2π Shift and Ligand-Swapping EXAFS Modeling Tricks in Applications to Catalysis and Biology

Alain MICHALOWICZ

Groupe de Physique des Milieux Denses Université Paris XII, Créteil

**With the very efficient collaboration of
Gilberto Vlaic and Emiliano Fonda**

Dipartimento di Scienze Chimiche, Universita` degli Studi di Trieste, and
XAFS group - ELETTRA, Sincrotrone Trieste SCpA

Also with **Frédéric Champloy** and Christoph Kratky (University of Graz, Austria, and Créteil, France)

And very useful discussions with **Dale Sayers, Edward Stern and James Penner-Hahn,** during the IXS S&C meetings.

2π Shift and Ligand-Swapping EXAFS Modeling Tricks in Applications to Catalysis and Biology

The reputation of EXAFS as a quantitative local structural probe is generally well established.
Error bars of ≈ 0.01-0.02 Å for the first absorber-neighbors distance assumed or estimated.

But

Some chemically *strange* unexplained results are still published, even recently.

- Very long metal-oxygen bond in metallic clusters in interaction with oxide surfaces.
-Very long metal-nitrogen bonds in metallo-enzymes.

The 2π Shift Trick in Applications to Catalysis

The facts :

Since 1988, several publications* in the frame of Catalysis works claim the existence of a very long M-O distance corresponding to the metallic cluster interaction with the oxide surface of the support.

R ≥ 2.50 Å instead of R ≤ 2.20 Å

* Martens et. al. 1988, Vaarkamp et. al. 1993, Miller et. al., 1993, Traiantafillou & Gates 1994, Purnel et. al. 1994, Kawi et. al. 1994, Koenigsberger & Vaarkamp 1995, Munoz-Paez & Koenigsberger 1995, Zhao &Gates 1996

The 2π Shift Trick in Applications to Catalysis

Since it was the subject of controversial discussions between EXAFS specialists and chemists, it is important to understand if this long M-O distance is real or due to an artefact in the EXAFS data analysis.

In the later case, is EXAFS definitely wrong, or is the artefact easy to understand and overcome ?

The 2π Shift Trick in Applications to Catalysis

When a long M-O distance was found, the corresponding Eo shift (when published) was systematically very important :
≤ -20 eV

In some cases the two distances (and Eo) were found in the same spectrum

R ≤ 2.20 Å, ΔEo ≥ 0.0eV
R ≥ 2.50Å, ΔEo ≤ -20eV

The 2π Shift Trick in Applications to Catalysis

FEFF Simulation of a theoretical RhO$_x$ model compound with
2 O at R = 2.20 Å Eo = 0 eV
6 Rh at R = 2.70 Å Eo = 0 eV
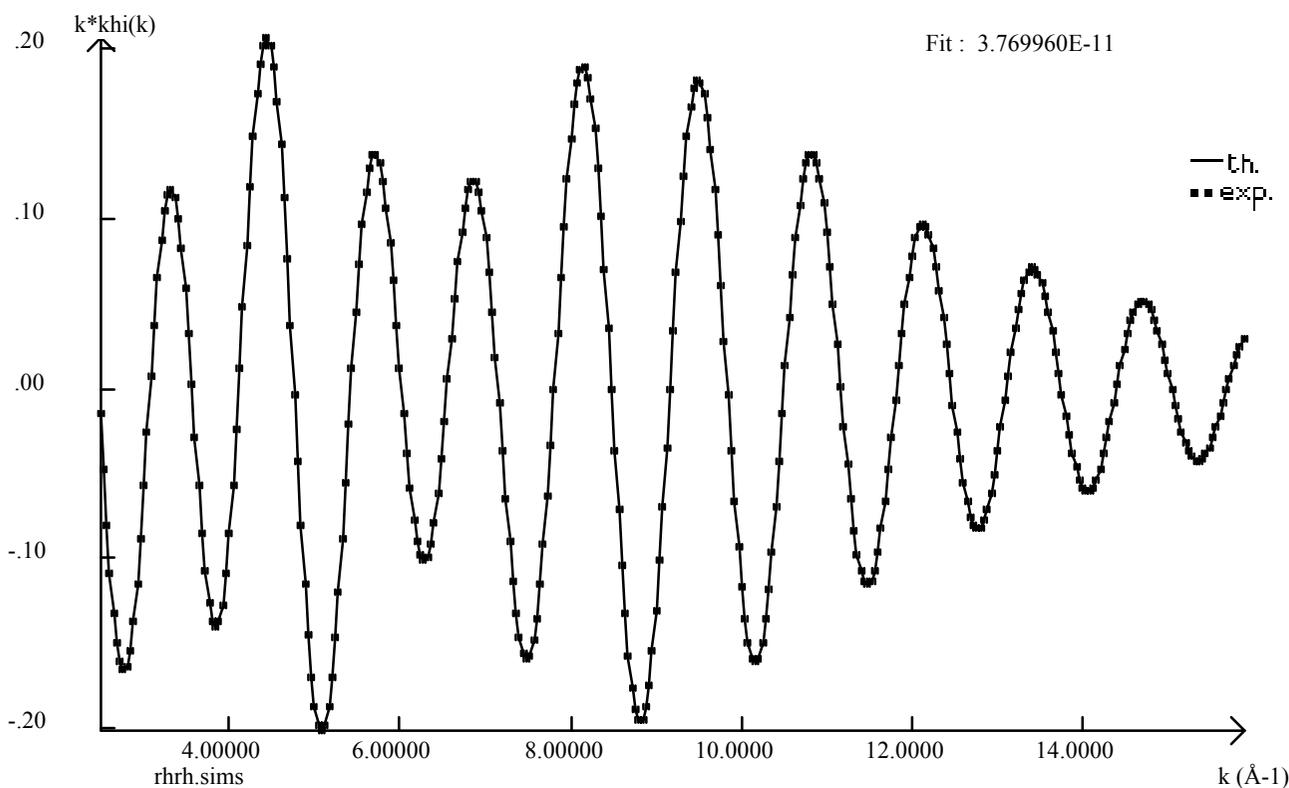
The 2π Shift Trick in Applications to Catalysis

Fit of the same FEFF Simulation with

3.5 O at R = 2.52 Å Eo = -23 eV
6 Rh at R = 2.70 Å Eo = 0 eV
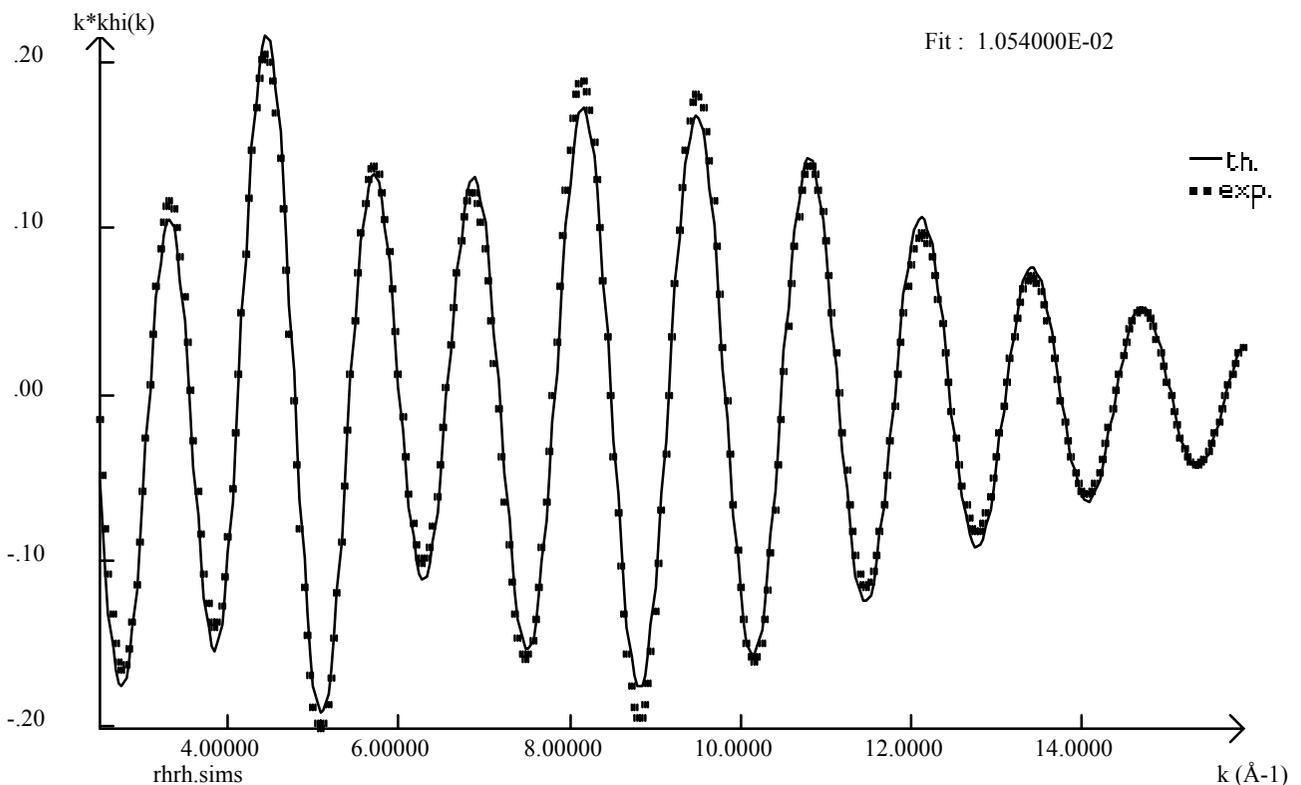
The 2π Shift Trick in Applications to Catalysis

Surface plot of $\Delta\chi^2(R, \Delta Eo)$
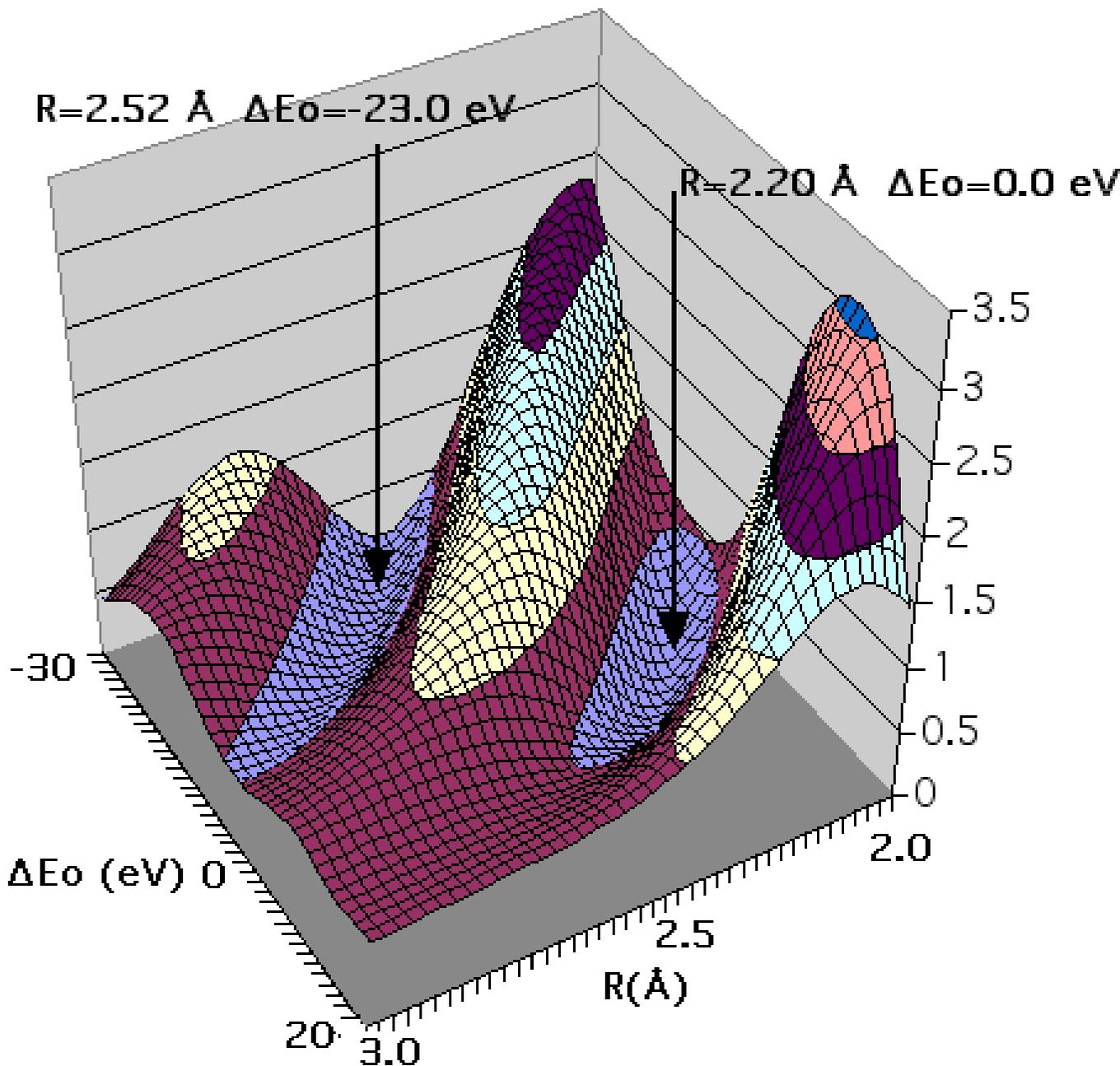
Two solutions

The 2π Shift Trick in Applications to Catalysis
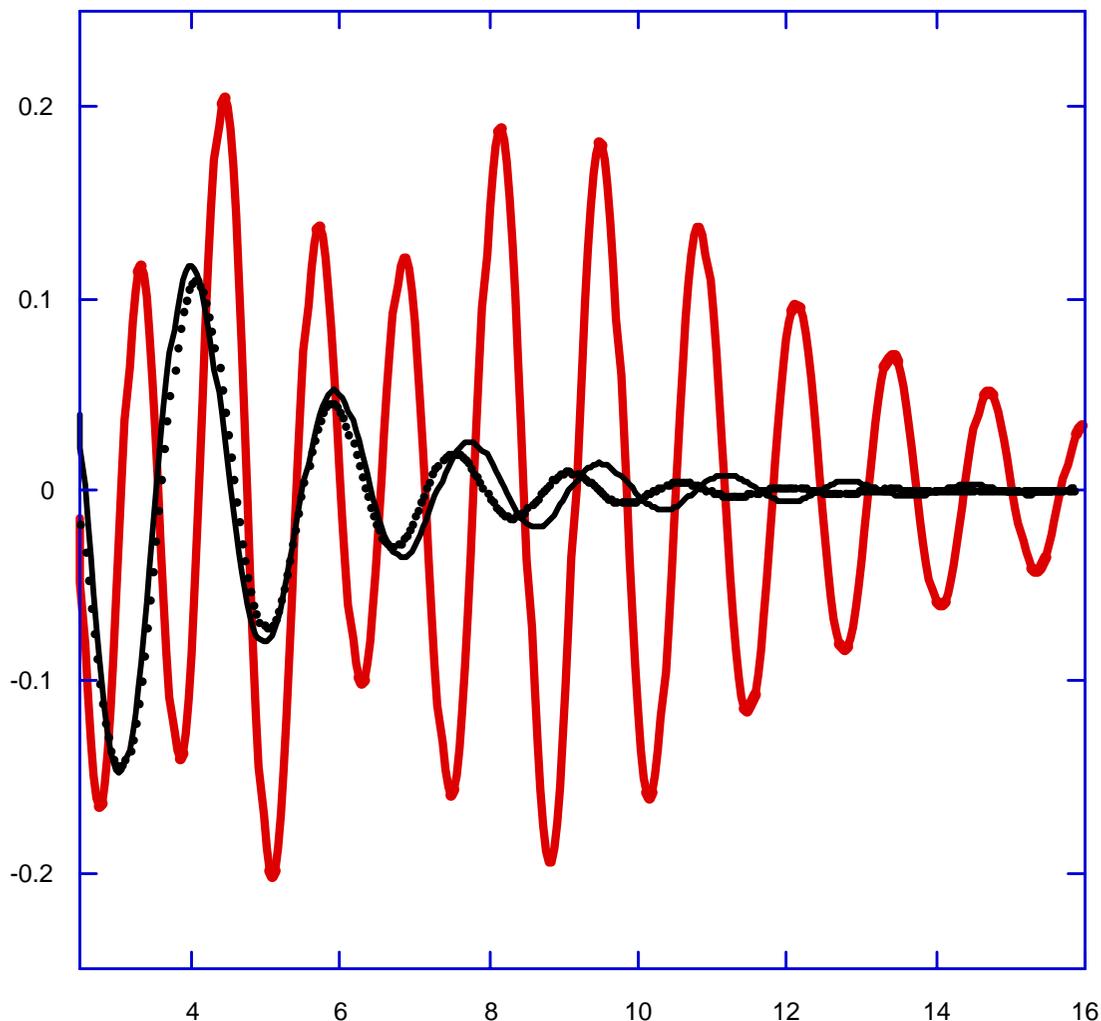
R = 2.20 Å, $\triangle Eo$ = 0.0eV
R' = 2.53Å, $\triangle E'o \leq$ -23eV
phase diference 2k'R' - 2kR $\approx 2\pi$
For k = 2.5 -> 8 Å^{-1}

2π Shift Trick

The 2π Shift Trick in Applications to Catalysis

Same result for a real experimental case
RhCl$_3$/MgO reduced sample
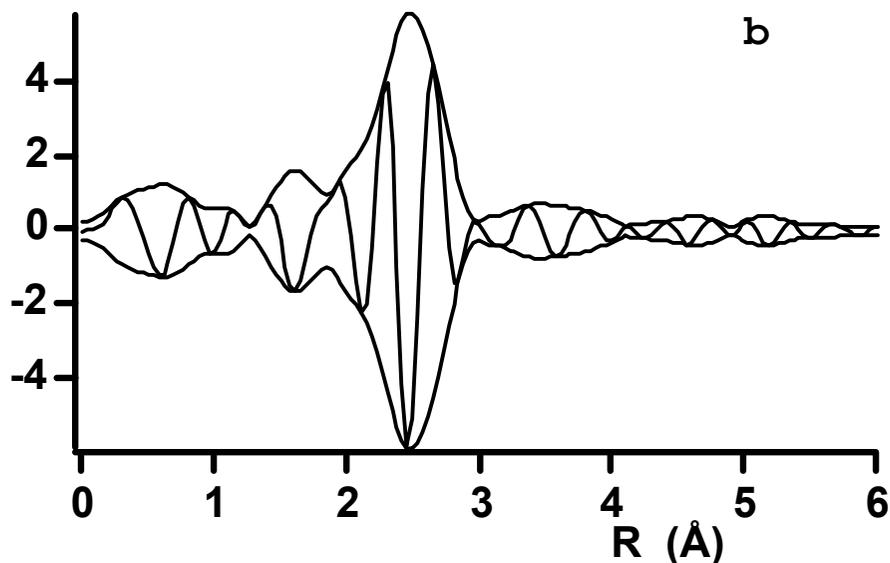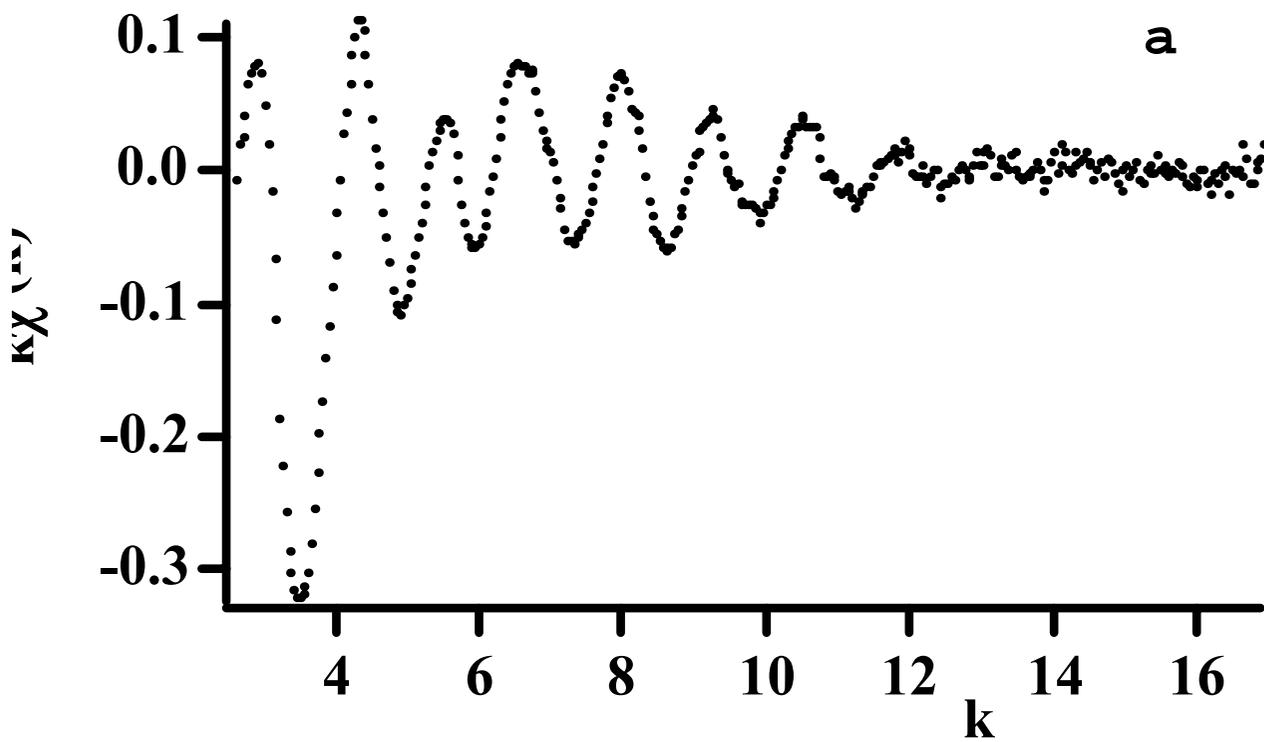
The 2π Shift Trick
A real experimental case

Fit with a short Rh-O distance
R_s = 2.07 Å ΔE_{os} = 3.7 eV
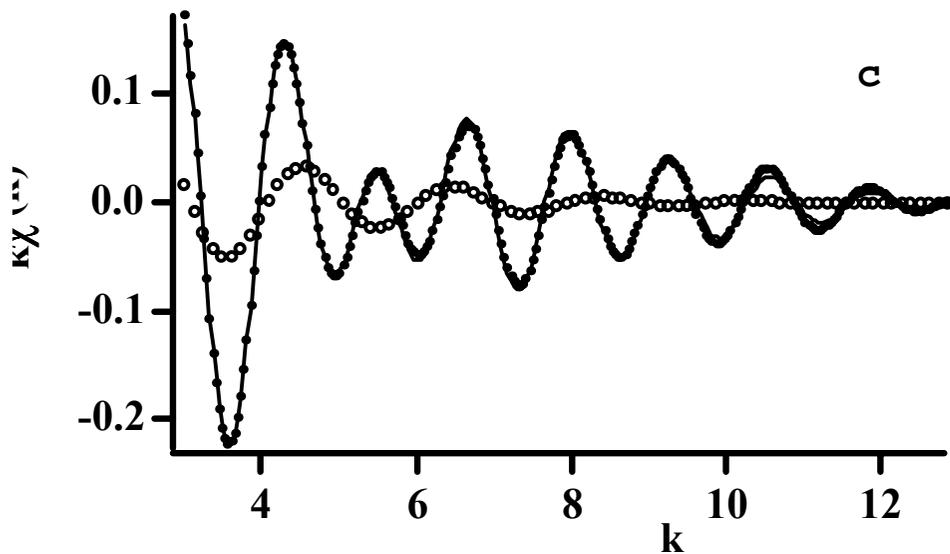
Fit with a long Rh-O distance
R_l = 2.44 Å ΔE_{ol} = -18.3 eV
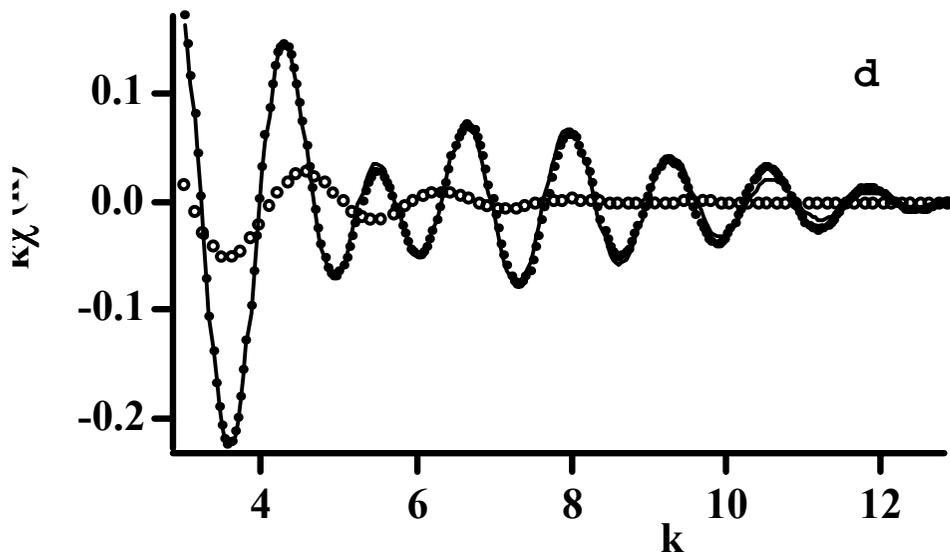
$$\Delta E_{os} - \Delta E_{ol} = 22 \text{ eV}$$

Some ideas to avoid the 2π shift trick

Alain MICHALOWICZ, Gilberto VLAIC

Is $\Delta Eo < -20$ eV (with Eo = inflexion point) physically reasonable ?
Is there any known model compound with such a ΔEo ?

If a chemically « special » long distances with very big negative ΔEo if found, look for other solutions.

EXAFS results, and especially strange ones, should be reproduced on experimental model compounds for validation.

The ligand-swapping trick

Example : B_{12} enzymes

- B_{12}-based enzymes are the only ones known cofactors containing a metal carbon-bond.
- Known B_{12} cofactors are alkyl-cobalamins (RCbl) consisting of a cobalt corrinoid with a pendant nucleotide coordinated to Co. The sixth ligand is CN (vitamin B_{12} itself) or a R group.

Vitmaine B12 = Cobalamine

adoCbl, R = 5'-deoxy-5'-adenosyl
MeCbl, R = Me
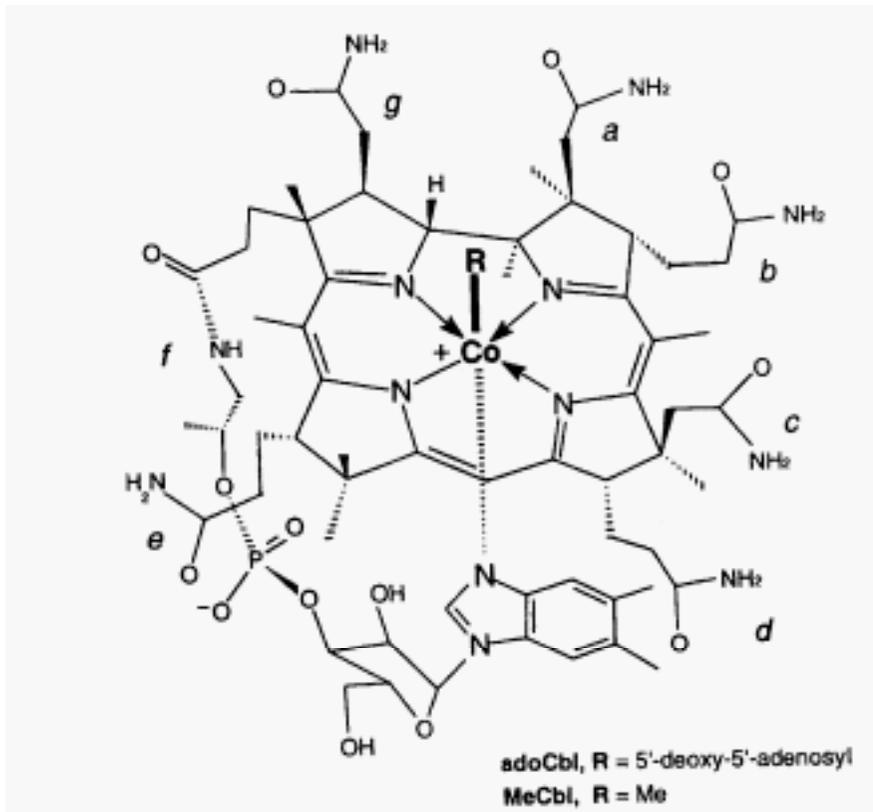
The ligand-swapping trick

Example of Model compounds : pyridine based cobaloximes

- Most important structural parameters are Co-N(base) and Co-L(axial) distances
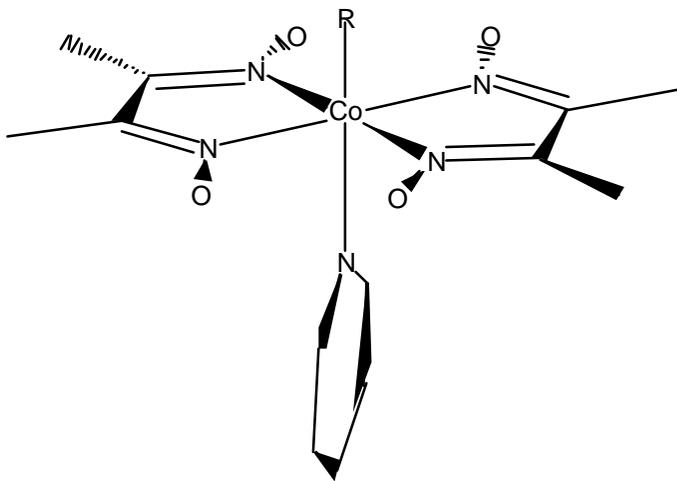
• A series of EXAFS studies on cobalamins and model compounds have been published in the last ten years.

• It has been found that many of the results were erroneous. I.e. Co-R or Co-L distances differed for more than 0.15Å from known crystal structure values.

The ligand-swapping trick

I. Sagi and M. R. Chance (1992) *J. Am. Chem. Soc.*, **114**, 8061-8066

Co-N in 5,6-DMB nonalkyl cobalamines

✶   correct (R=Methyl , R=adenosyl);

✶   erroneous (R=CN,H_2O);

In R=CN R=H_2O, the Co-N(DMB) EXAFS distance is respectively 0.15Å and 0.22Å longer than XRD values

C. Kratky et al. (1995) *J. Am Chem. Soc.,* **117**, 4654-46670

F. Champloy et al. (1999) *J. Am. Chem. Soc.*, **121**, 11780-11789

+ W. Meyer-Krautke, EMBL Outstation, Hamburg, Germany

The ligand-swapping trick
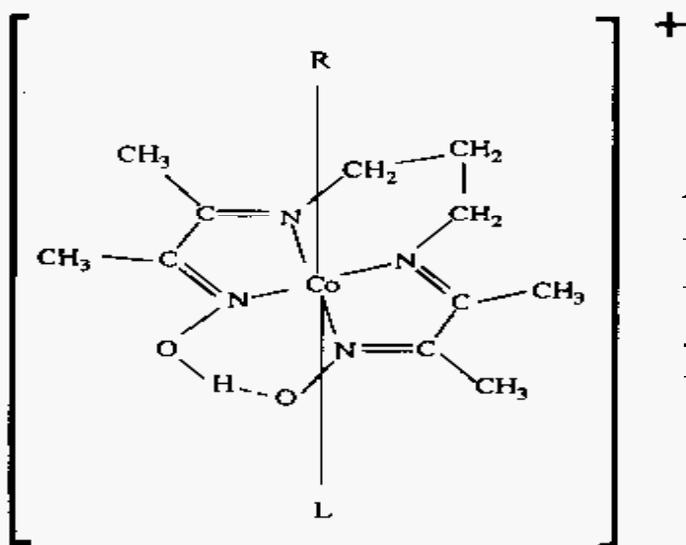
A semi-constrained EXAFS (GNXAS) fit

$[LCo(DO)(DOH)_{pn}R]ClO_4$ where L=H_2O

R = isopropyl, isobutyl, benzyl, methyl

Co-L distance is in perfect agreement with XRD

R= methyl acetate, 2,2,2-tri-fluoro-ethyl

Co-L distance differs more than 0.15Å from the value found in a successive XRD study.

L. Randaccio and S. Geremia (1997) *Organometallics* **16**, 4951

The ligand-swapping trick

A complete work by Emiliano Fonda
Constrained EXAFS (FEFF) fit
with $\Delta\chi^2$ mapping
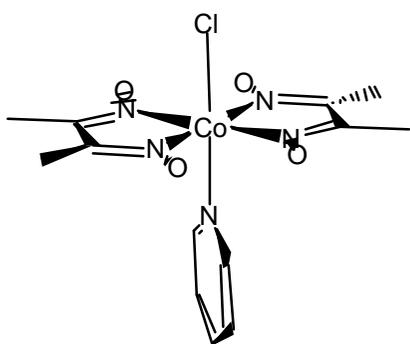
Co(DH)$_2$(Py)Cl
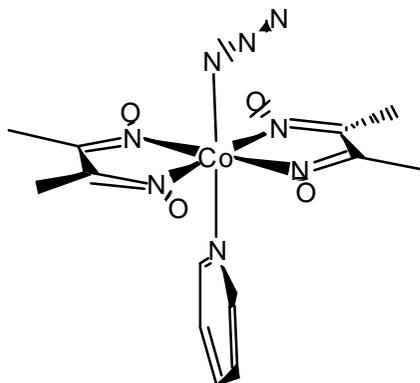
Co(DH)$_2$(Py)N$_3$
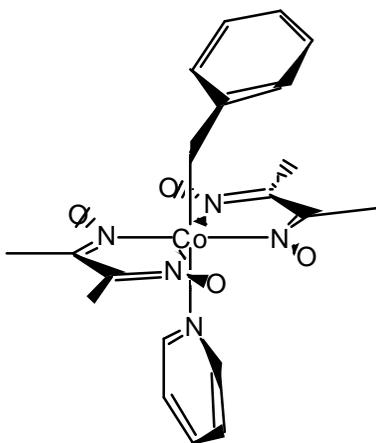
Co(DH)$_2$(Py)(CH$_2$Ph)
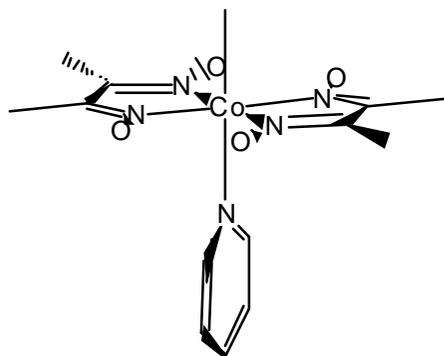
Co(DH)$_2$(Py)Me
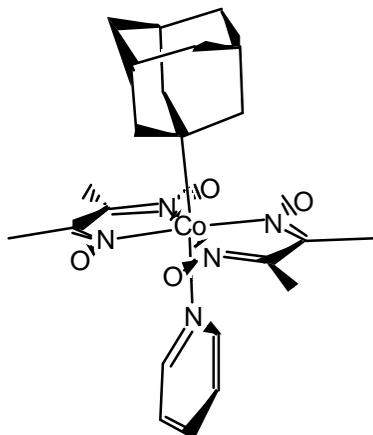
Co(DH)$_2$(Py)(adamantyl)

The ligand-swapping trick

R=Cl

R=N$_3$

R=CH$_2$Ph

R=Me

R=adam

χ k^2 (k)

k(Å^{-1})
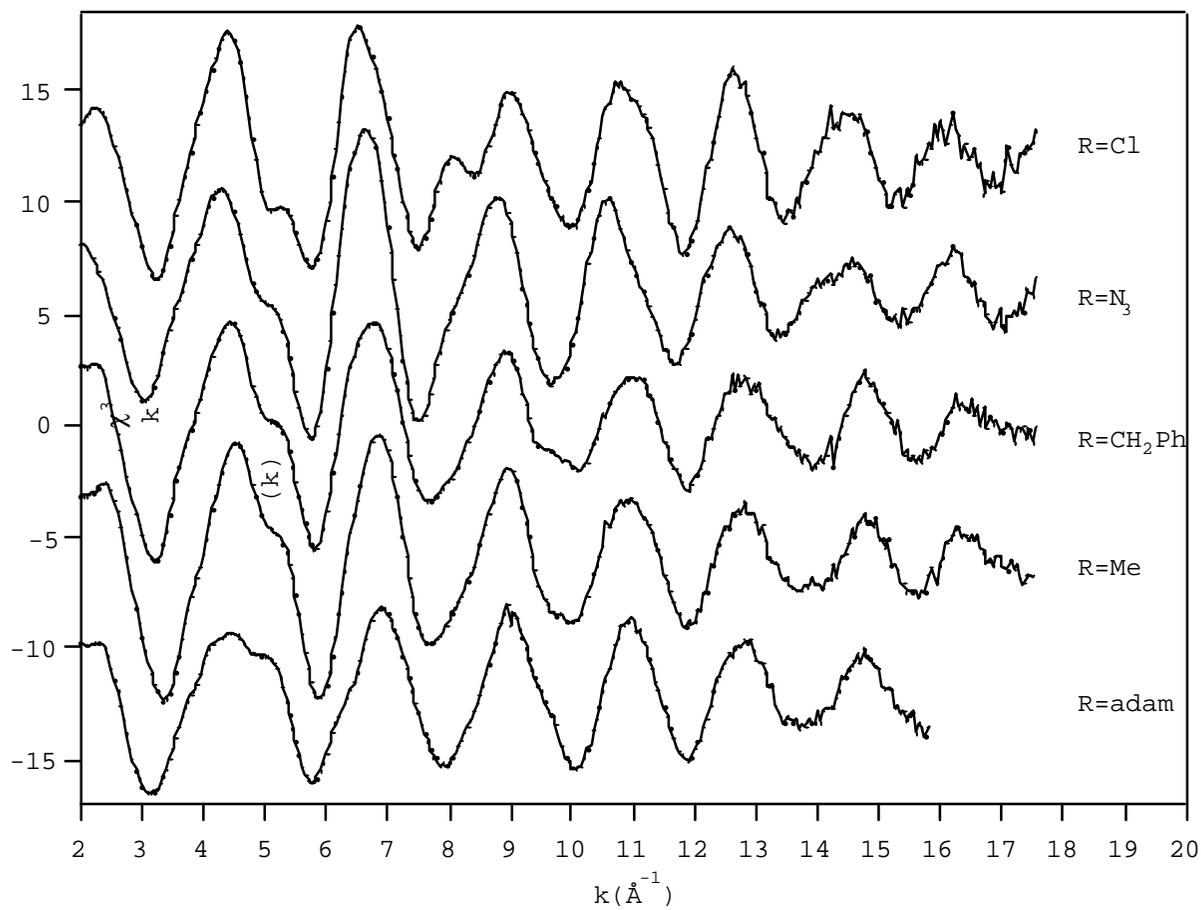
The ligand-swapping trick
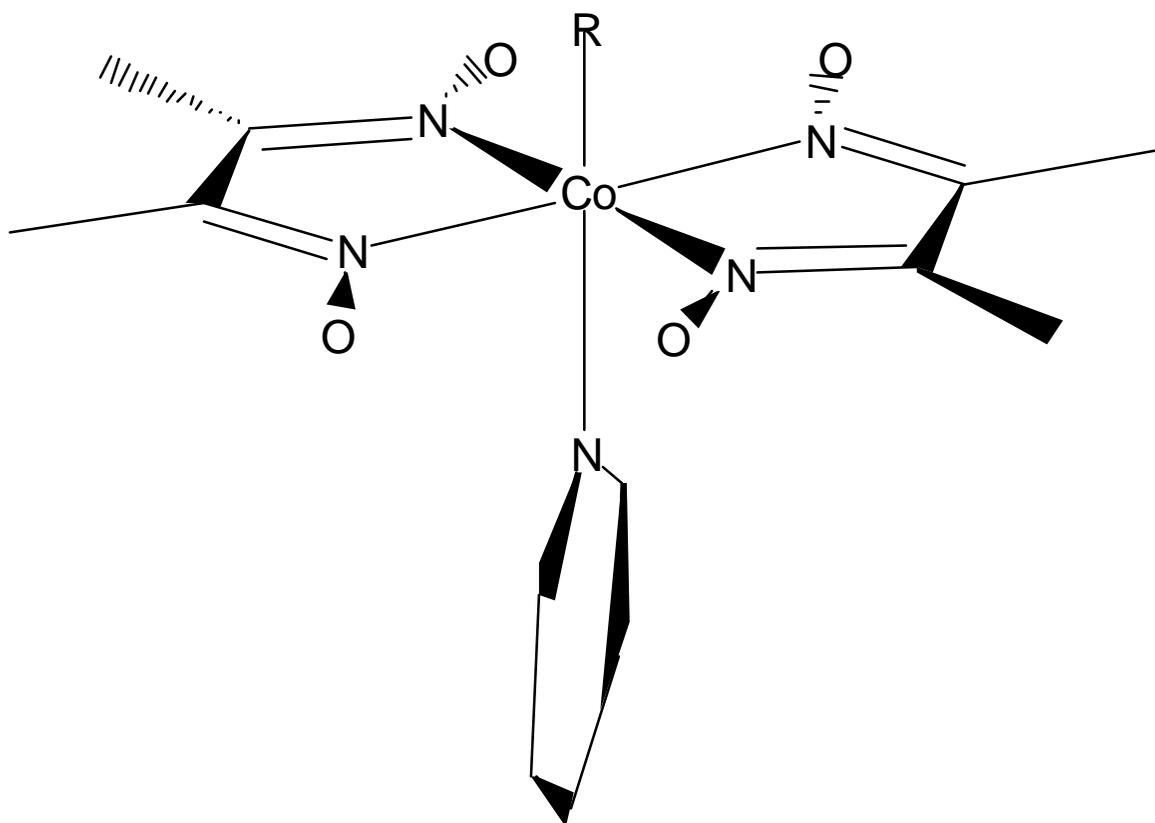
R-pyridine-cobaloximes.

The ligand-swapping trick

single and multiple scattering in the equatorial and the axial ligands

Second (Co-C) distance

First (Co-N) distance)

$R=N_3$

Experiment
Theory

Co-N (DH)$_2$

Co-N (Py)

Co-N (N$_3$)

Co-C (DH)$_2$

Co-N (N$_3$)

Co-O (DH)$_2$

Co-C (Py)

Total MS signal of Co(DH)$_2$

Total MS signal of Co(Py)

Total MS signal of Co(N$_3$)

R(Å)
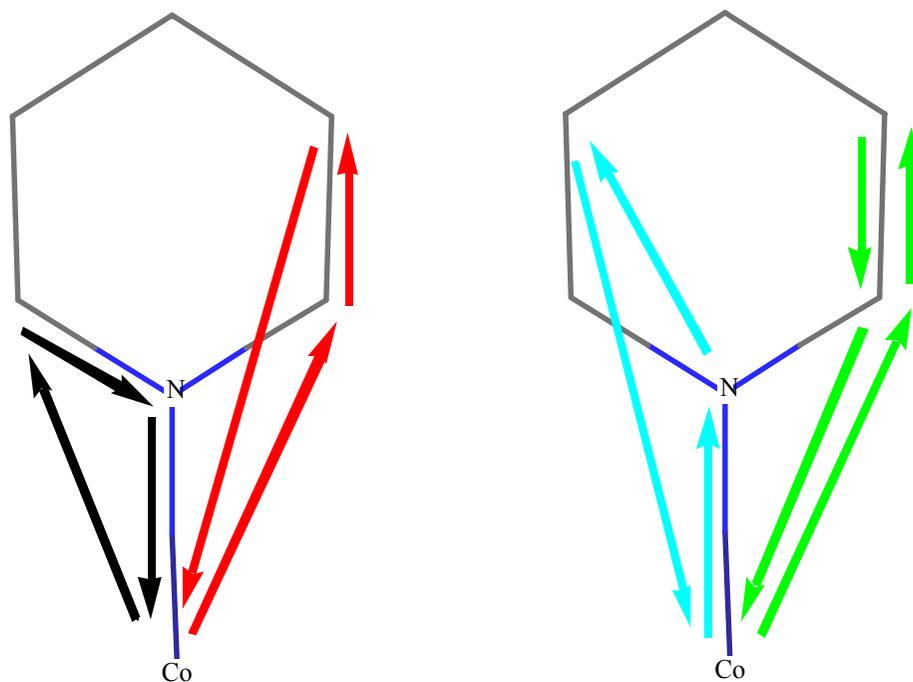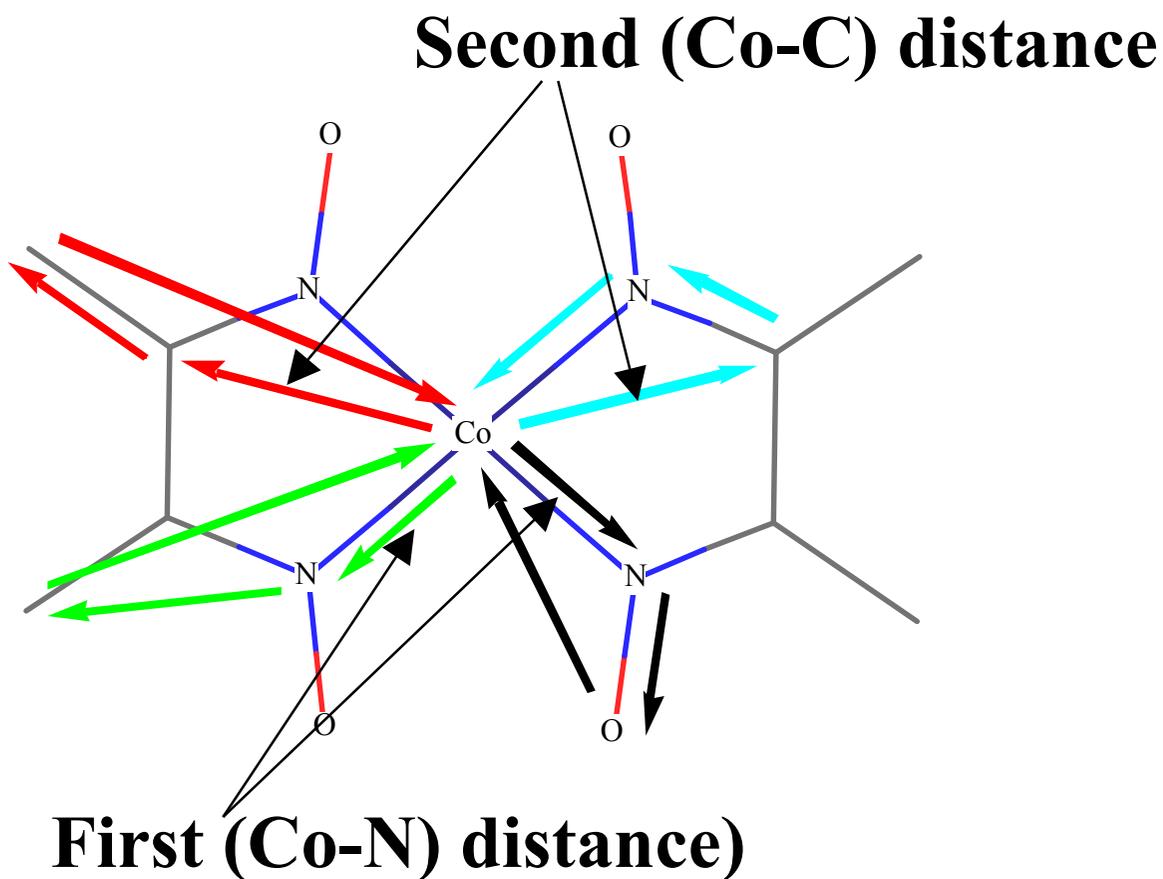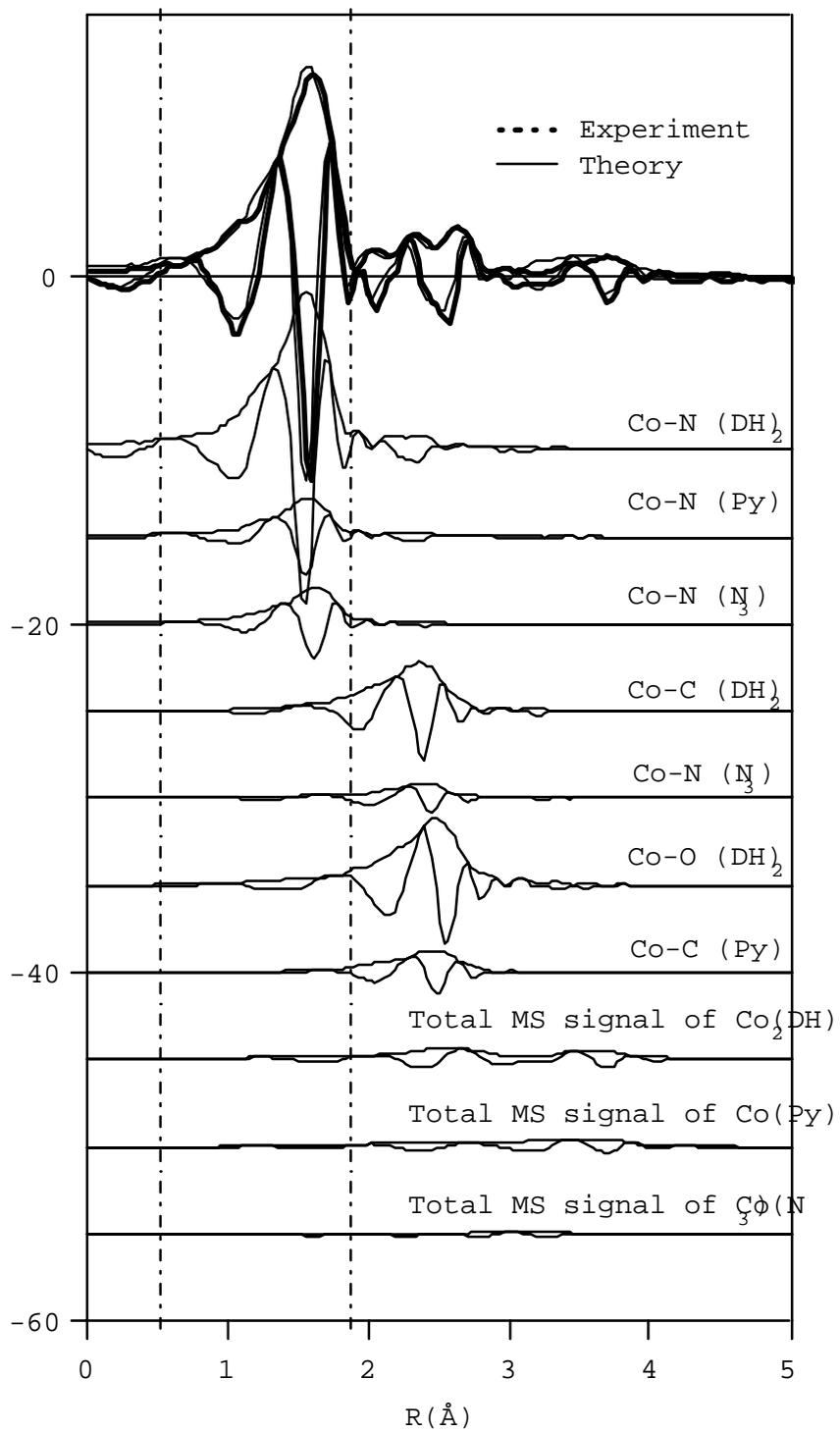
R=adam
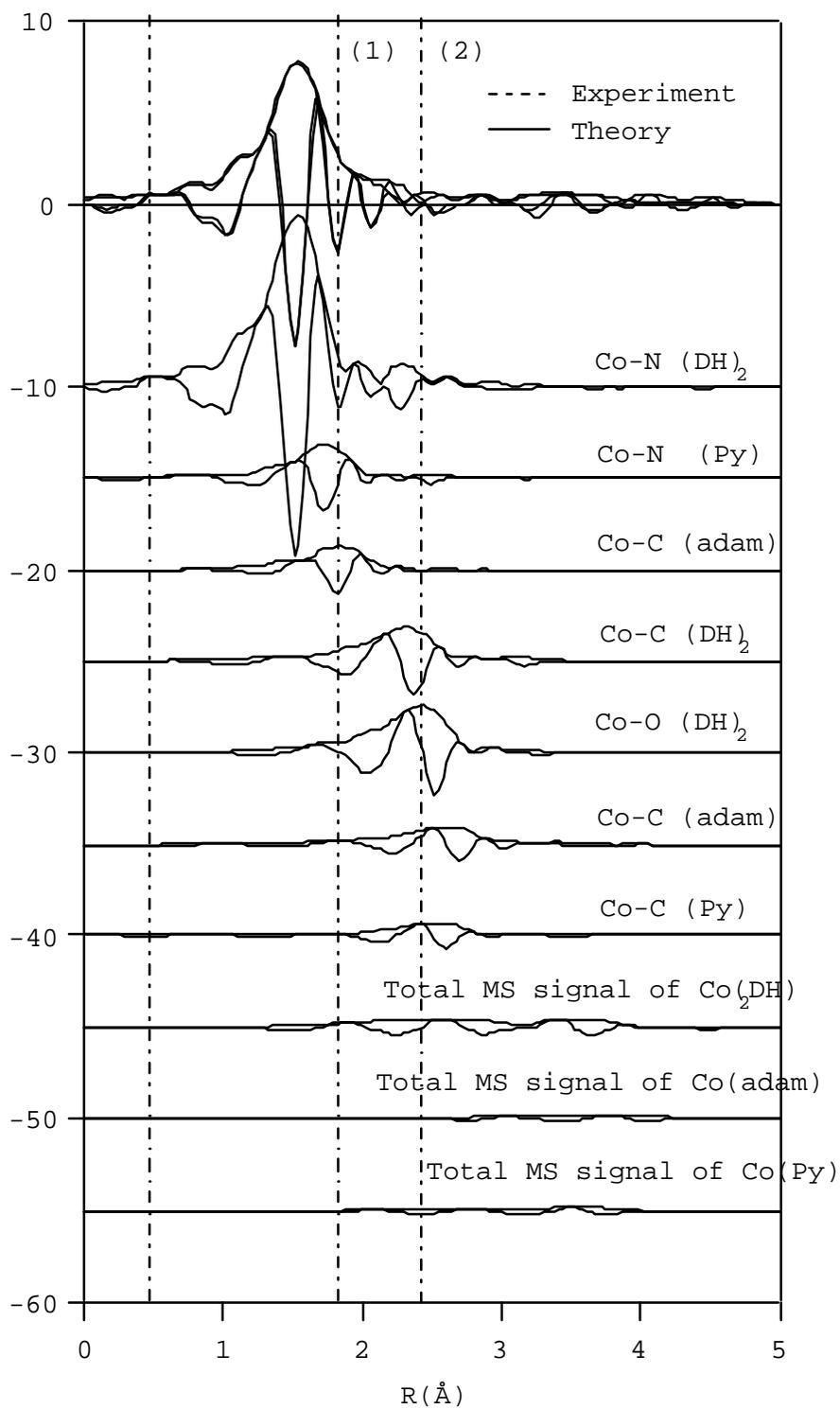
$\Delta\chi^2$ Mapping

$$\Delta\chi^2 = \sum_i \frac{[f_{i(th)} - f_{i(exp)}]^2}{\sigma_i^2}$$

• $\Delta\chi^2$ is calculated with FEFF, for each geometry.

• We map $\Delta\chi^2$ as a function of Co-N and Co-R distances

• Constrained mapping : axial and equatorial ligands geometries are fixed. The only changes are the Co-N and Co-R distances.

• Free refinement : Other parameters (distances, DW,…) are optimized for each (Co-N, Co-R) point with FEFFIT in a given range in R space.

a)
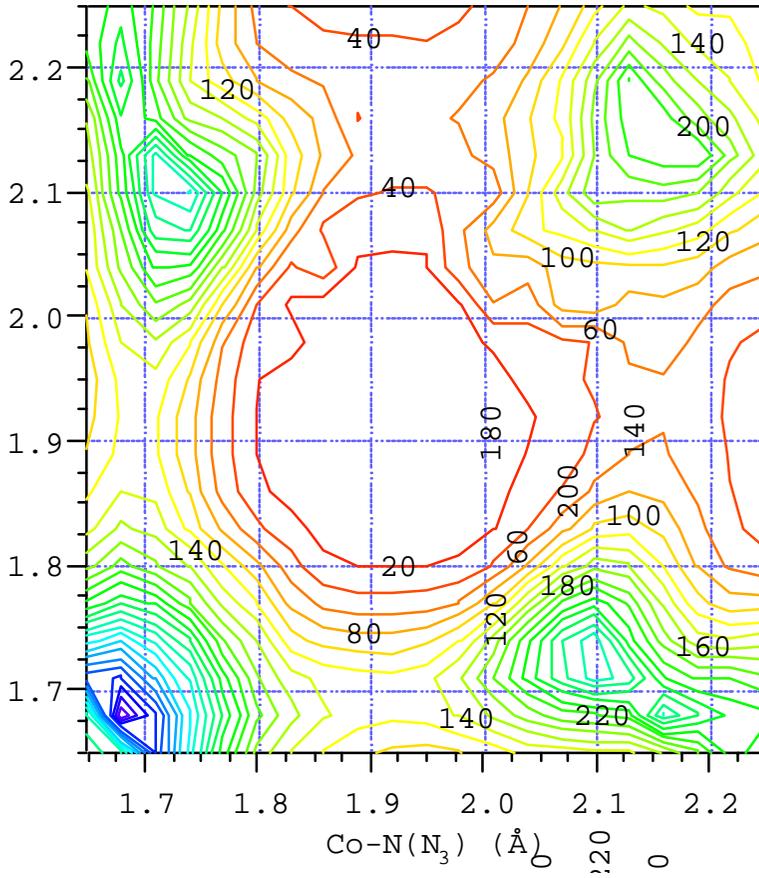
Free parameters Fit

b)

Constrained fit

a) **Free parameters For the whole Structure Swapping of the two axial ligands**

b) **Constrained map, but only in the range 0-3 Å**

c) **Constrained map with multiple Scattering, up to 4 Å**

a)
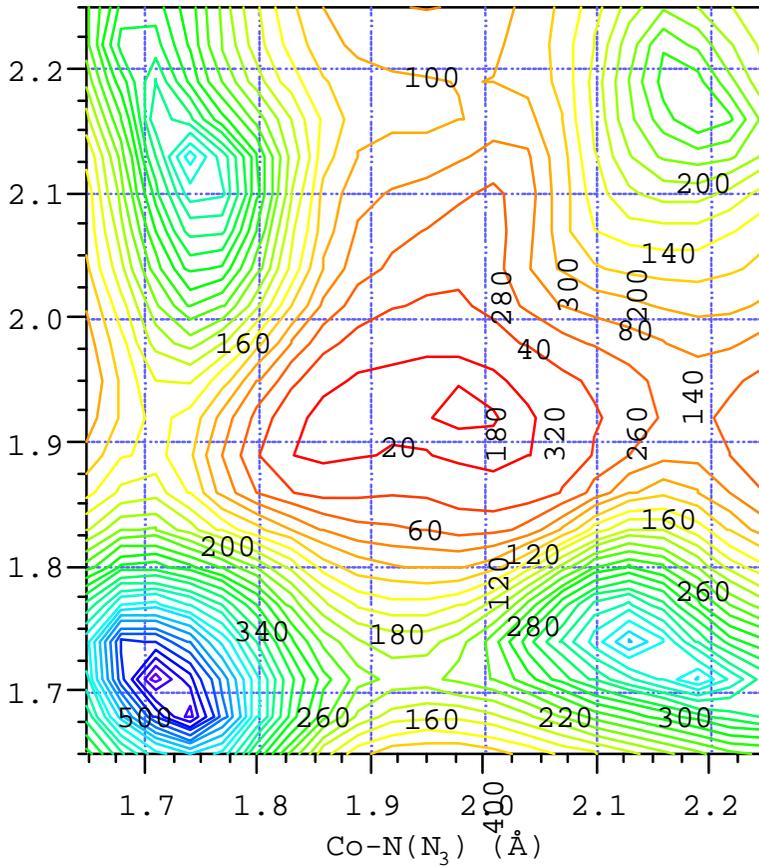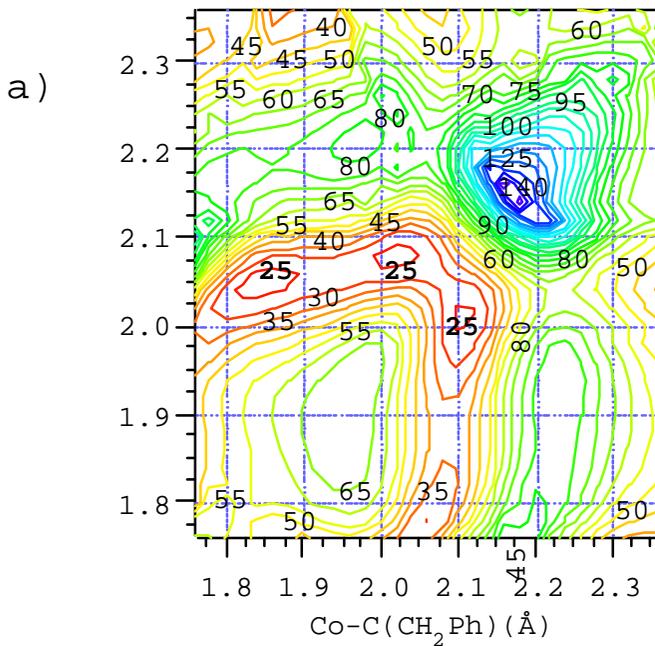
A very short
Co-N axial
distance
Appears :

Swapping with the
Equatorial
Co-N distance

b)
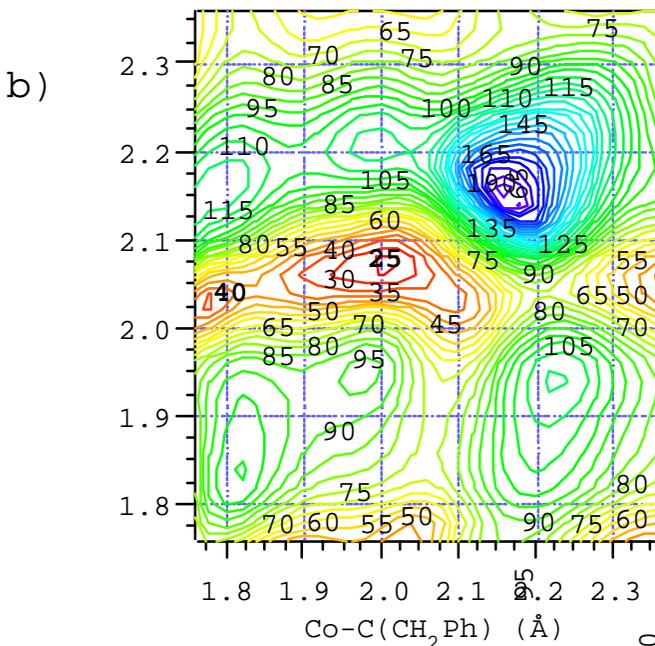
There is also
a very long Co-N
Distance solution :
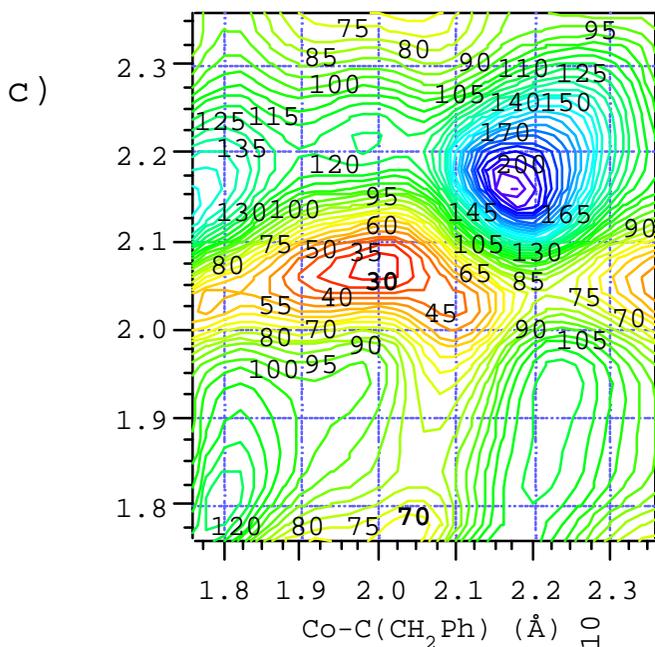
Swapping with the
Equatorial
second neighbors
Co-C

c)

An example of ligand swapping trick in biological samples
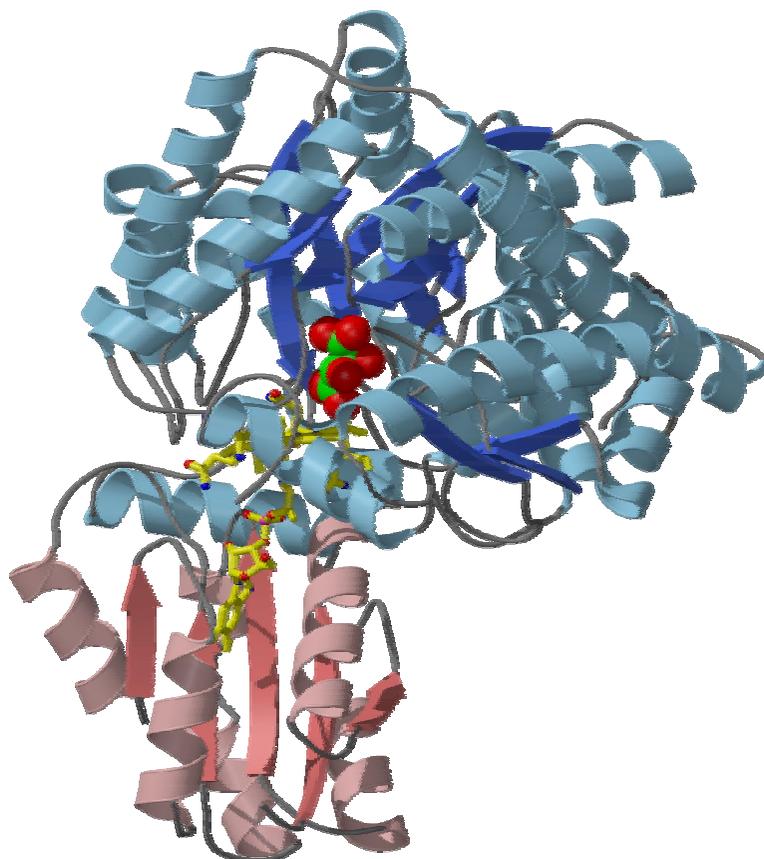
Co-N(DMB) $= 2.18$ Å (free MetCbl)

≥ 2.55 Å for H_2OCbl

Complexed with several enzymes

Crystallography and EXAFS (Chance)

Methyl Cobalamine complex with Glutamate mutase
F. Champloy, C. Kratky
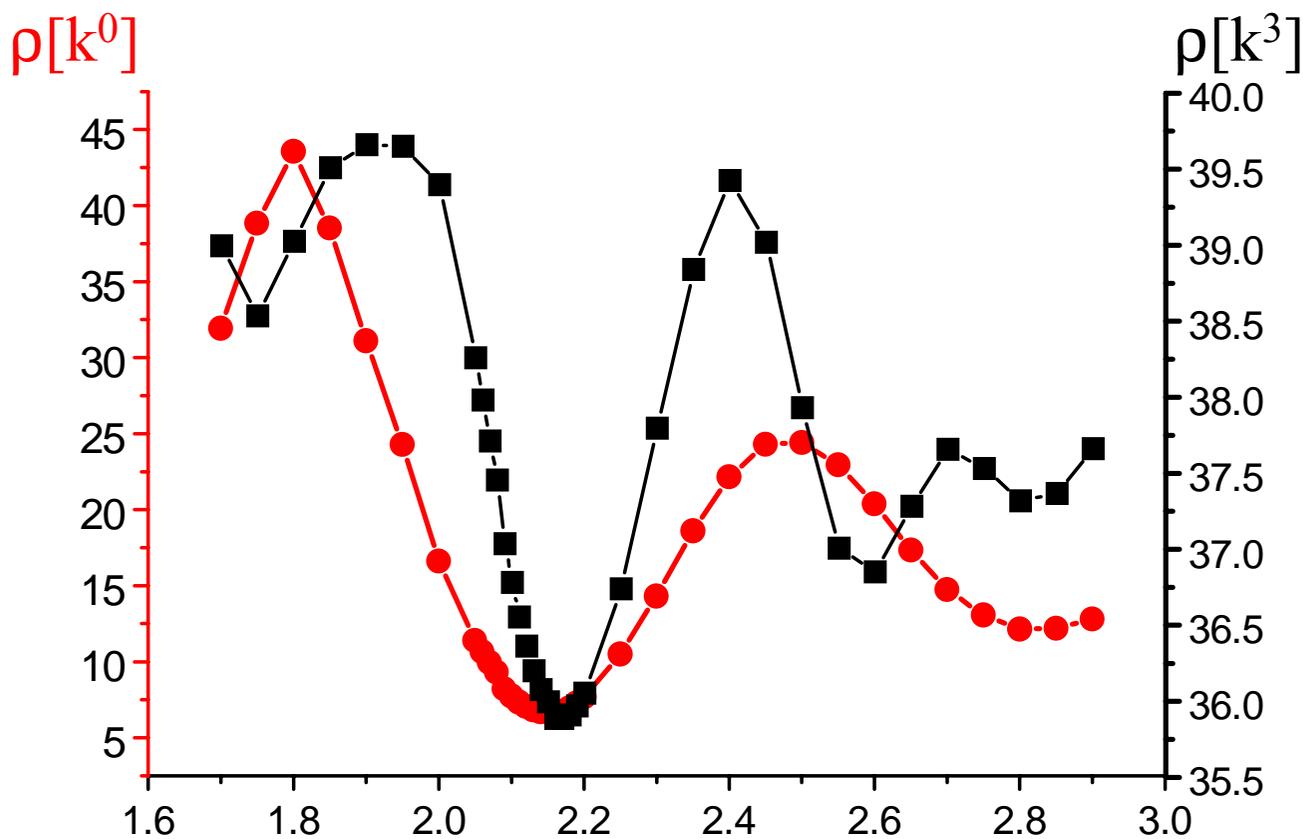
The residual is calculated for the whole structure, up to 4 Å, including the multiple scattering

Free Methyl cobalamine
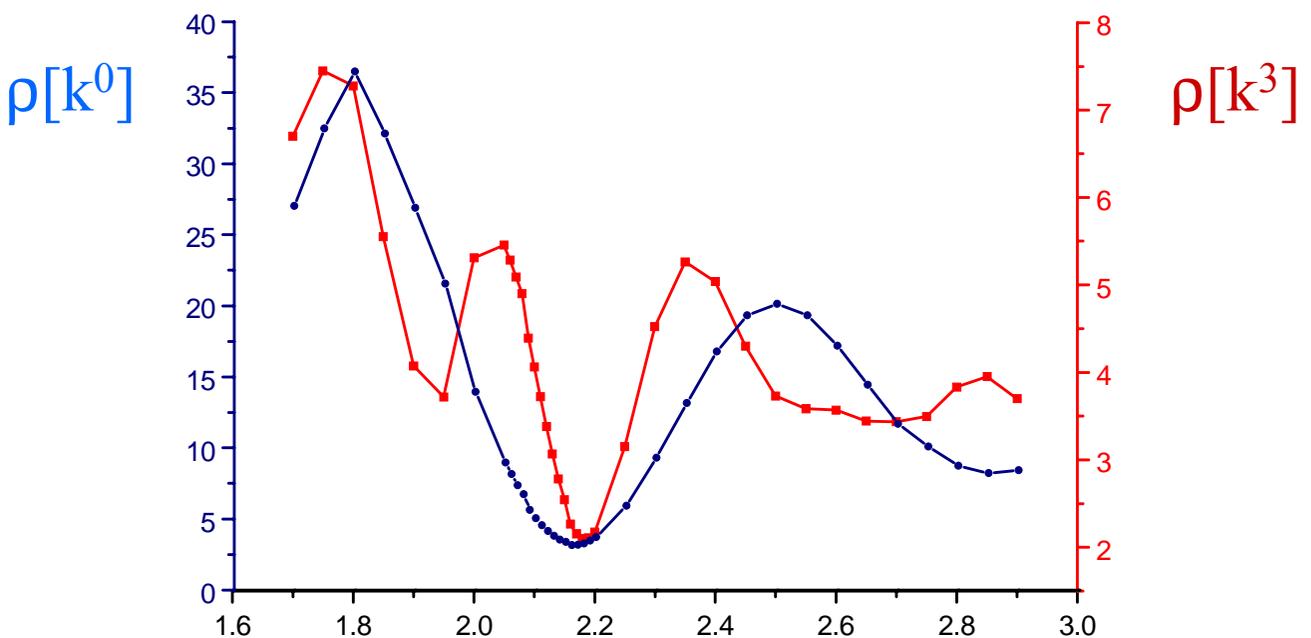
The secondary long distance minimum occurs even for the free model compound, in the solid state, where the accual distance (2.18 Å) is undoubltly known. The true minimum do not vary with the fitting weight.

The long distance minimum is unstable, sensitive to the fitting weight k^n, and close to the Co-C (2nd neighbors) distance (2.95 Å)

Fitting the amplitude parameters (Debye-Wallers, N) can lead to a dangerous minimization of the FALSE solution.

Free and enzymz-bound B12 have the same EXAFS spectrum (except the noise) : assuming different structures is UNJUSTIFIED

Conclusions

We have identified two specific EXAFS data modeling tricks :
a) « 2π shift » of the theoretical curve
b) « ligand swapping »

These two tricks are certainly more dangerous with poor resolution and poor signal/noise spectra, but their nature is resolution & noise -independant : they can occur even for a theoretical simulation or a good experimental spectrum.

Other tricks are also discussed during this workshop

Chance 's group was unlucky :
The cobalamine-enzyme
complex crystal structure they
used as reference
(aquocobalamine) was false.
Why ???

Radiation dammage
sensitivity to   **UV-Vis**   **X-rays**
Methyl-cobalamine   **yes**   **no**
Aquo-cobalamine   **no**   **yes**

X-Ray dammage : photoreduction
The crystal was a Co(III)-Co(II) mixture)

Champloy et. al., JSR, 2001

Conclusions

2π shift and ligand swapping tricks
Common features :

1) Both are not directly due to the data quality. They can occur even for a perfect noisde-free spectrum

2) Both lead to multiple fitting solutions. Nead to explore the $\Delta\chi^2$ vs fitting parameters map. The first solution you fond is not necessary the good (or the bad) one !

3) Both tricks are not due to buggy programs : FEFF(FIT), GNXAS, EXCURVE, even my own program…, All ,can lead to these traps.

Conclusions

2π shift and ligand swapping traps :
Differences.

1) 2π shift should be obvious to avoid.
Long M-L distances associated with
large negative ΔE_0 should be suspect
Try another solution and restrain the fit
to « reasonable » $\Delta \varepsilon_0$
In case of doubt, use model compounds

2) Ligand swapping is less obvious
Long M-L distances can be due to the
2nd M-C distance => chemically
irrelevant

Conclusions

2π shift and ligand swapping traps :
Differences.

Swapping between axial ligands can
lead to false but acceptable distances
$\Delta\chi^2$ constrained mapping can help. Fit in
R space is preferable.
Look at the 3-4 Å region.