study!

The difference between a simply reduced Pd/C sample (hydrided) and one subsequently blown out by He flow (dehydrided)



Example: Application of EXAFS to Pd,Pt/C Catalysts (d)



Catalytic properties:

- The catalytic activity in toluene and benzene hydrogenation was found to exceed the activity of conventional Pd/Al₂O₃ and Pt/Al₂O₃ fourfold for Pd/C and almost ten-fold for Pt/C.
- If the reduction temperature exceeds 350°C the activity of both catalysts sharply decreases.

The EXAFS study made it possible to exclude intense metal sintering, or Pd carbide formation as possible reasons of the activity drop.

Stakheev et al., *Russ.Chem.Bull.Int.Ed.* **53** (2004) 528

What we can learn from XANES: a) Pre-edge Peak

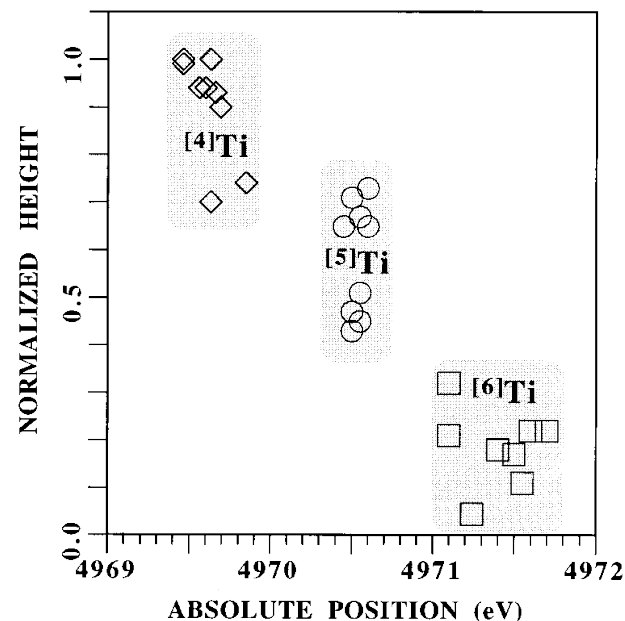
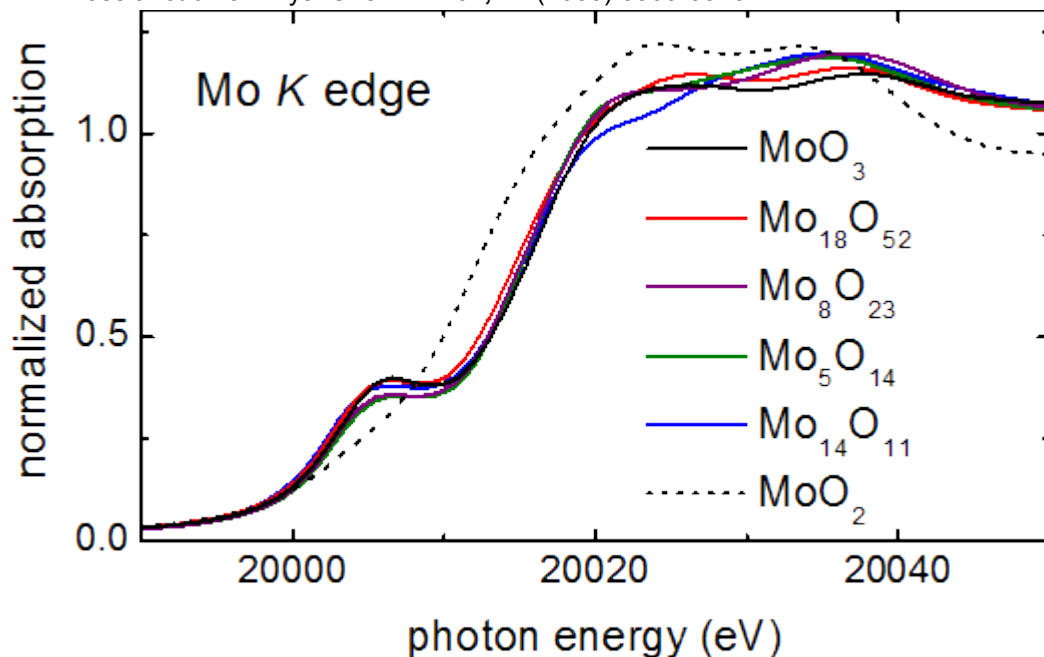
Dipole selection rule (only in central-symmetric case!): $\Delta l = \pm 1$

Consider K -absorption for transition metals:

- initial state = $1s$ ($l=0$)
- states near E_F are formed by nd electrons ($l=2$)

central-symmetry	non-central symmetry
no resonance	resonance (pre-edge peak)

T. Ressler et al. J. Phys. Chem. B **104**, 27 (2000) 6360-6370

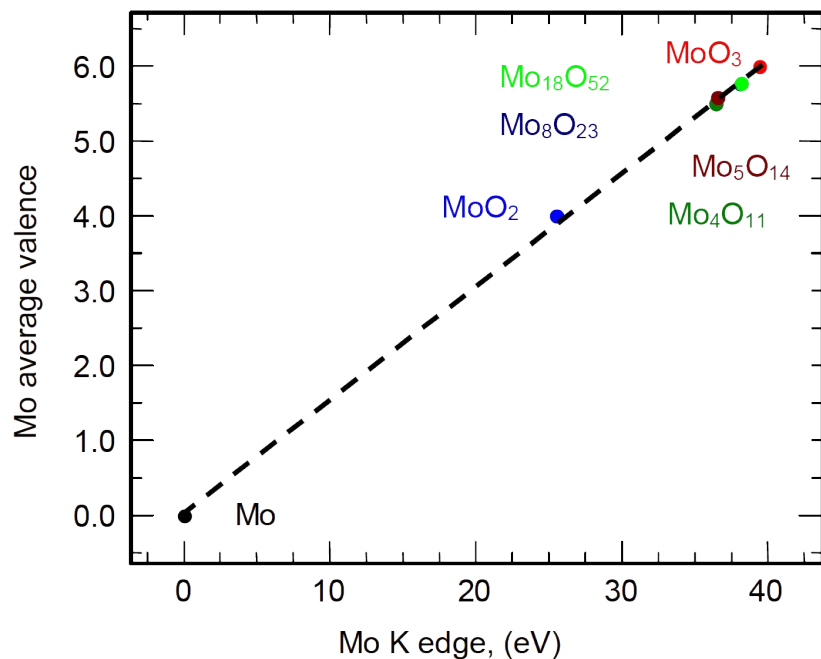


from [F. Farges, G. E. Brown, J. J. Rehr, Phys. Rev. B **56** (1997) 1809]

What we can learn from XANES: b) Edge Shift

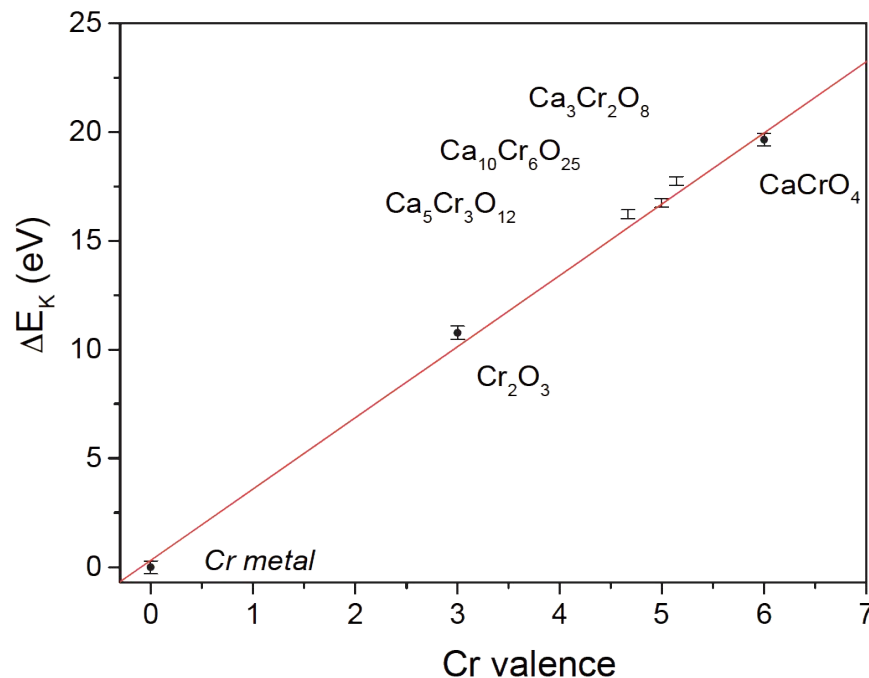
T. Ressler, R. E. Jentoft, J. Wienold, M. M. Günter and O. Timpe:

J. Phys. Chem. B **104**, **27** (2000) 6360-6370



I. Arčon, B. Mirtič, A. Kodre,

J. Am. Ceram. Soc. **81** (1998) 222–224



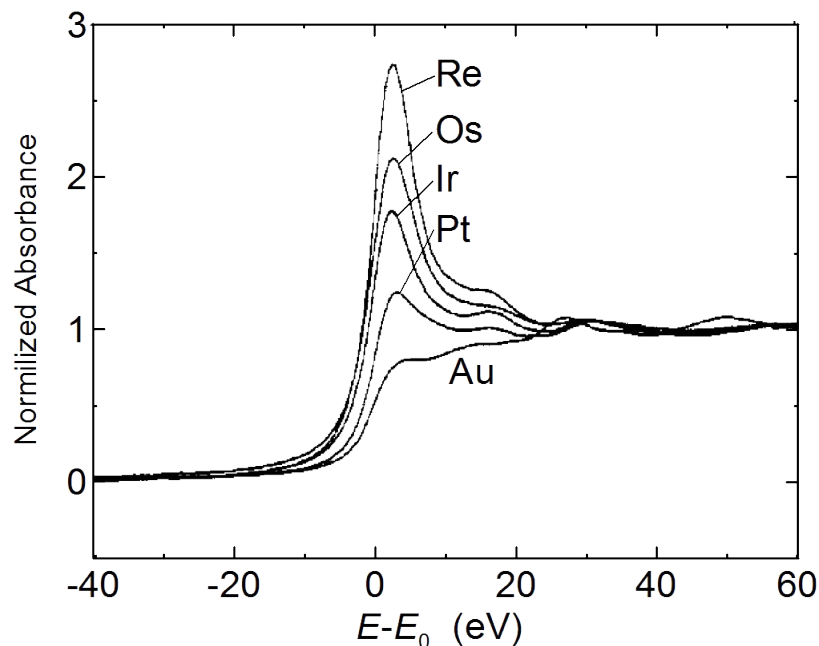
Why does it shift?

- 1) Electrostatic: it is harder for the photoelectron to leave a positive (oxidized) atom
- 2) Shorter bonds at higher oxidation states $\Rightarrow$ Fermi energy is higher

What we can learn from XANES: c) White Line

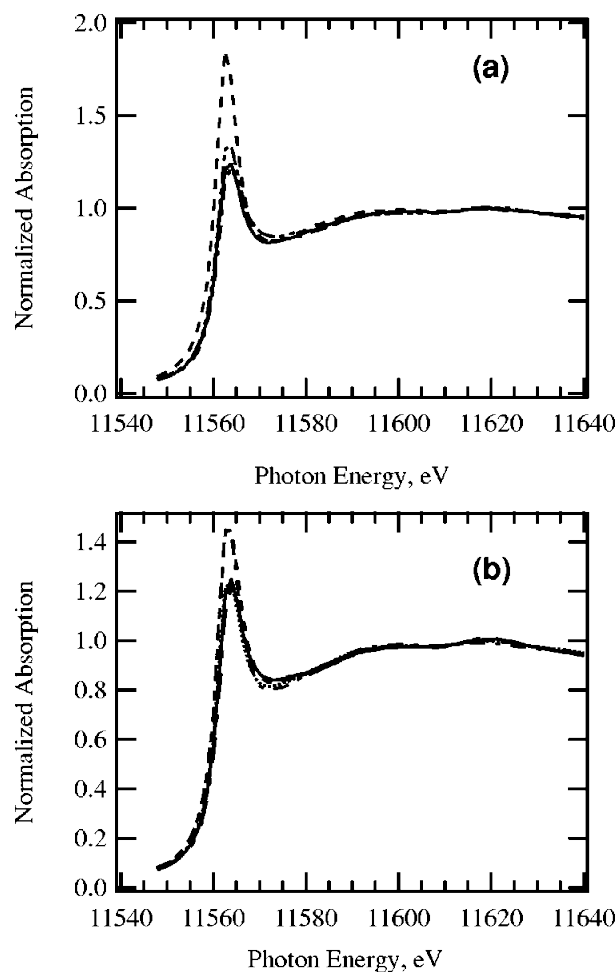
L_3 absorption edges for 5d metals:
(transition $2p_{3/2} \rightarrow 5d$)

G. Meitzner, G. H. Via, F. W. Lytle, and J. H. Sinfelt,
J. Phys. Chem. **96** (1992) 4960



Intensity is proportional to the number of free 5d states and also depends on valence state. But...

...white line also depends on particle size and morphology:

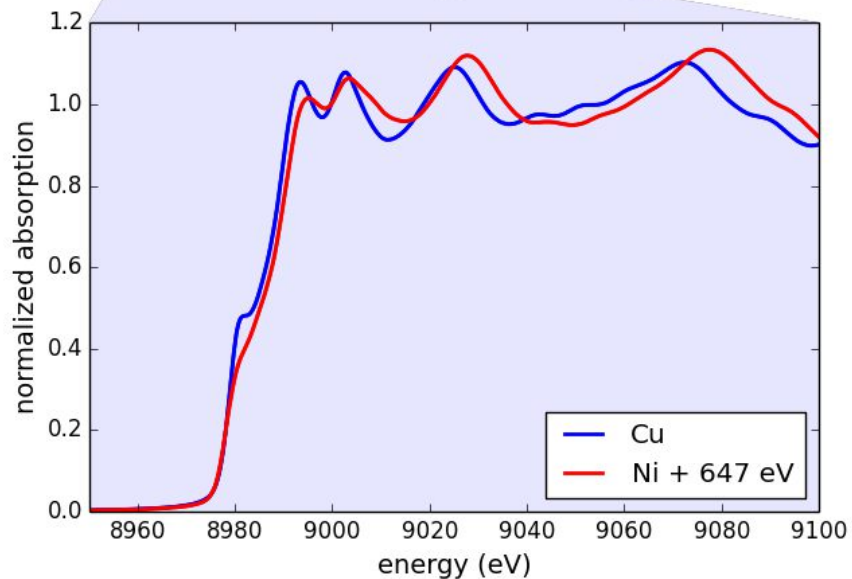
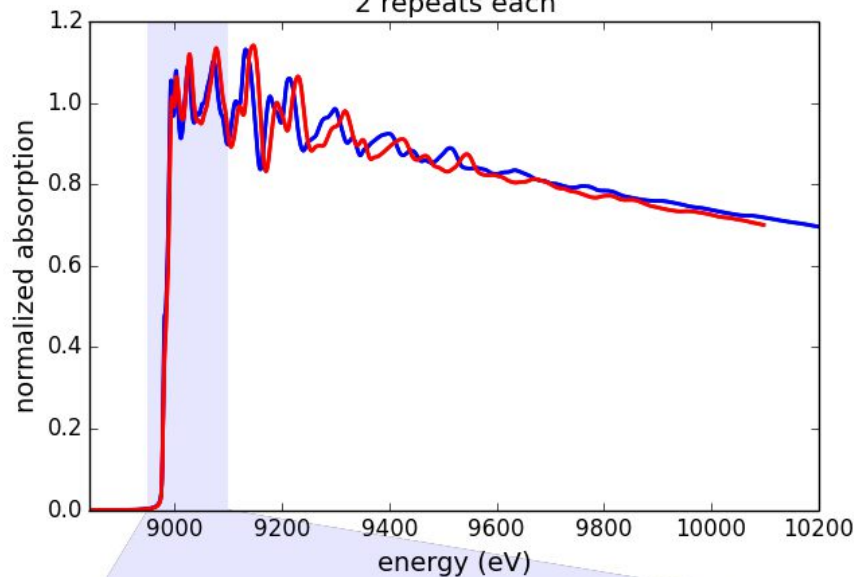


a) Pt₃ triangle (dashes), Pt₄ tetrahedron (solid), Pt₅ triangular bipyramid (dash-dot), and Pt₆ octahedron (dash-dot-dot);
(b) Pt₇ and Pt₈ clusters of different shape: planar "honeycomb" (dashes), D_{5h} bipyramid (solid), single-capped octahedron (long dash-dot), Pt₄ tetrahedron (dots), and Pt₄ planar rhombus (dash-dot).

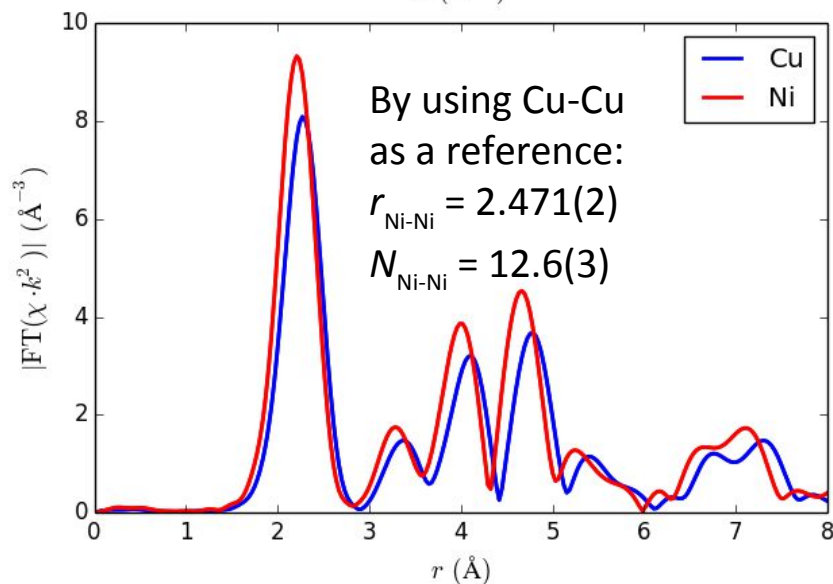
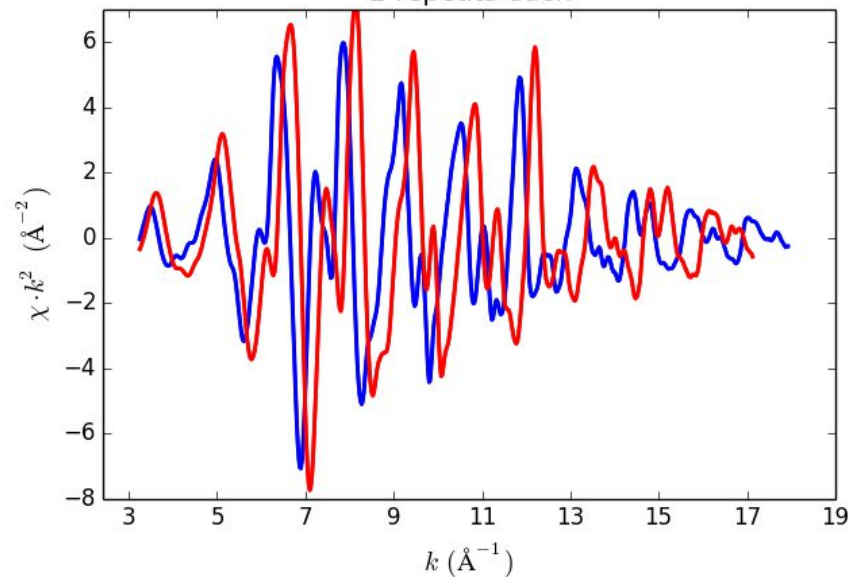
from A. L. Ankudinov, J. J. Rehr, J. J. Low, and S. R. Bare, J. Chem. Phys. **116** (2002) 1911

Spectra of similar structures

Absorption spectra of copper and nickel foils LNT,
2 repeats each

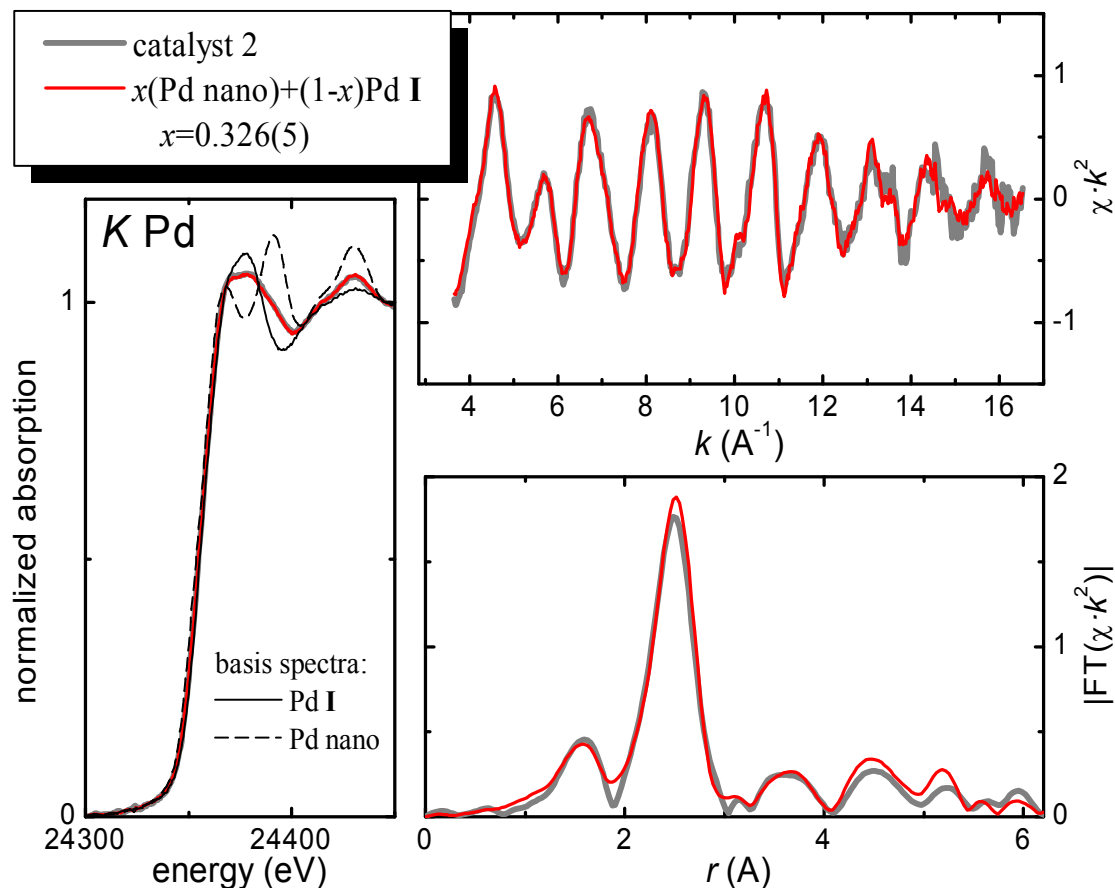


EXAFS spectra of copper and nickel foils LNT,
2 repeats each



Linear combination of spectra

1. *Basis spectra*: precursor (Pd I) and metallic Pd particles.
2. The spectrum “catalyst 2” shows coincidence with its *target transformation*.
3. Linear combination fitting of **XANES** of “catalyst 2” by the two basis spectra.
4. The found linear combination is then successfully applied to **EXAFS**.



Palladium Nanoparticles immobilized on Mesoporous Silica Support – New Efficient Catalysts for Aerobic Alcohol Oxidation in Supercritical Carbon Dioxide
Z. Hou et al., *J. of Catalysis* **258** (2008) 315

Conclusions

- XAFS (XANES and EXAFS) spectroscopies:
 - suitable under reaction conditions
 - does not require long-range order
 - element specific
- XANES spectroscopy for:
 - symmetry information from the pre-edge peaks
 - valence state from the edge shift
 - analysis of mixtures using basis spectra
- XANES is experimentally simpler than EXAFS
 - signal is stronger (one can measure faster and at lower concentrations)
 - does not depend on T (if without phase transitions, of course)
- EXAFS gives:
 - inter-atomic distances and coordination numbers
 - identification of neighbor atoms