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

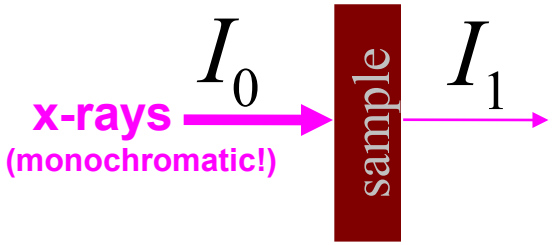
Main intentions:

- 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**

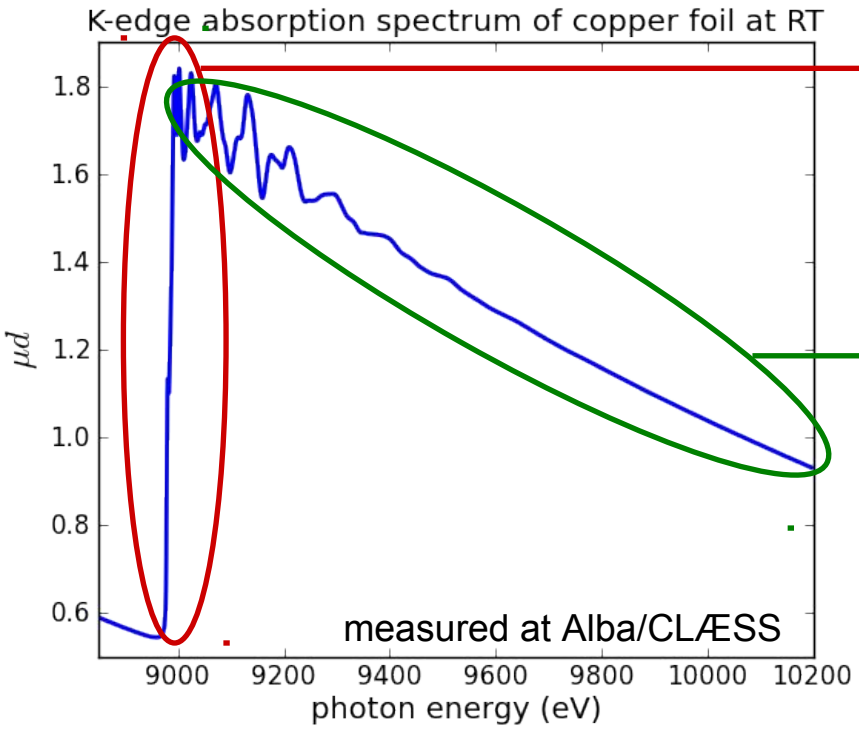
- Basic definitions and qualitative picture of XAFS (slide 3)
- Qualitative picture of XAFS (slide 4)
- The EXAFS formula and the need for amplitudes and phases (slides 5–7)
- XAFS at various T (slide 8)
- Experimental XAS setup (slides 9–10)
- An example of EXAFS study (slides 11–14)
- Using XANES without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

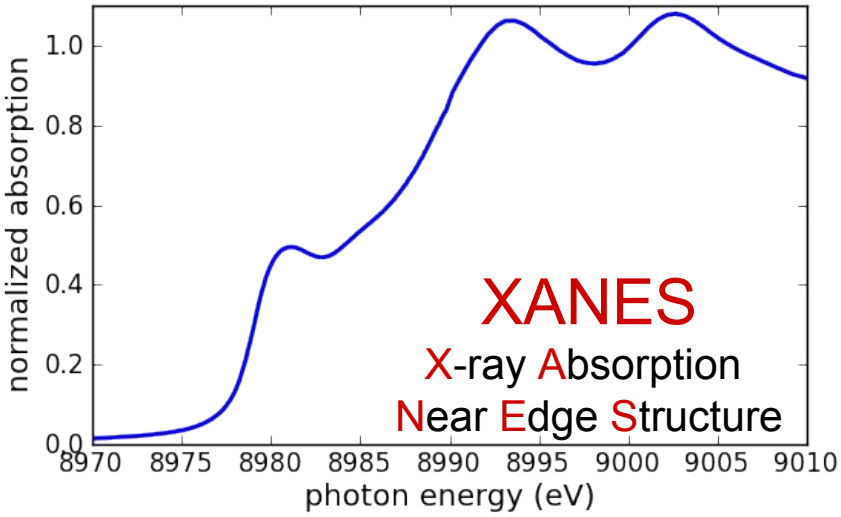
X-ray Absorption Spectra

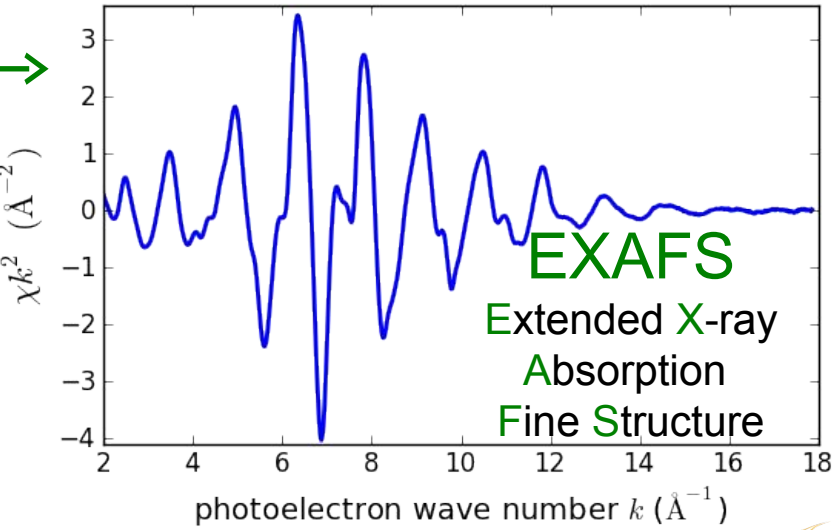
transmission experiment



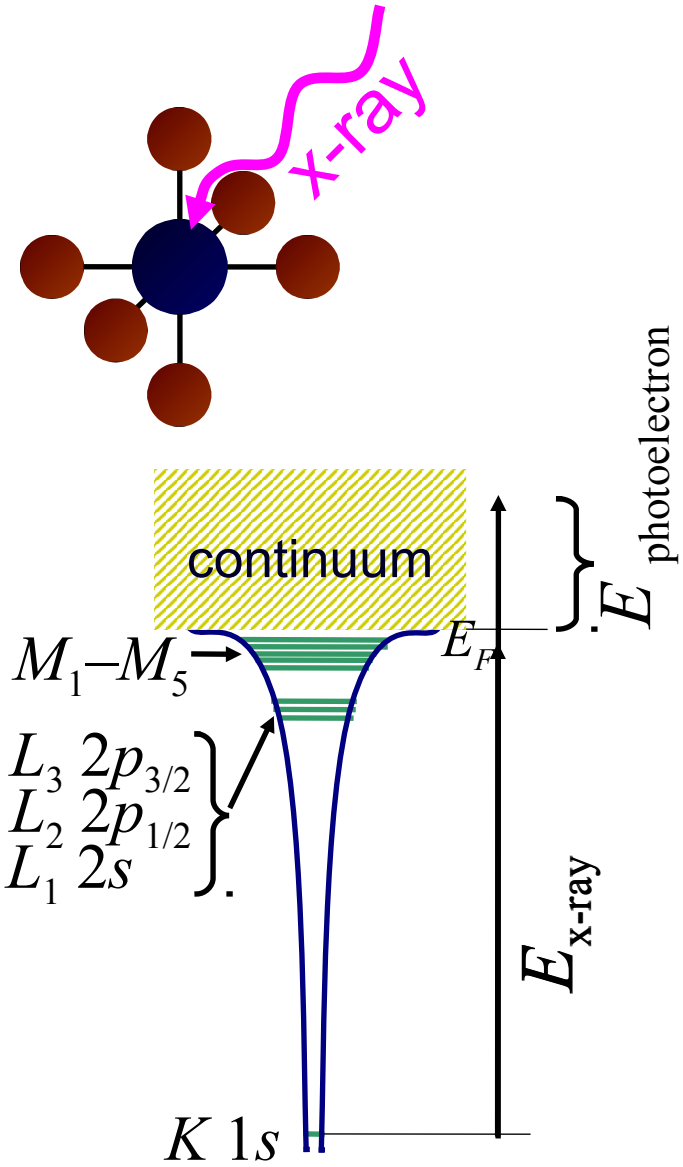
$$I_1 = I_0 e^{-\mu d}$$

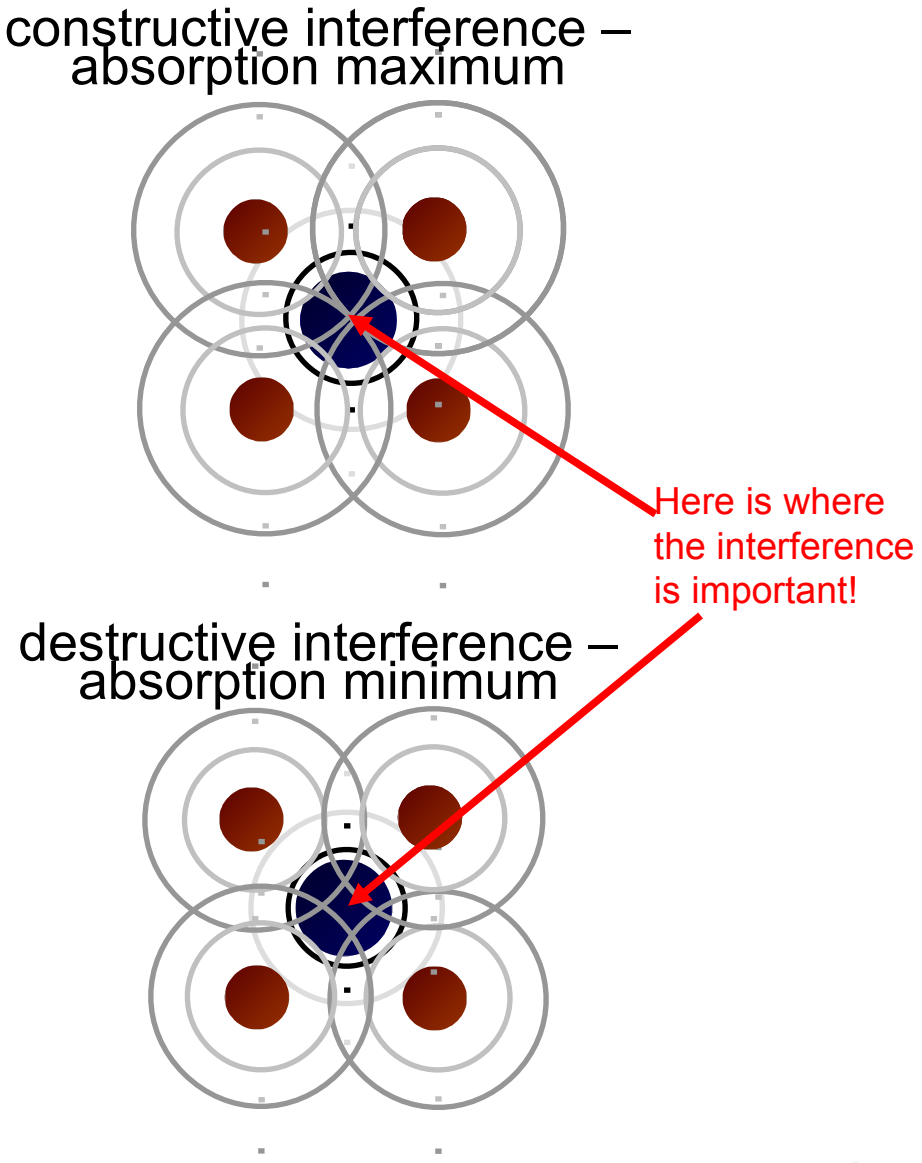






Qualitative Picture of XAFS





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:

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

For each coordination shell j:

R_j, N_j, σ^2_j 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.

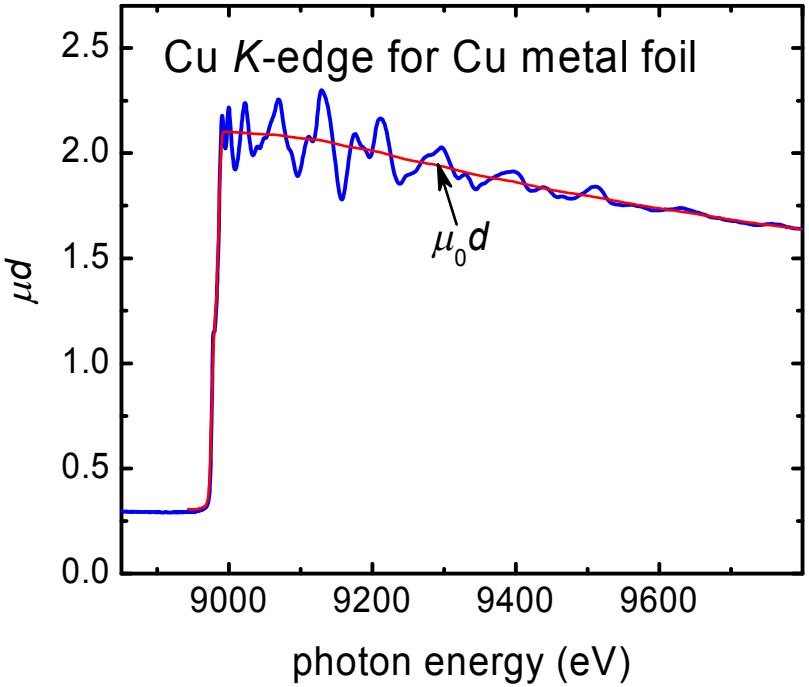
- For XANES region this is a problem, because μ_0 there is a rapidly changing function with features comparable with χ.
- In EXAFS region μ_0 is a smooth function and can be constructed empirically.

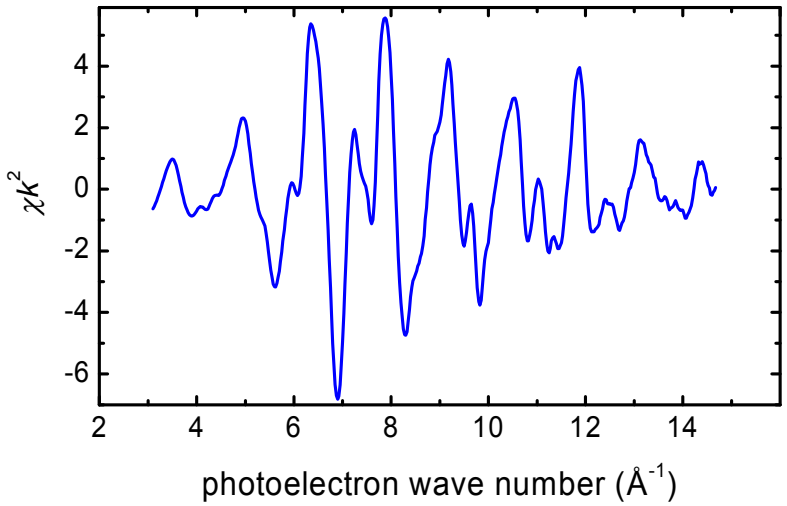
Thus, XANES spectra are mostly *interpreted*, not analyzed. EXAFS spectra can be analyzed quantitatively.

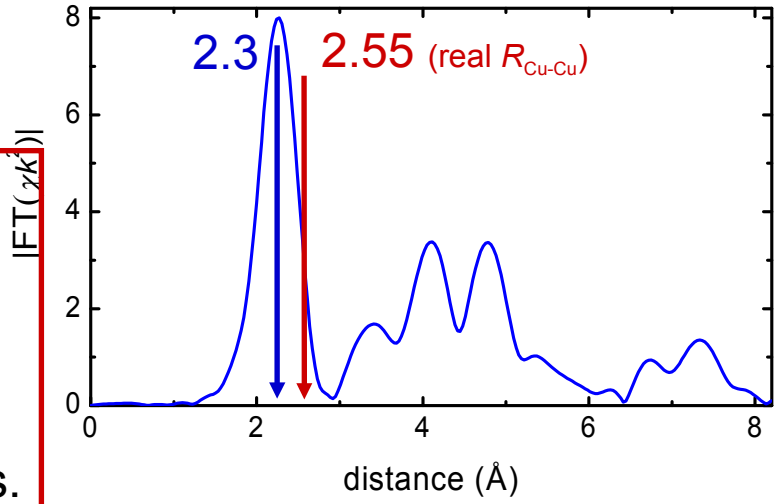
See more in the "*Theory*" lecture

Importance of EXAFS phases

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



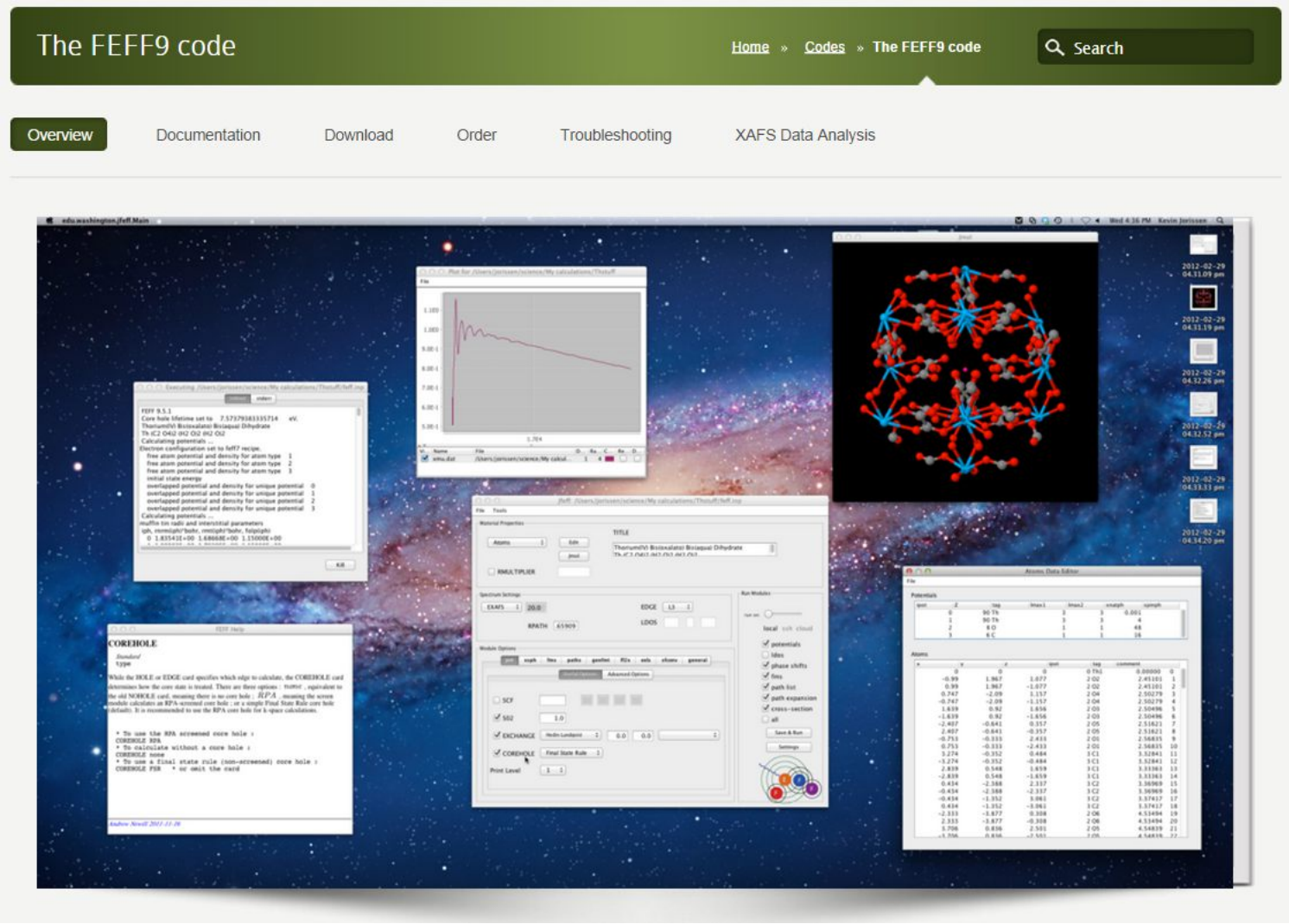




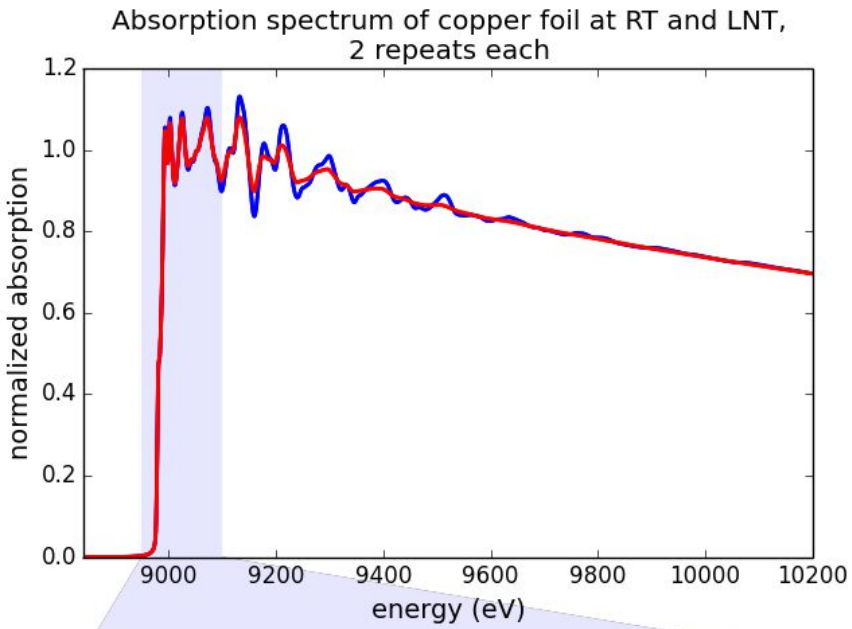
Unpleasant thing about EXAFS:
FT positions are shifted towards small distances.
More unpleasant: Each FT peak has its own shift.
Because of the phase shifts, extracting the structural information from EXAFS requires curve fitting with assumed (calculated) phase shifts.

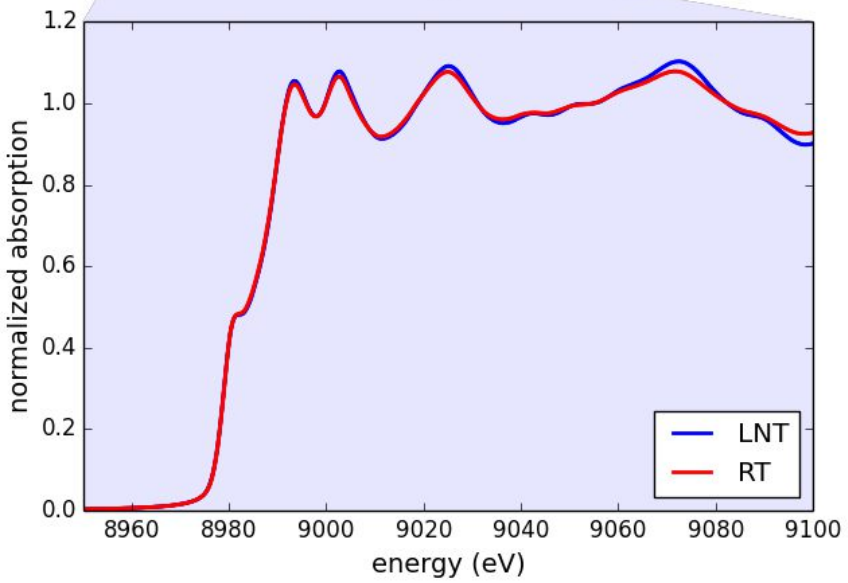
EXAFS amplitudes and phases

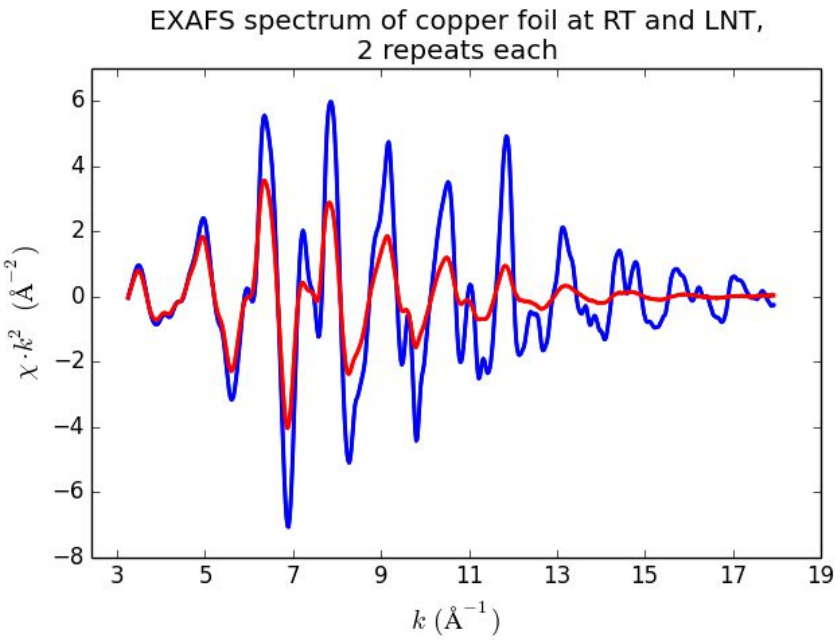
http://feffproject.org/

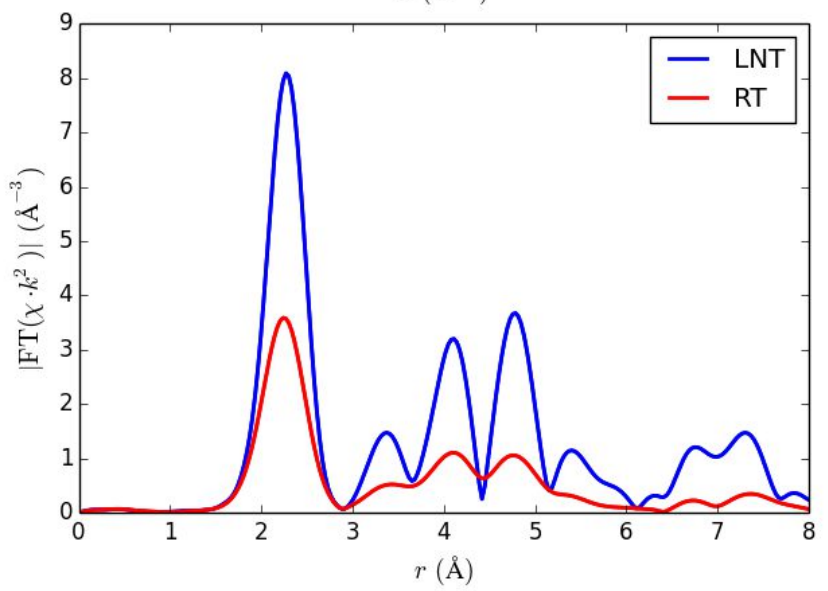


XAS spectra at various T

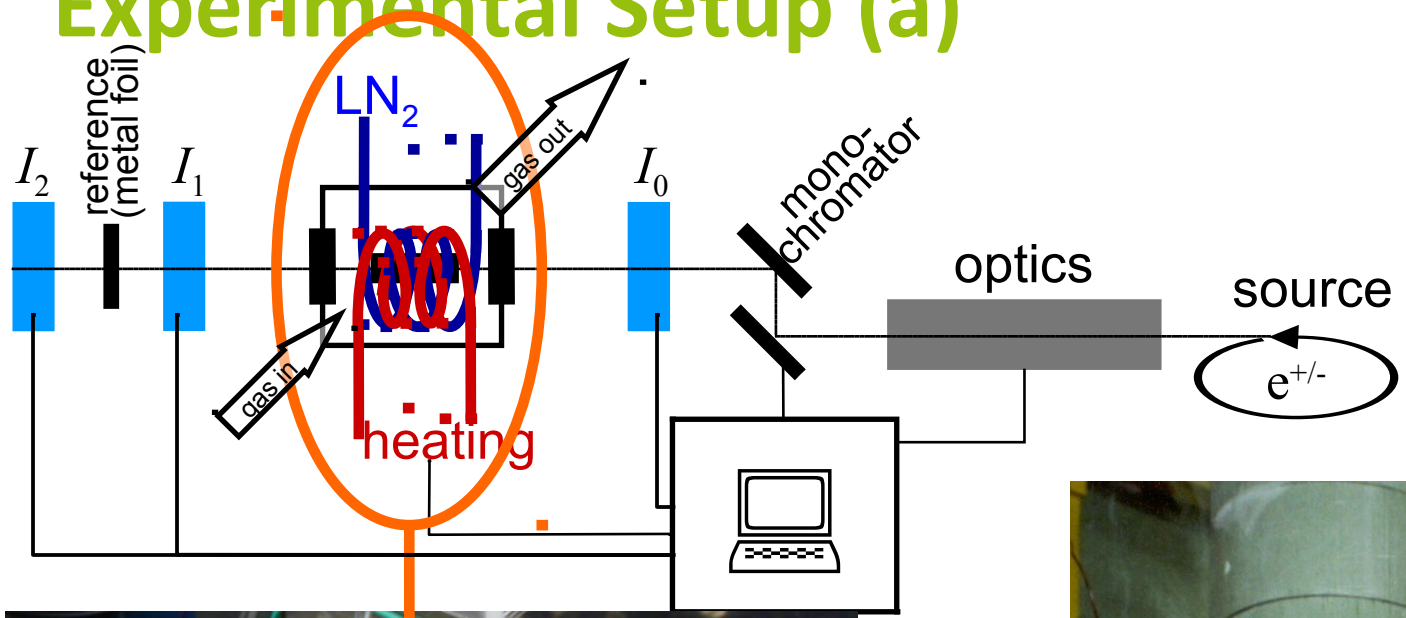


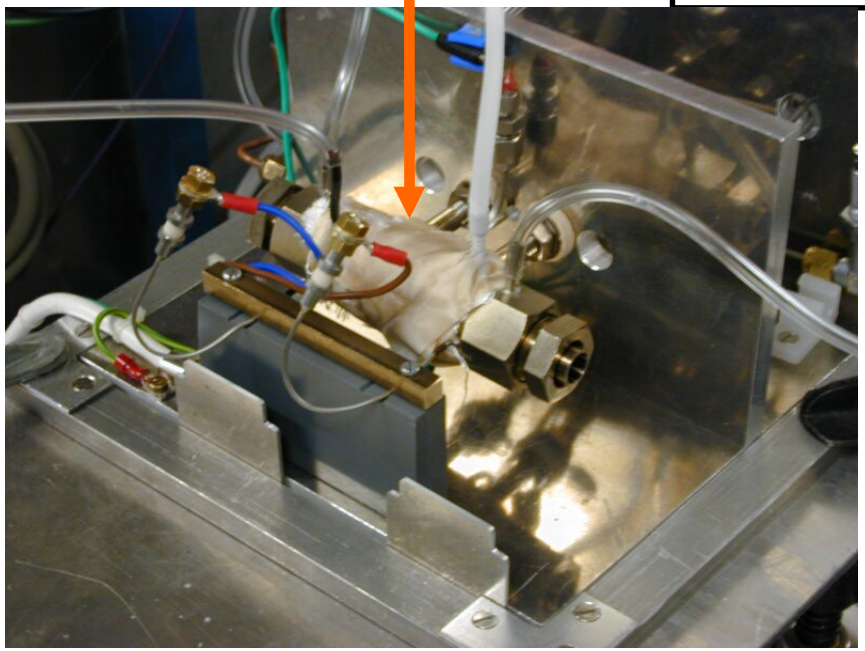




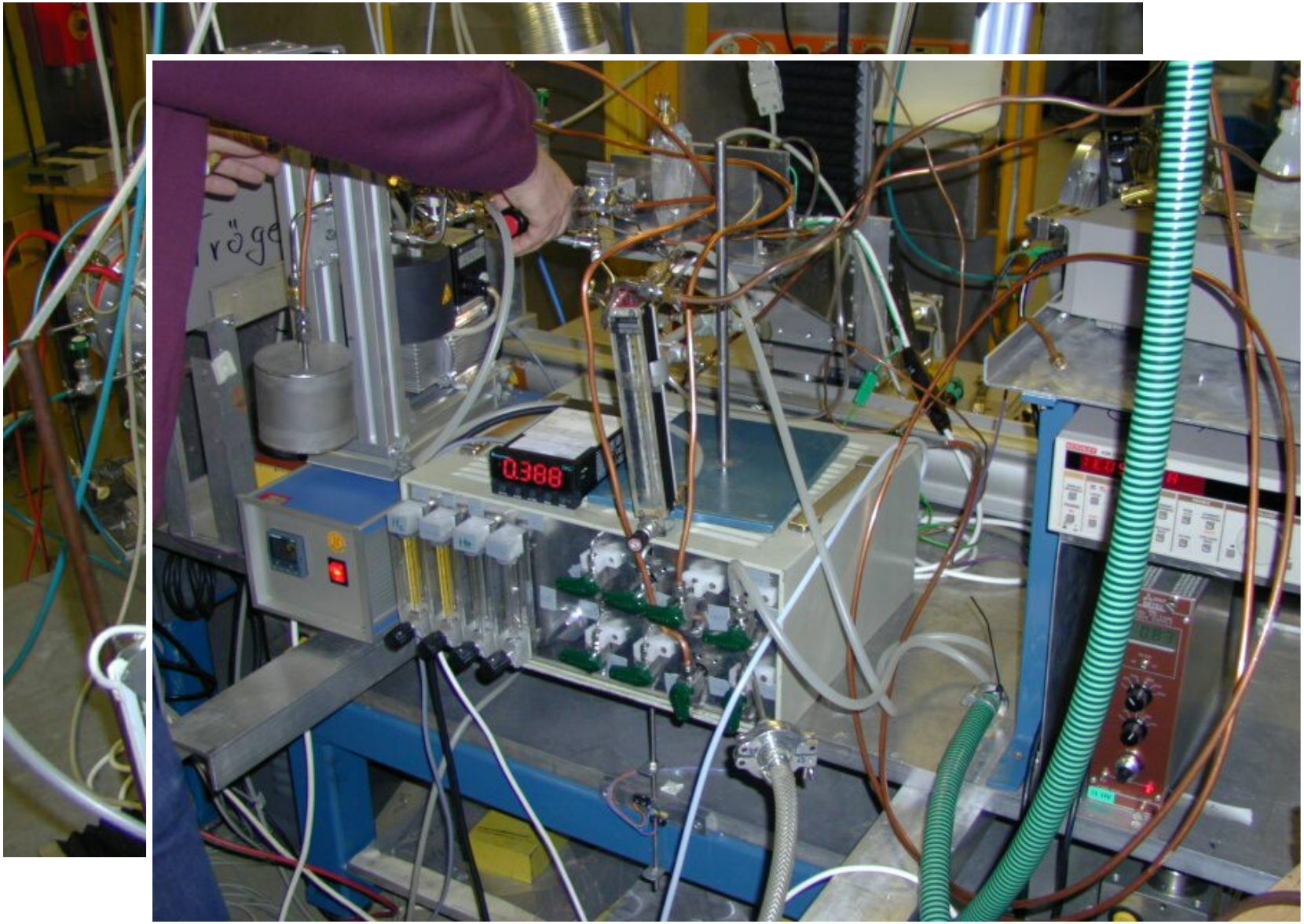


Experimental Setup (a)





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 $\rightarrow$ 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

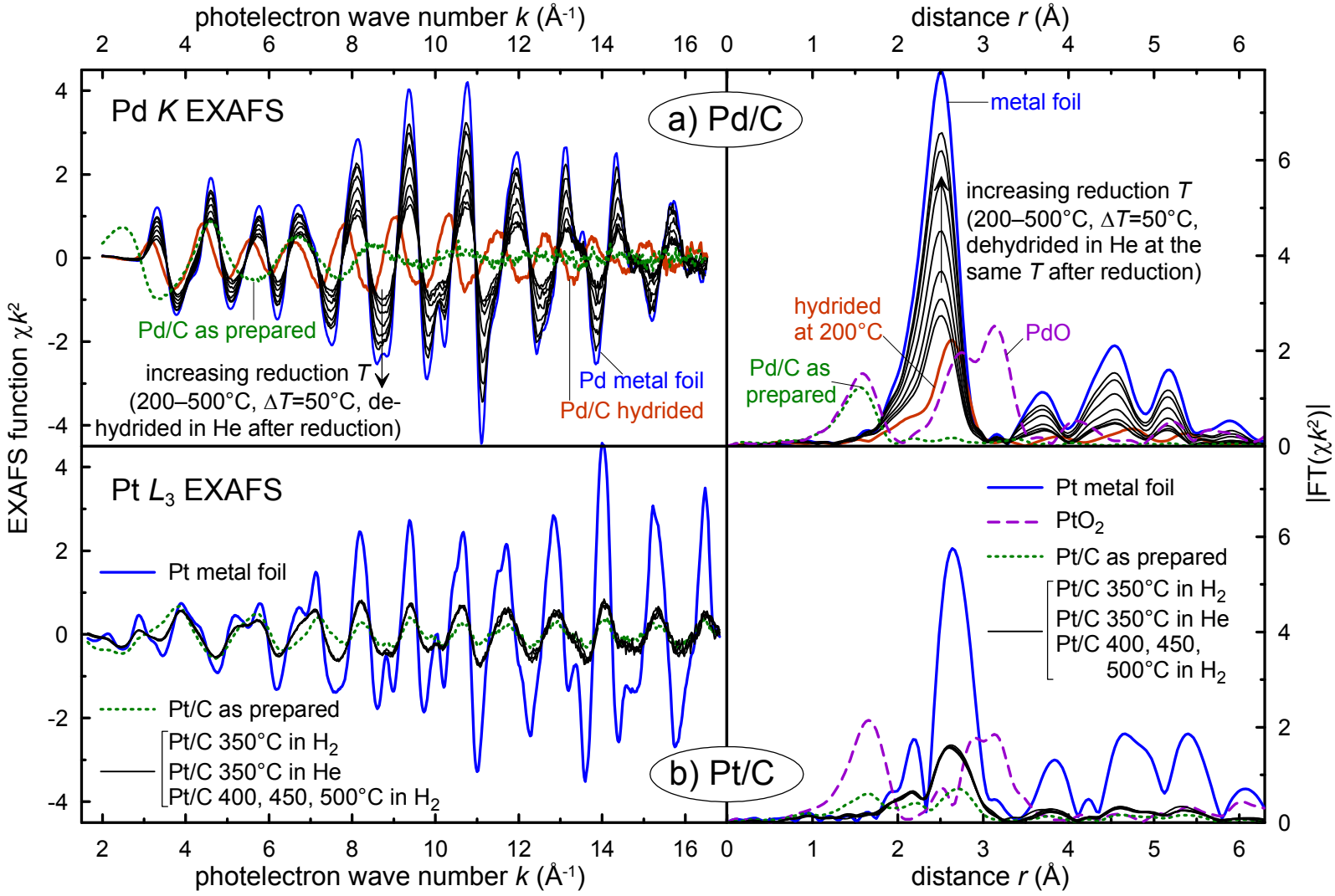
XAFS measurements

- 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)

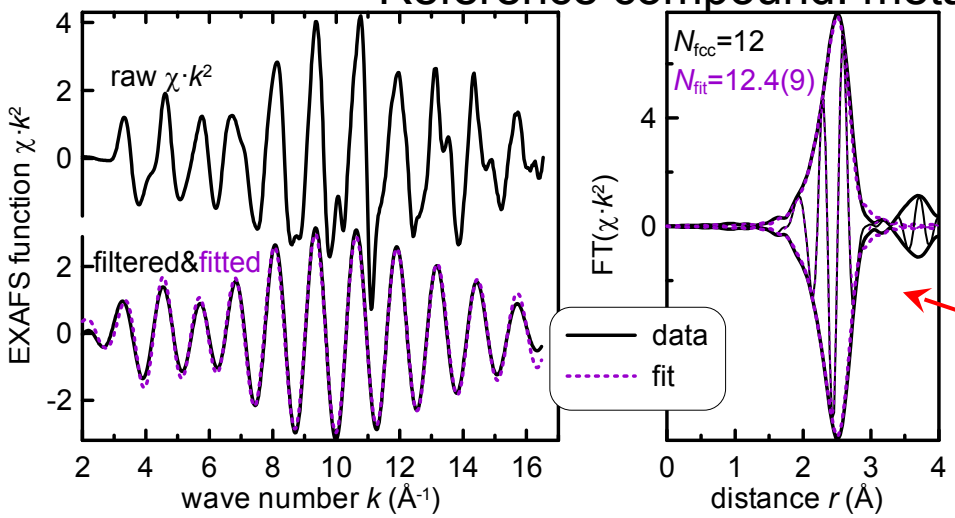
Reduction treatment: in 5%H_2/He atmosphere, stepwise with ΔT=50°C.

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.



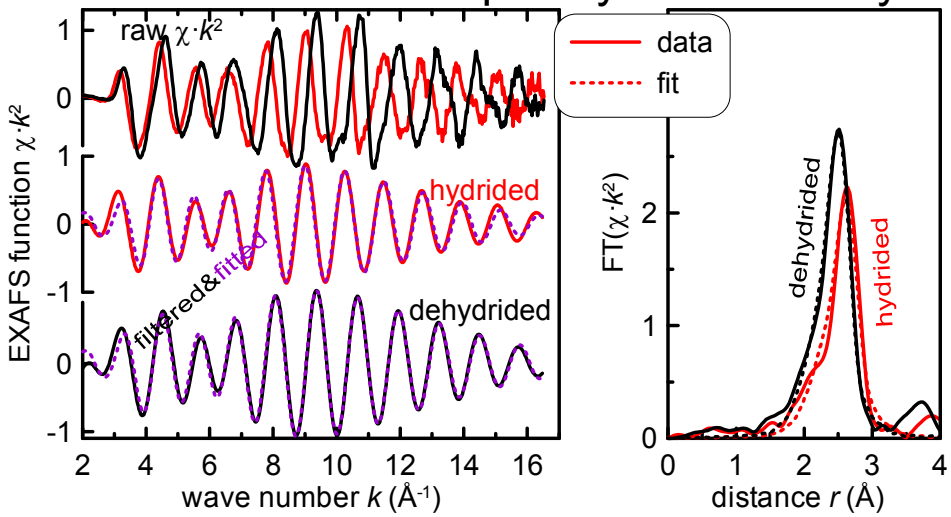
Example: Application of EXAFS to Pd,Pt/C Catalysts (c)

Reference compound: metallic Pd foil

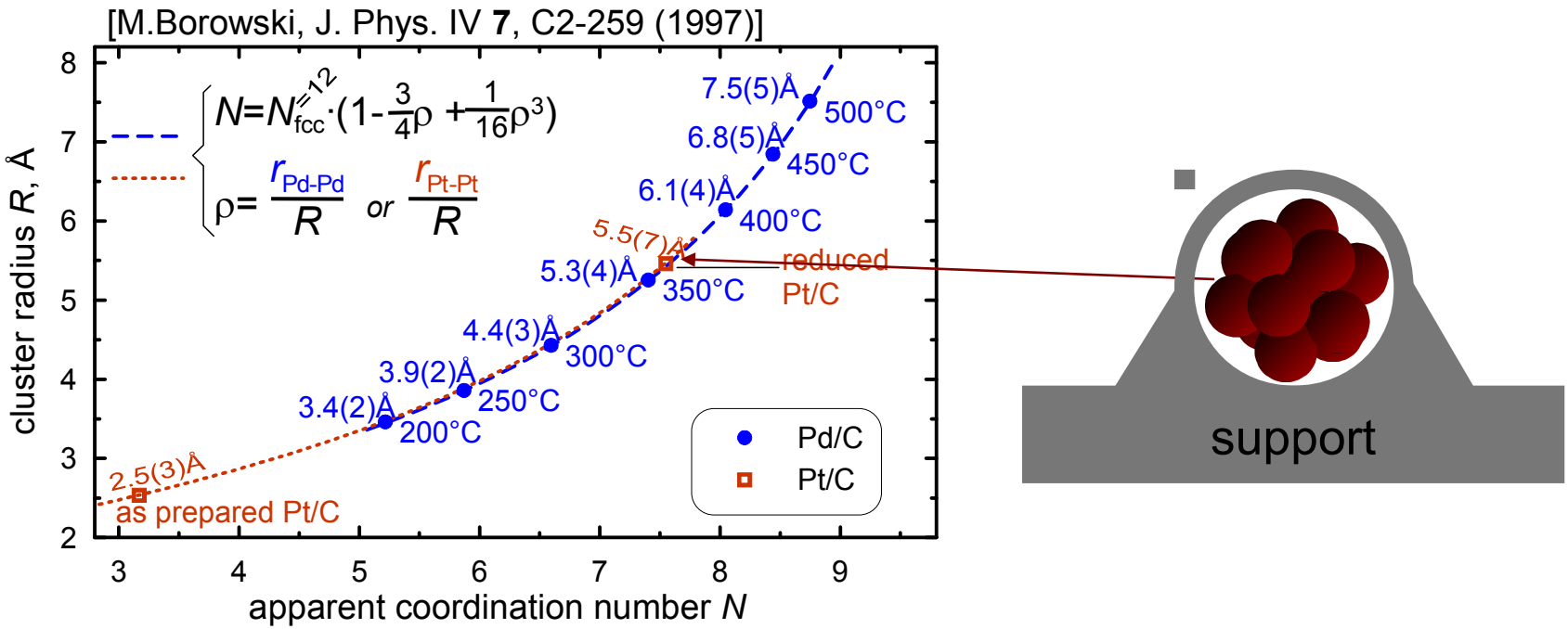


Checking your amplitudes and phases with reference spectra must be always the first step in every EXAFS study!

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/Al_2O_3 and Pt/Al_2O_3 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

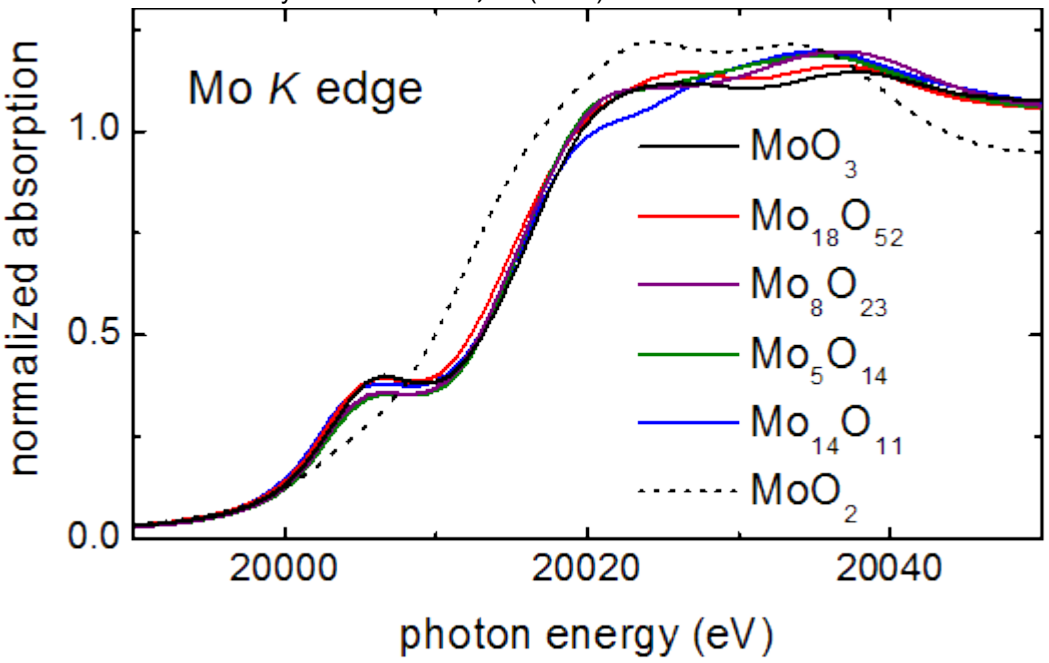
Dipole selection rule (only in central-symmetric case!): $\Delta l = \pm 1$

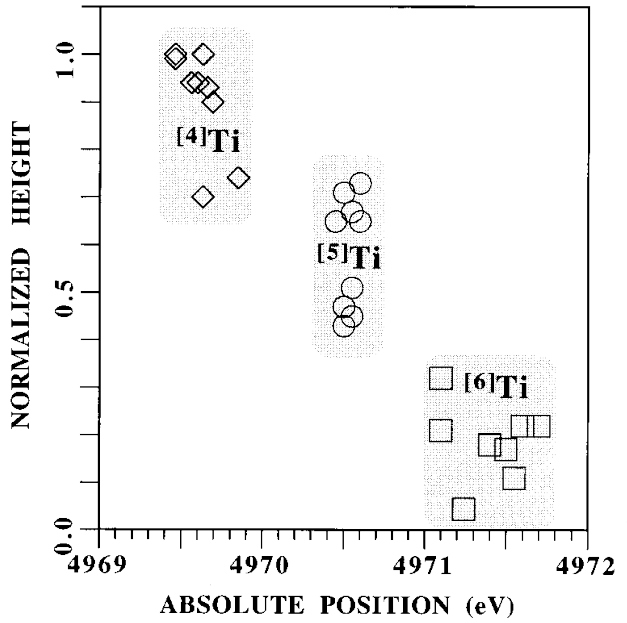
Consider *K*-absorption for transition metals:

- 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

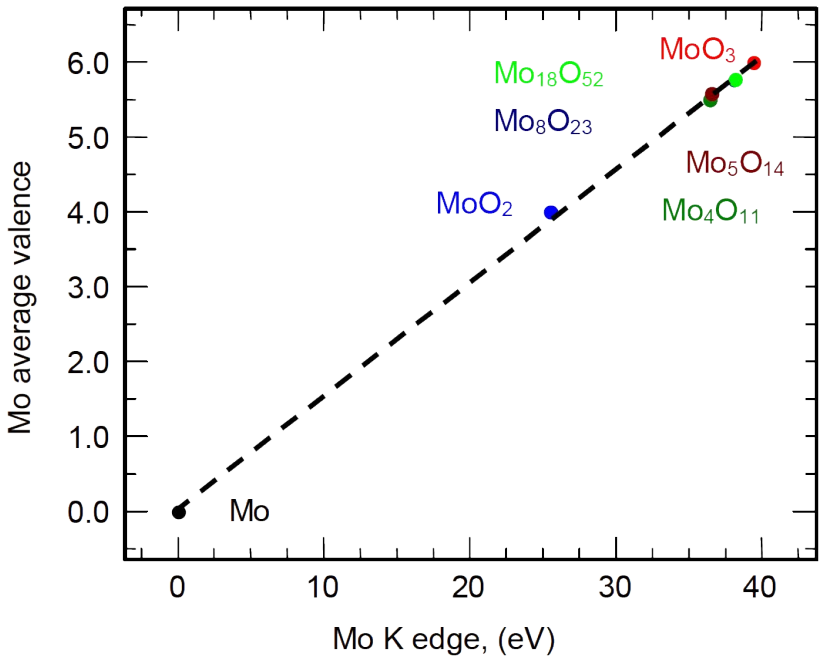




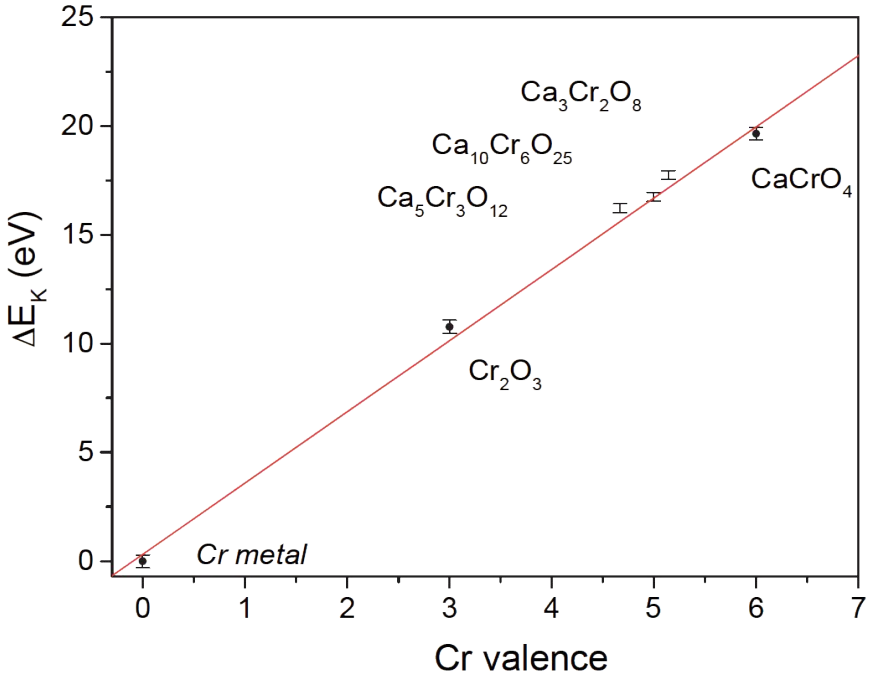
from [F. Farges, G. E. Brown, J. J. Rehr, *Phys. Rev. B* **56** (1997) 1809]

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

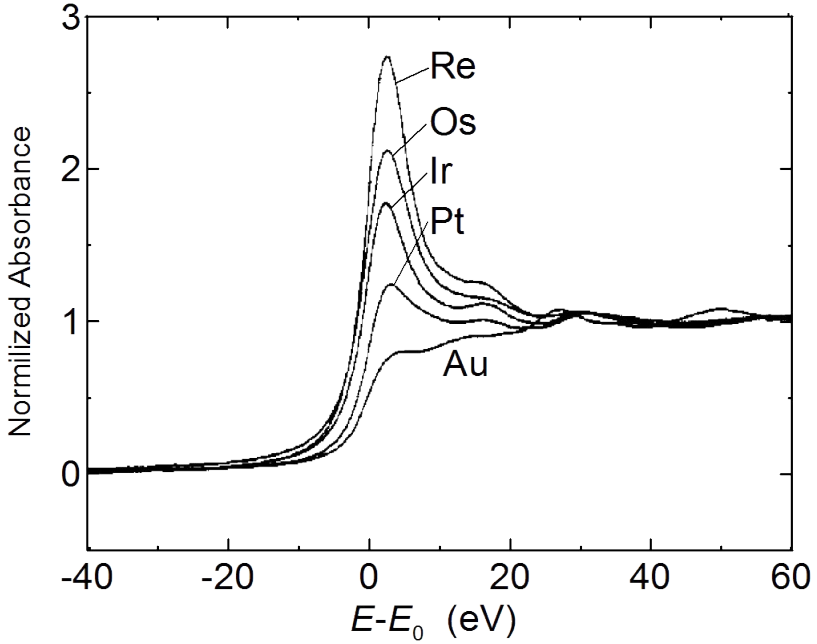
2) Shorter bonds at higher oxidation states ⇒ Fermi energy is higher

What we can learn from XANES: c) White Line

L_3 absorption edges for 5*d* metals:

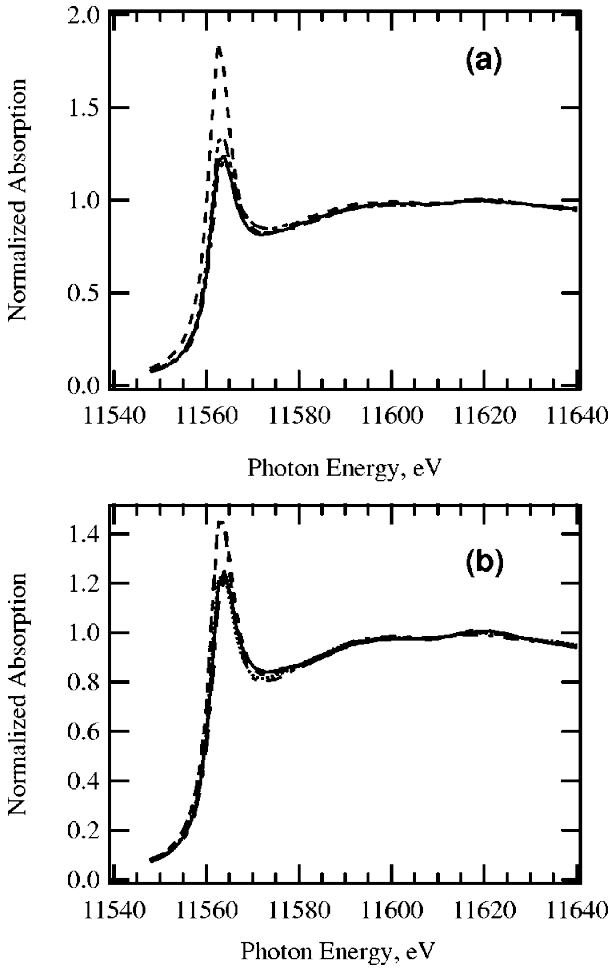
(transition $2p_{3/2} \rightarrow 5d$)

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 5*d* states and also depends on valence state. But…

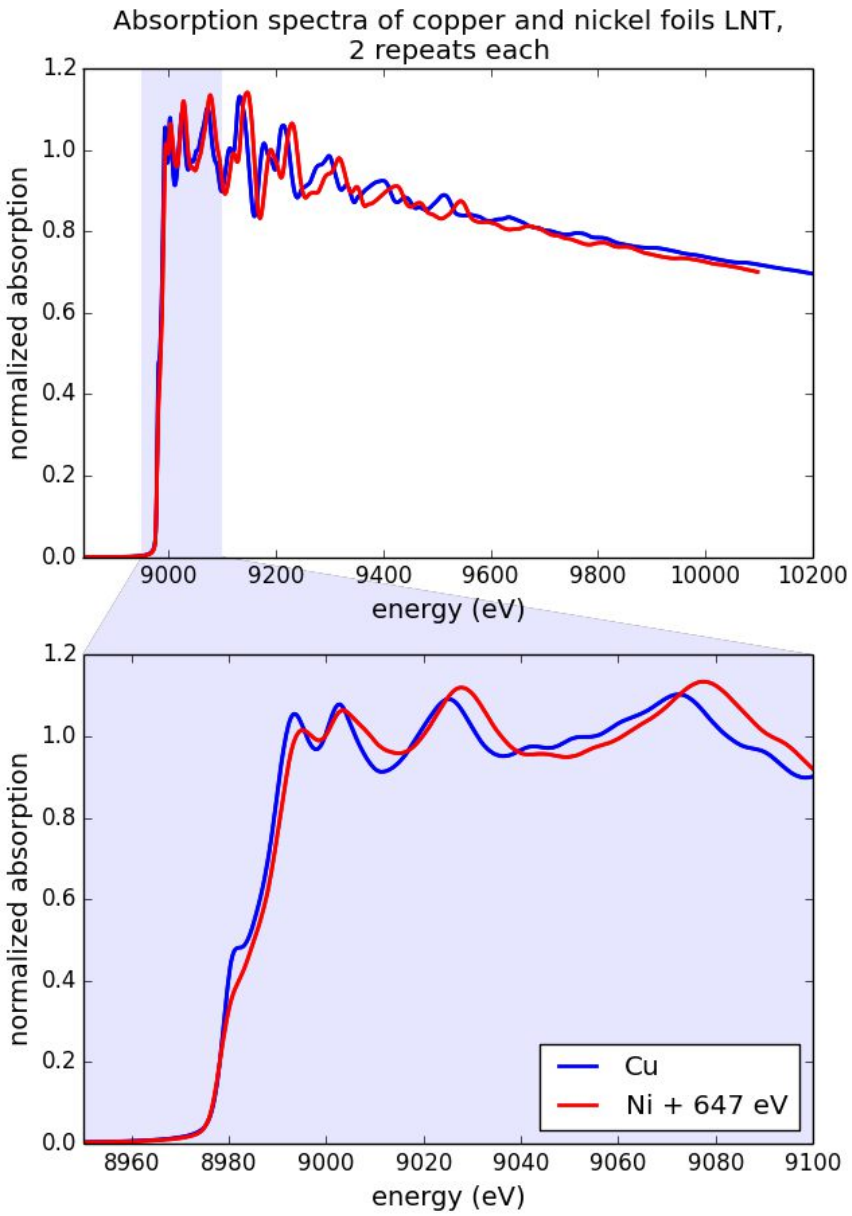
…white line also depends on particle size and morphology:

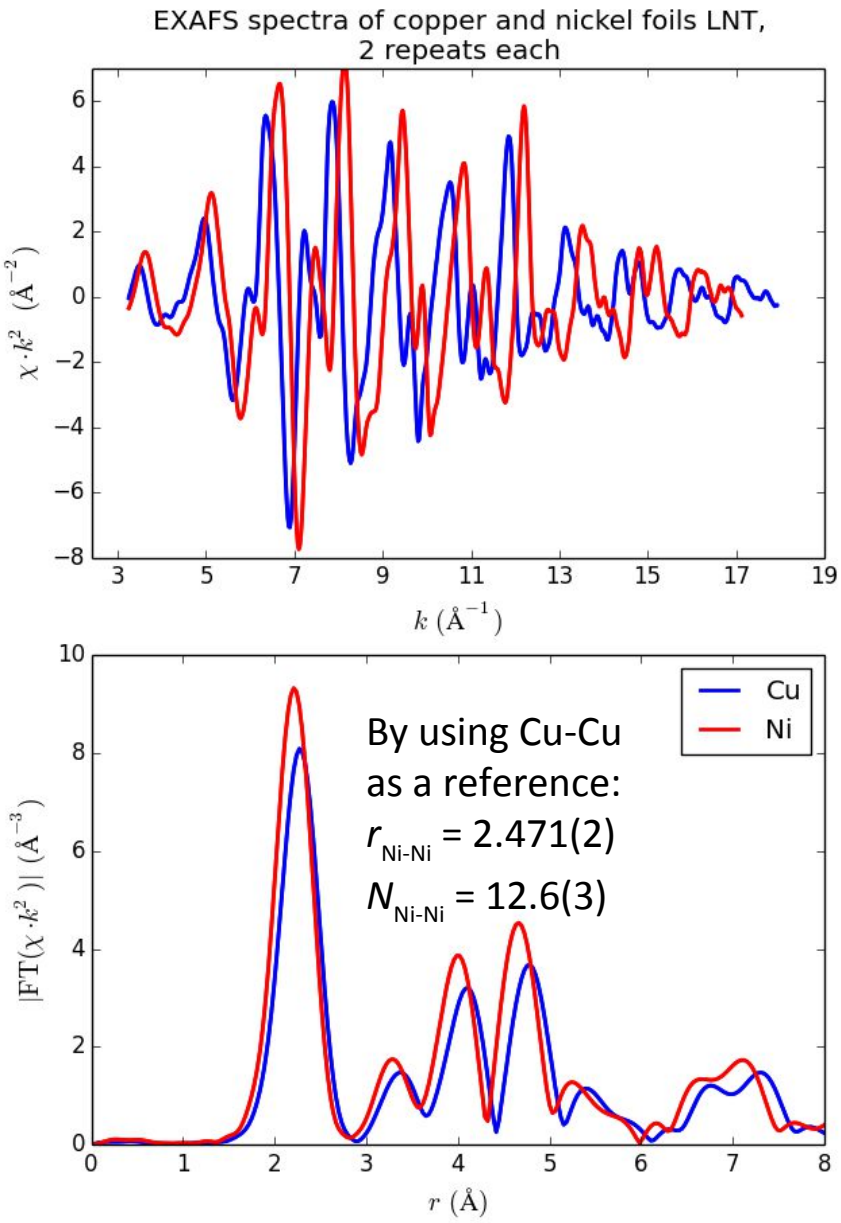


a) Pt_3 triangle (dashes), Pt_4 tetrahedron (solid), Pt_5 triangular bipyramid (dash-dot), and Pt_6 octahedron (dash-dot-dot); (b) Pt_7 and Pt_4 clusters of different shape: planar "honeycomb,(dashes), *D5h* bipyramid (solid) , single-capped octahedron (long dashdot), Pt_4 tetrahedron (dots), and Pt_4 planar rhombus (dash-dot).

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

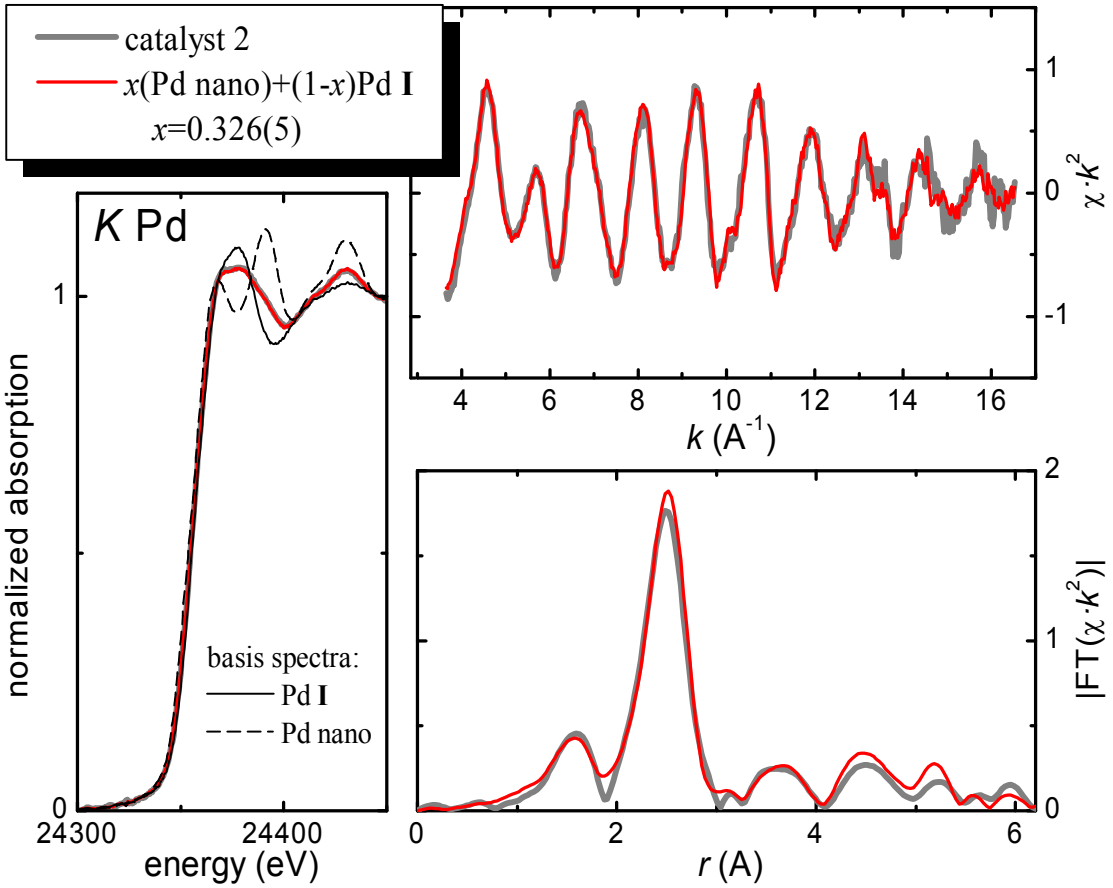
Spectra of similar structures





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