Wavelet Analysis of EXAFS Spectra

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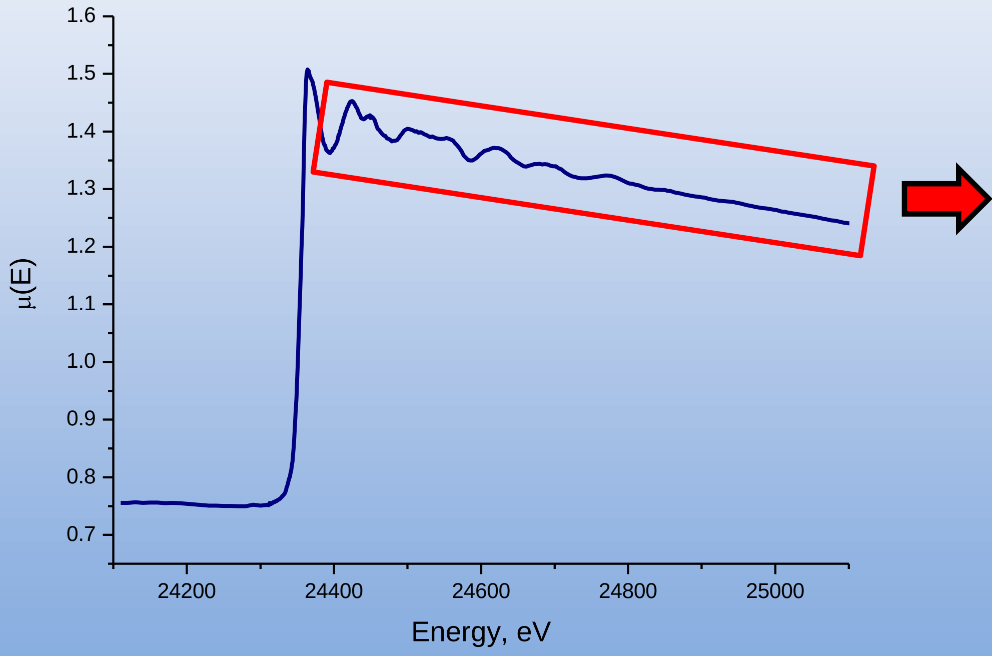
TIPS RAS

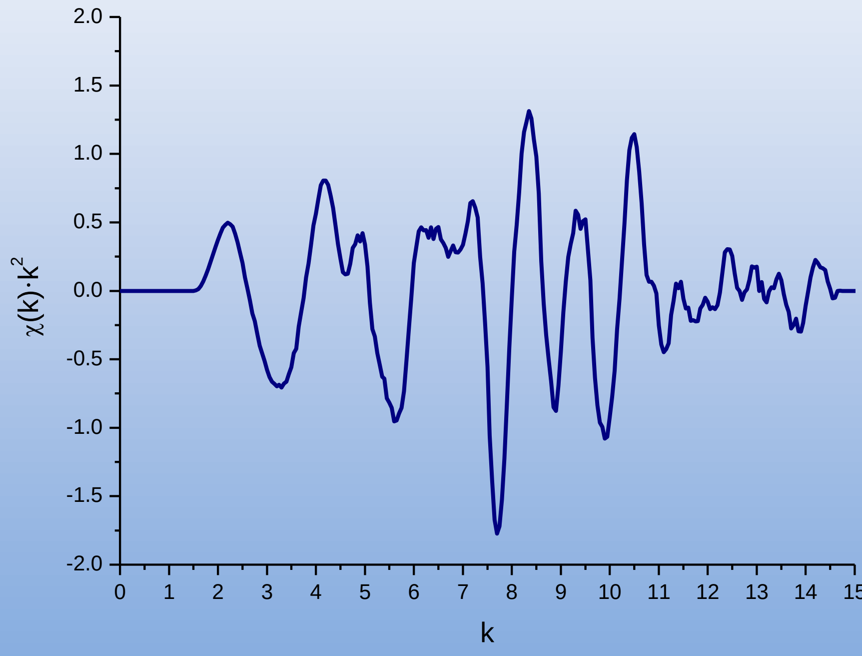
EXAFS

Extended X-ray Absorption Fine Structure

X-ray absorption coefficient

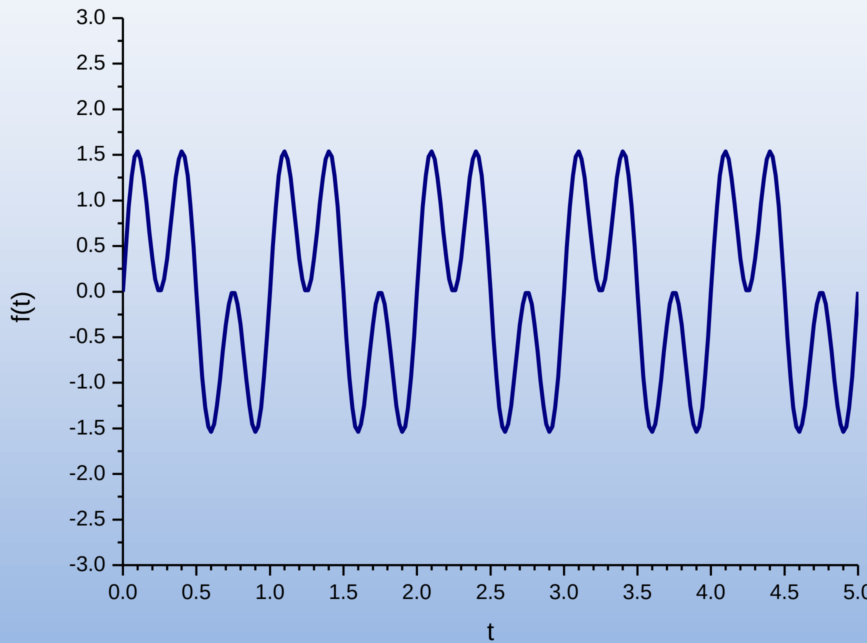


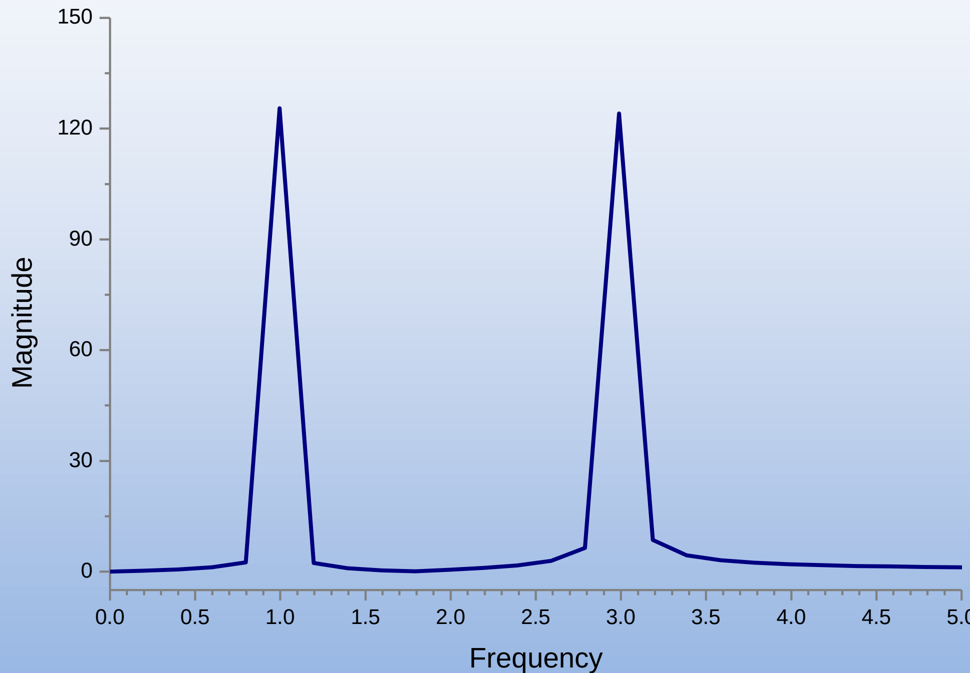
Normalized EXAFS function χ(k)



Fourier Transformation(FT)

Signal f(t) → Frequency FT(ω)

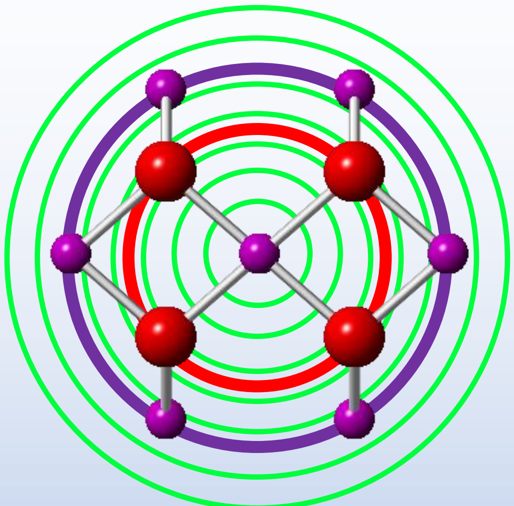


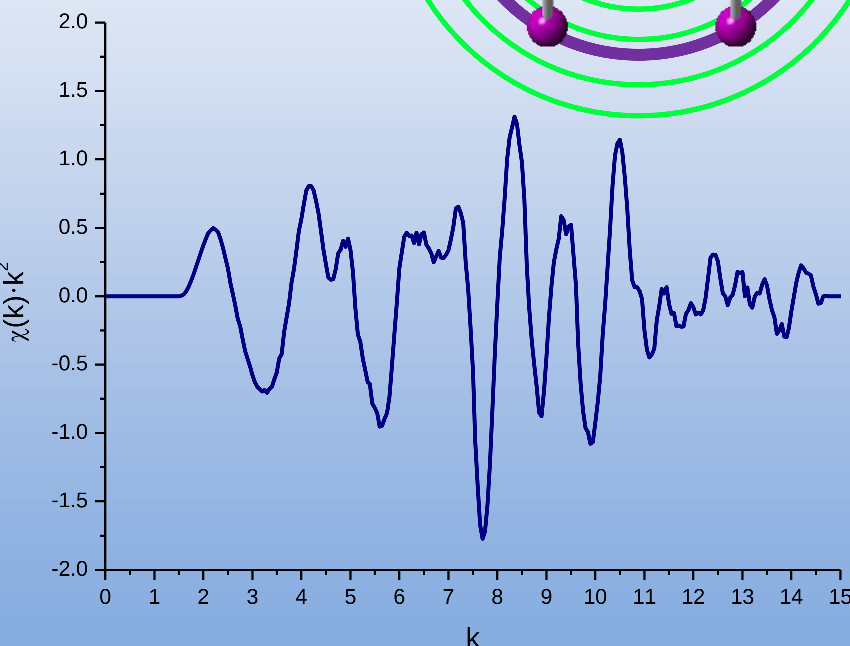


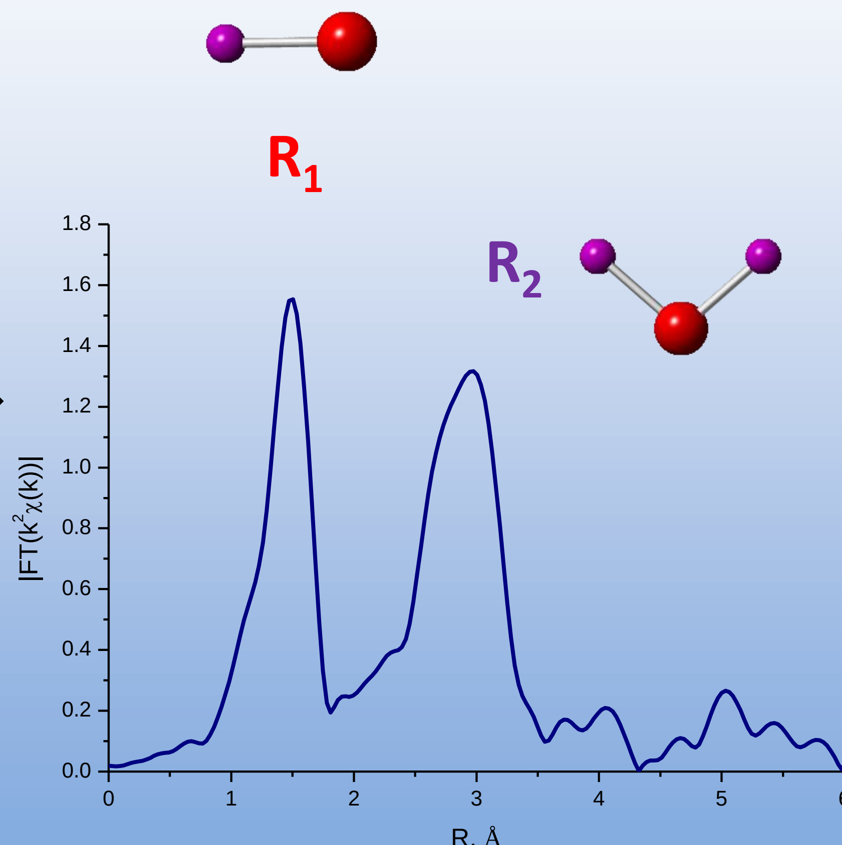
$$f(t) = \sin(2\pi t) + \sin(6\pi t)$$

$$FT(\omega) = \int_{-\infty}^{+\infty} f(t) e^{-i\omega t} dt$$

Fourier Transformation(FT) of EXAFS spectra







$$\chi(k) = \sum_R S_0^2 N_R \frac{|f(k)|}{kR^2} \sin(2kR + \delta_c + \Phi) e^{-2R/\lambda(k)} e^{-2\sigma^2 k^2}$$

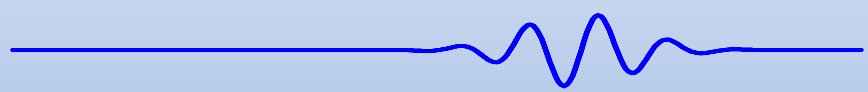
$$FT(R) = \int_{-\infty}^{+\infty} \chi(k) g(k) e^{-i\omega k} dk$$

Wavelet Transformation (WT)

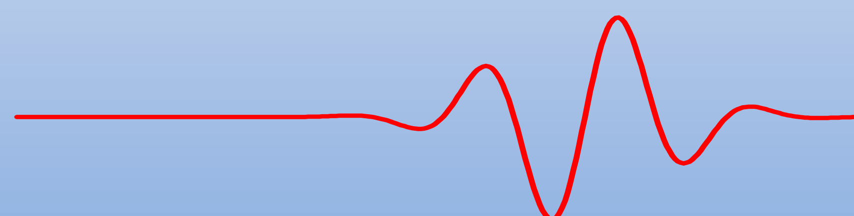
$$WT(a,b)=\frac{1}{\sqrt{a}}\int_{-\infty}^{+\infty} f(t)\psi^{*}\left(\frac{t-b}{a}\right)dt$$

ψ – “Mother wavelet” function

b – translation parameter



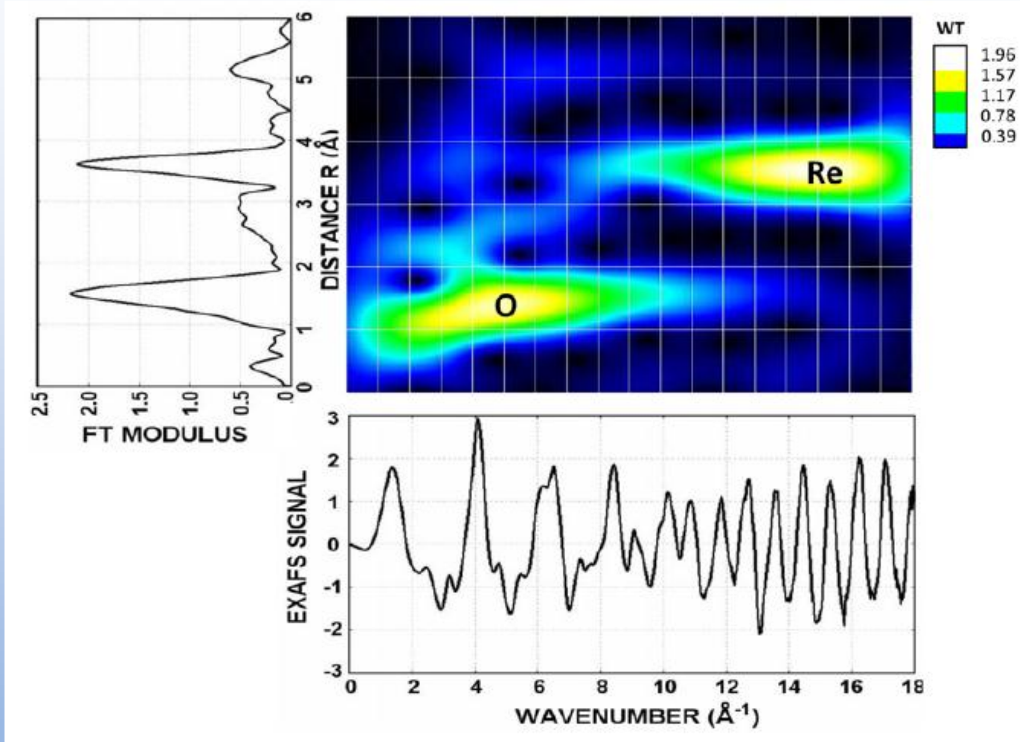
a – scaling parameter



Information about signal localization becomes available!

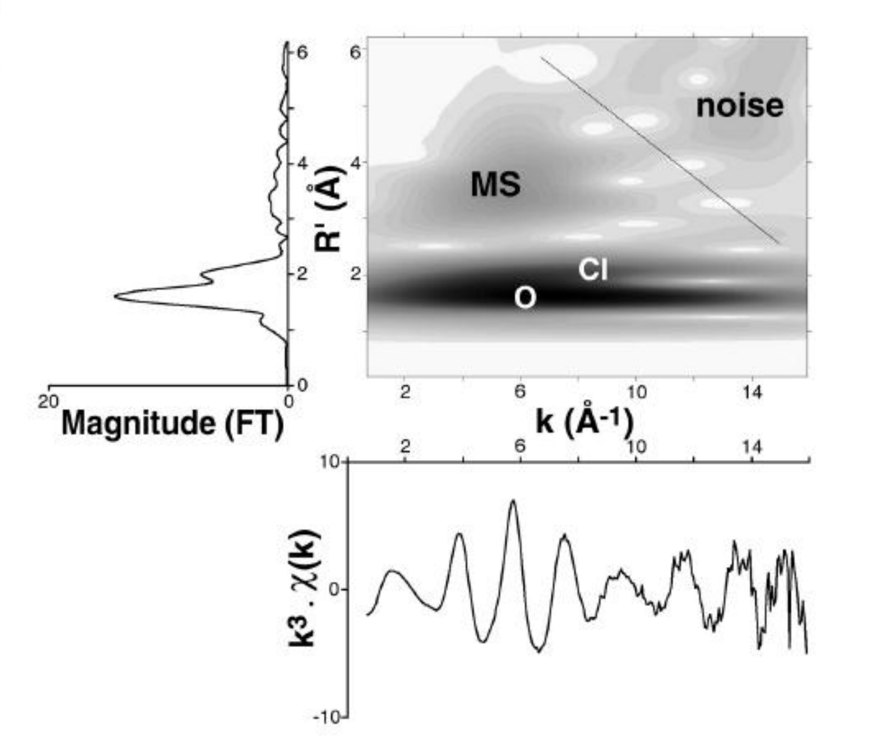
WT for EXAFS

ReO_3



J. Timoshenko, A.Kuzmin. *Comp. Phys. Comm.* 180 (2009) 920-925.

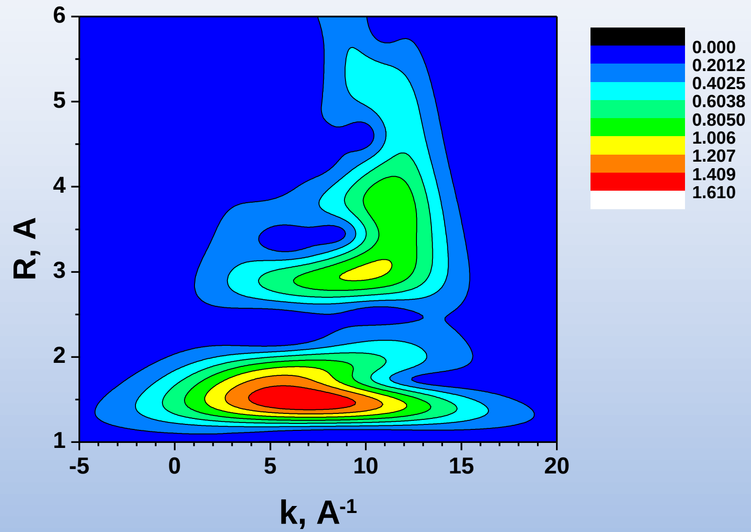
Aqueous solution of $AuCl_3$



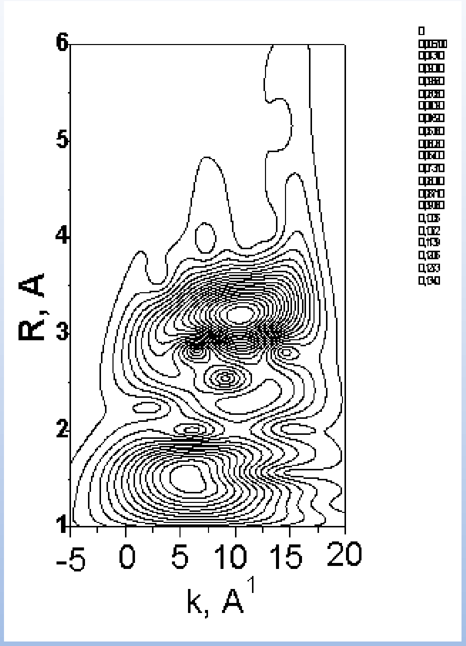
M.Munoz, P. Argoul, F.Farges. *Am. Mineralogist.* 88 (2003) 694-700.

WT for EXAFS

$GdHfO_{1.75}$



Tc-DTPA

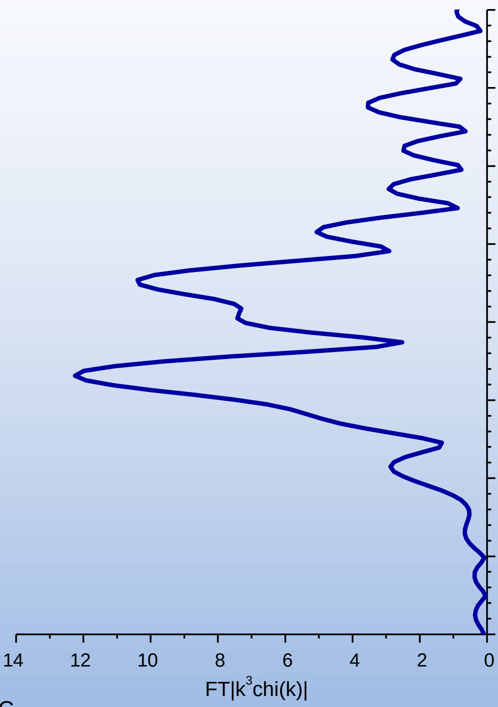


A.A. Shiryaev, Ya. V.Zubavichus et.al. MRS Proceedings 2010.

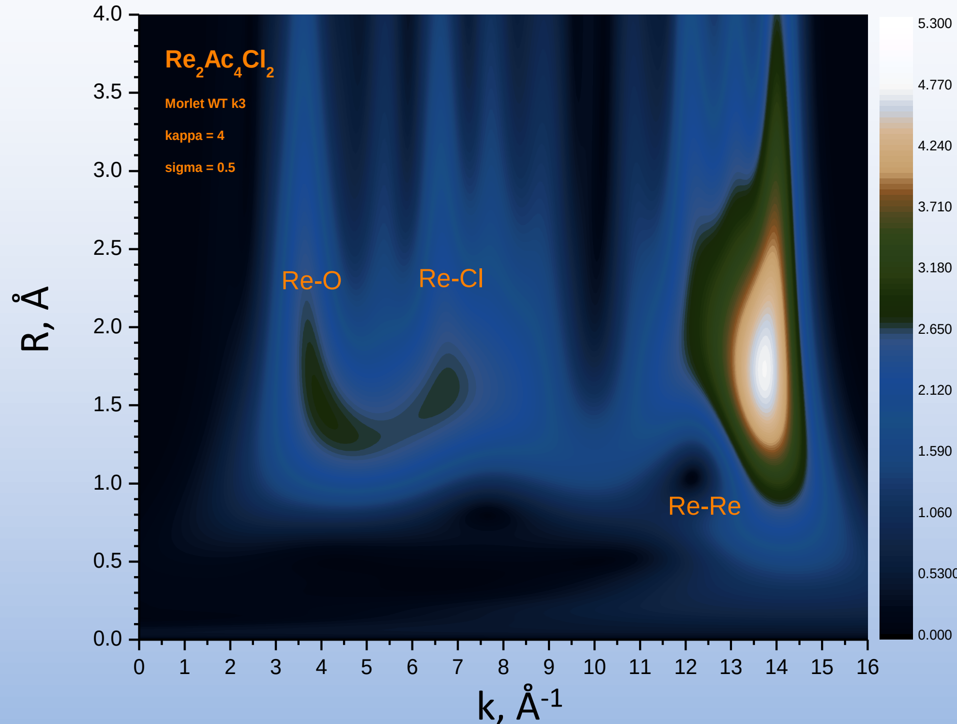
K.E. German, A.B. Melentiev, S.N. Kalmykov, N.N. Popova, A.A. Shiryaev, I.G. Tananaev, Ya.V. Zubavichus.
In Technetium and other radiometal in chemistry and medicine Edited by U. Mazzi, W.C. Eckelman, W.A. Volkert, SGEditorial, Padova, Italy, 2010, pp. 47-50

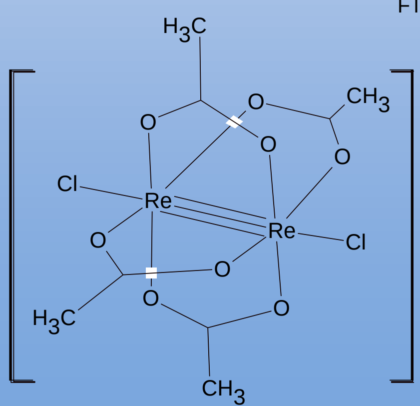
FT vs. WT

Fourier Transformation



Wavelet Transformation



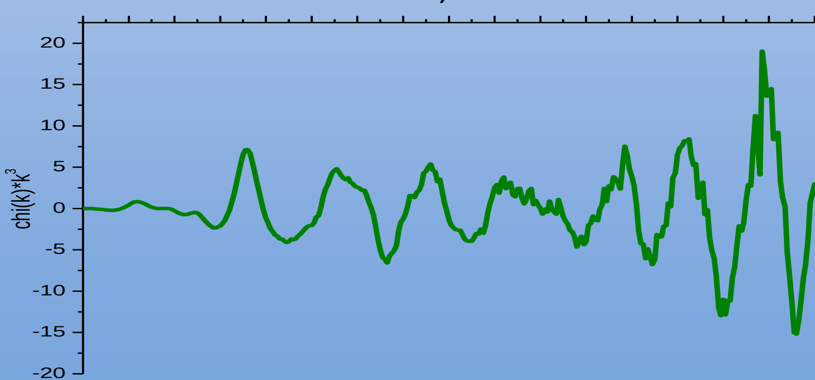


Contributions:

4 Re-O

1 Re-Cl

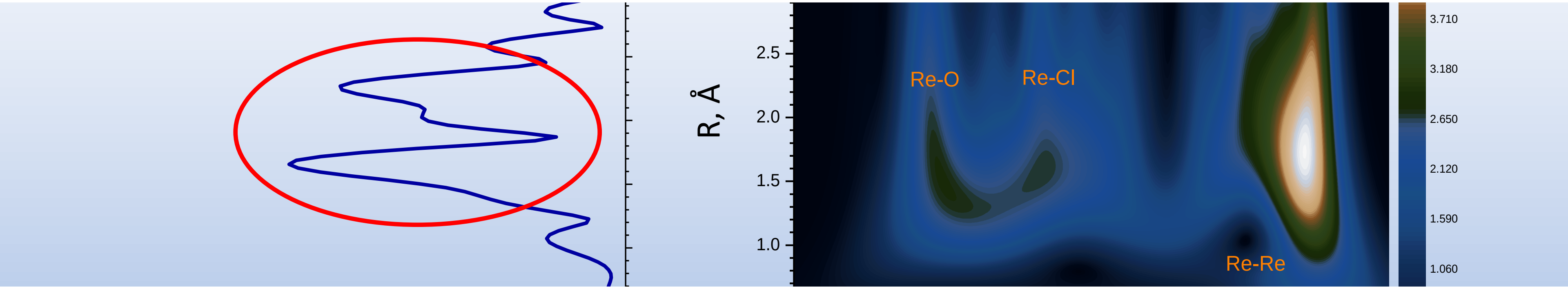
1 Re-Re



FT vs. WT

Fourier Transformation

Wavelet Transformation



Problem:

If several groups of atoms are at close distances their contributions combine in a complicated way.

Solution:

The contributions become distinguishable with the help of wavelet transformation. The position at k-axis mostly depends on atomic number of the scattering atom. The higher Z is – the larger k-position of the peak.

FT vs. WT

Key points:

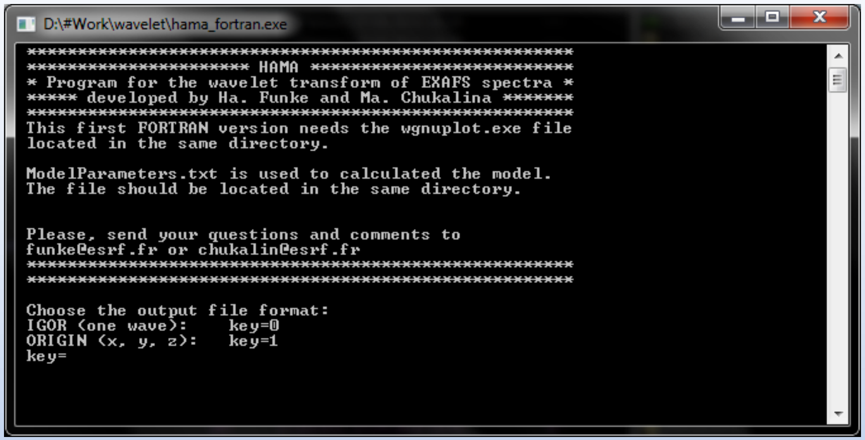
1. **Wavelet transformation is just another way of processing EXAFS data. No modifications of an experiment are required.**

2. **With Fourier transformation you get the best resolution in R-space. WT gives you information about k-dependence at the cost of resolution in R-space. The higher resolution in k-space is, the lower resolution in R-space you get.**

3. **The position of peaks at k-axis mostly depends on atomic number of the corresponding element. With higher Z you get larger k.**

Software for WT of EXAFS

HAMA

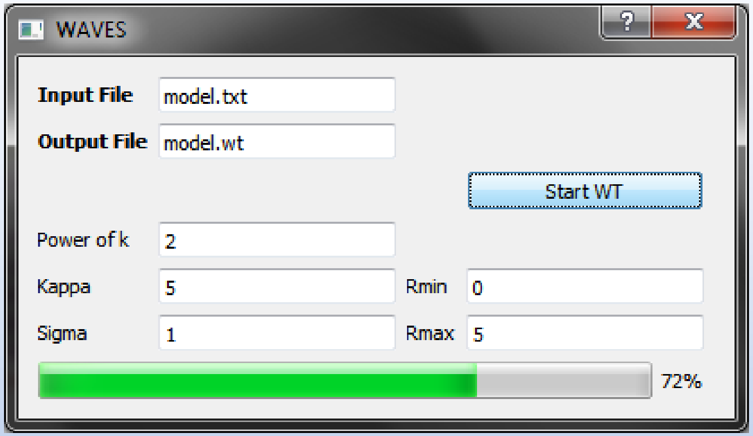


Developed by
Harald Funke (IRC-FZR)
Marina Chukalina (IMT-RAS)

Funke, H.; Scheinost, A. C.; Chukalina, M. *Physical Review* **2005**, B 71, 094110.

Funke, H.; Chukalina, M.; Scheinost, A. C. *Journal of Synchrotron Radiation* **2007**, 14, 426-432.

WAVES



Wavelet
Analysis &
Visualization for
EXAFS
Spectroscopy

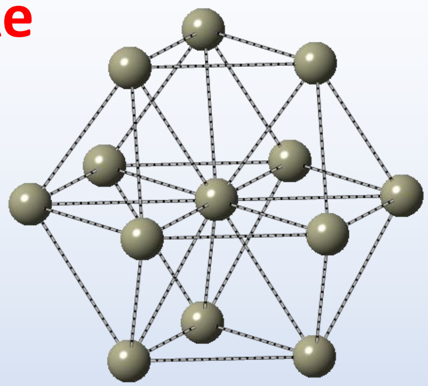
under development
Vadim Murzin (NRC “KI”, TIPS RAS)

Application:

1. Separation of different contributions in EXAFS spectra for Re polynuclear complexes
2. Precipitation of Tc complexes from TcDTPA solution
3. Non-stoichiometric Re & Tc carbide nanoparticles
4. Monitoring of PdZn alloy nanoparticles formation

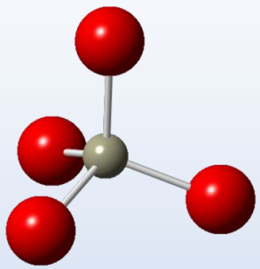
Some standard compounds

Re

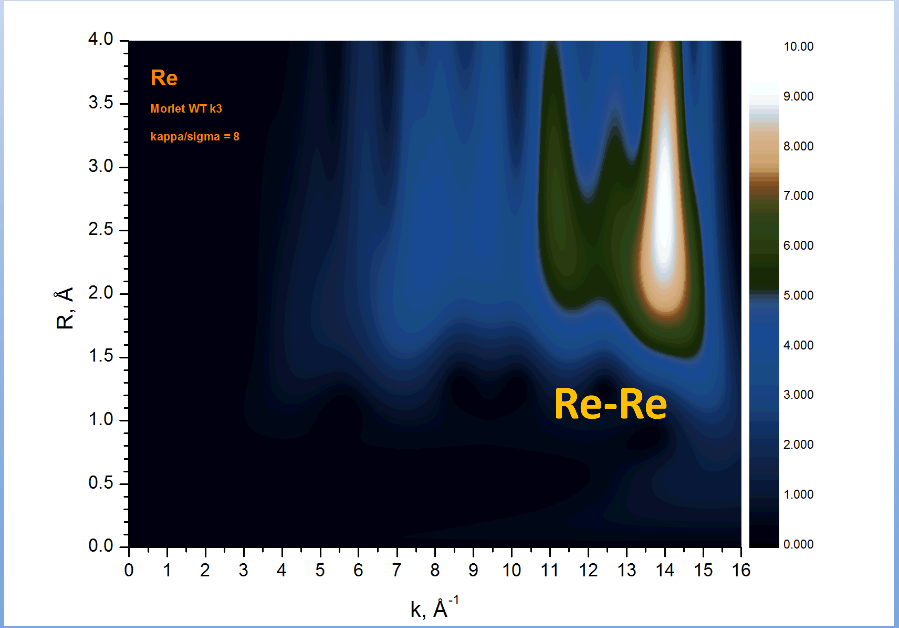


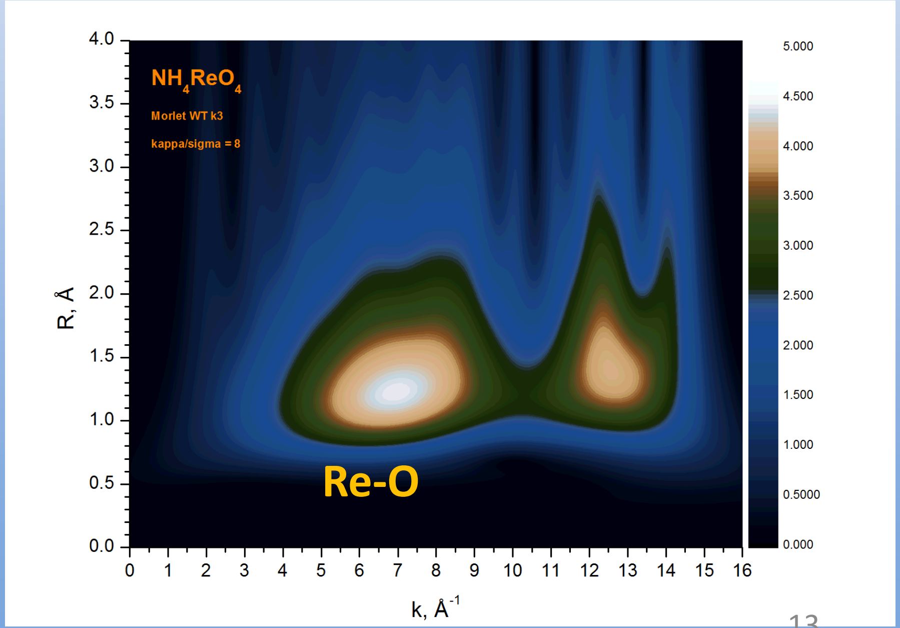
12 Re-Re

NH_4ReO_4

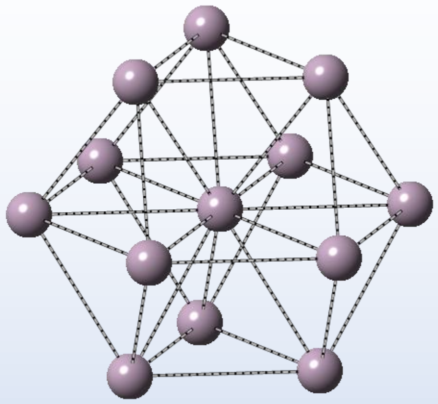


4 Re-O



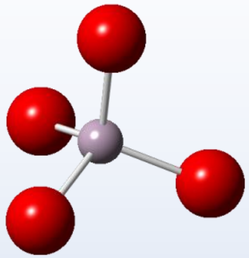


Tc

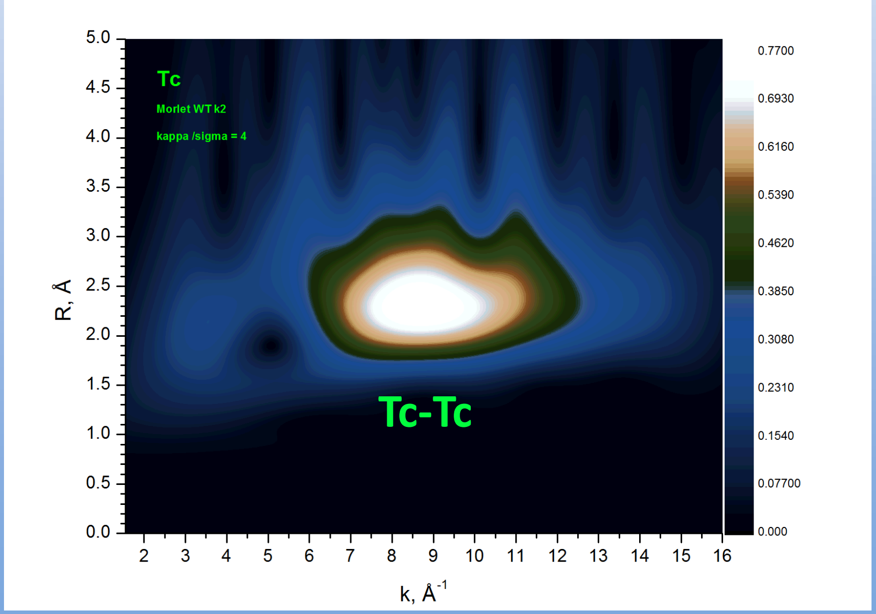


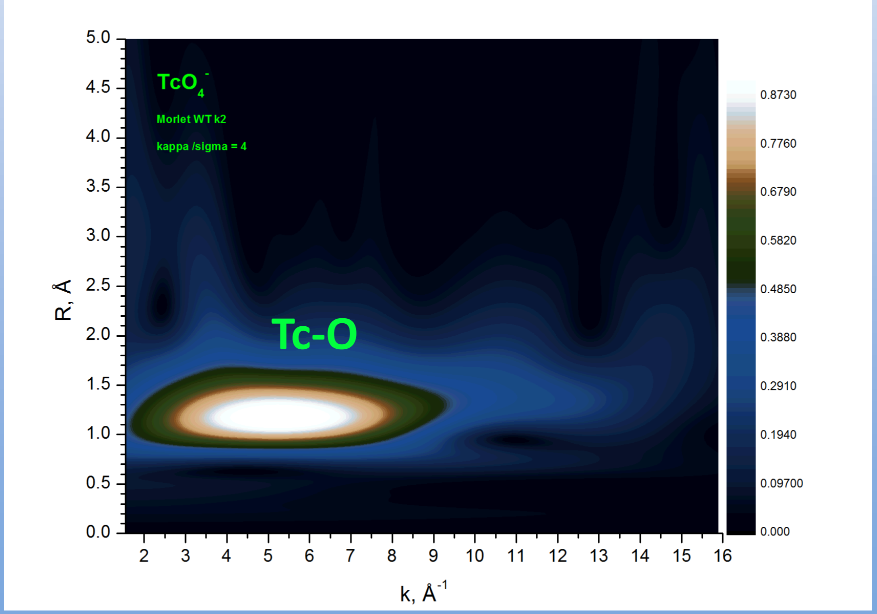
12 Tc-Tc

NH_4TcO_4

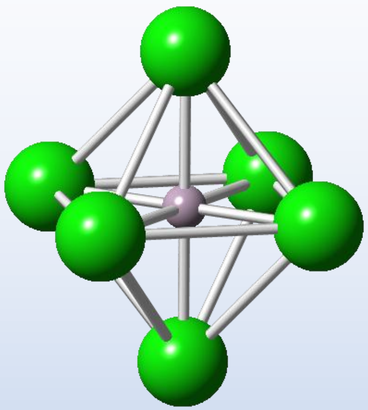


4 Tc-O

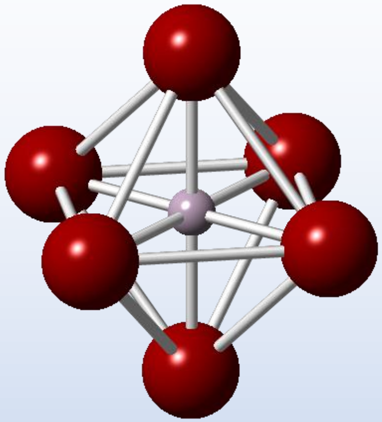




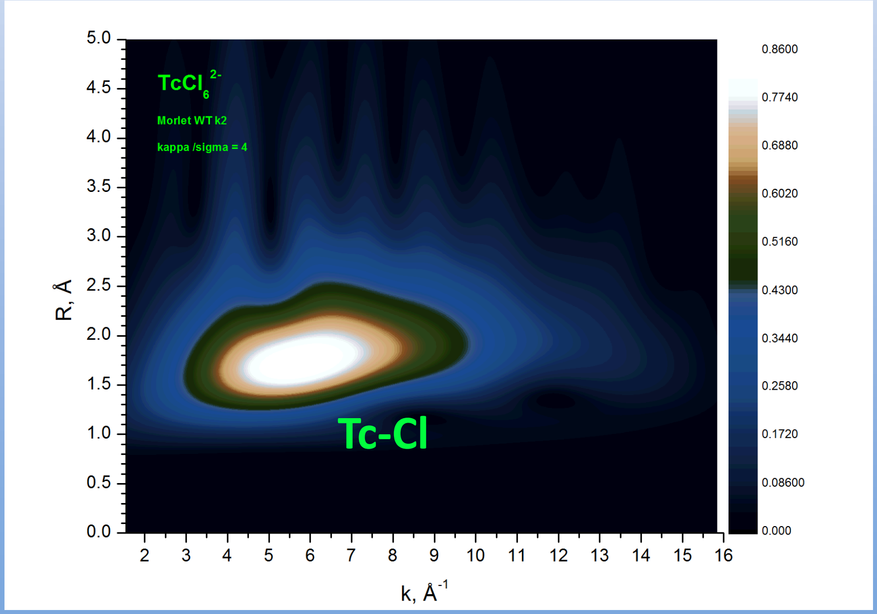
$(TEA)_2TcCl_6$ | $(TMA)_2TcBr_6$

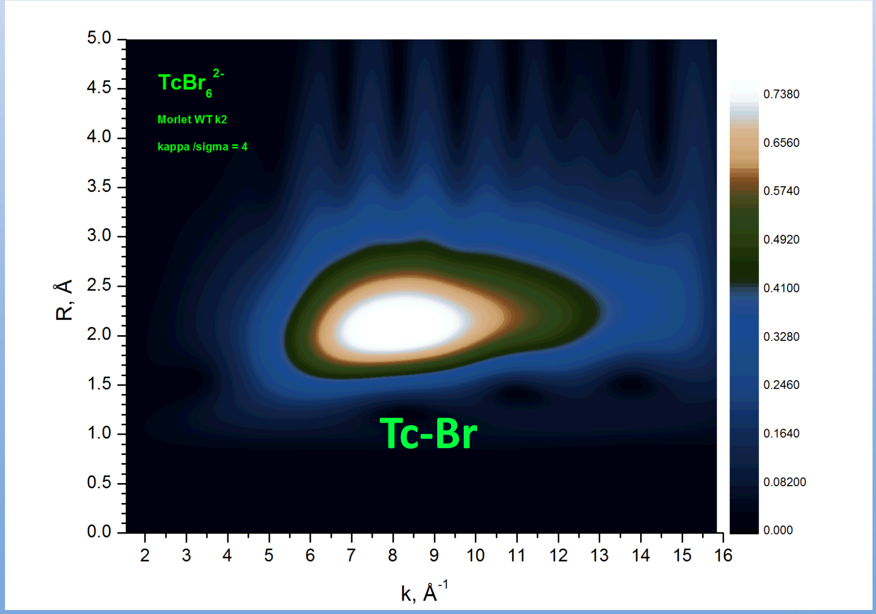


6 Tc-Cl

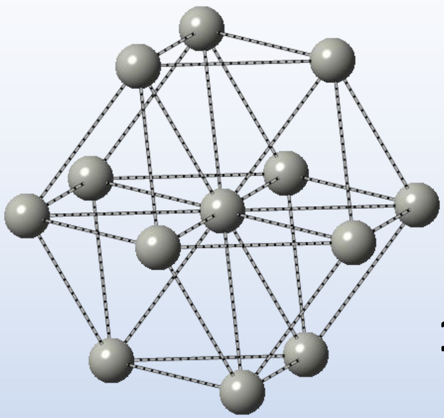


6 Tc-Br



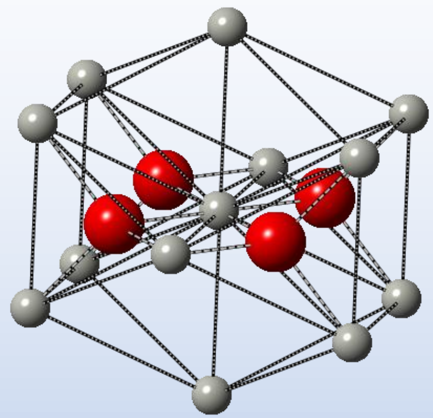


Pd

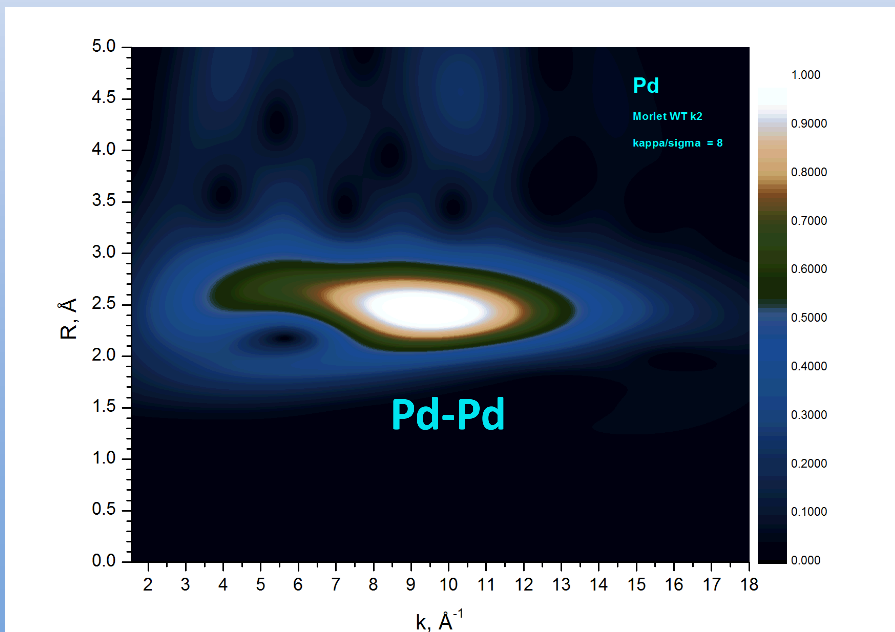


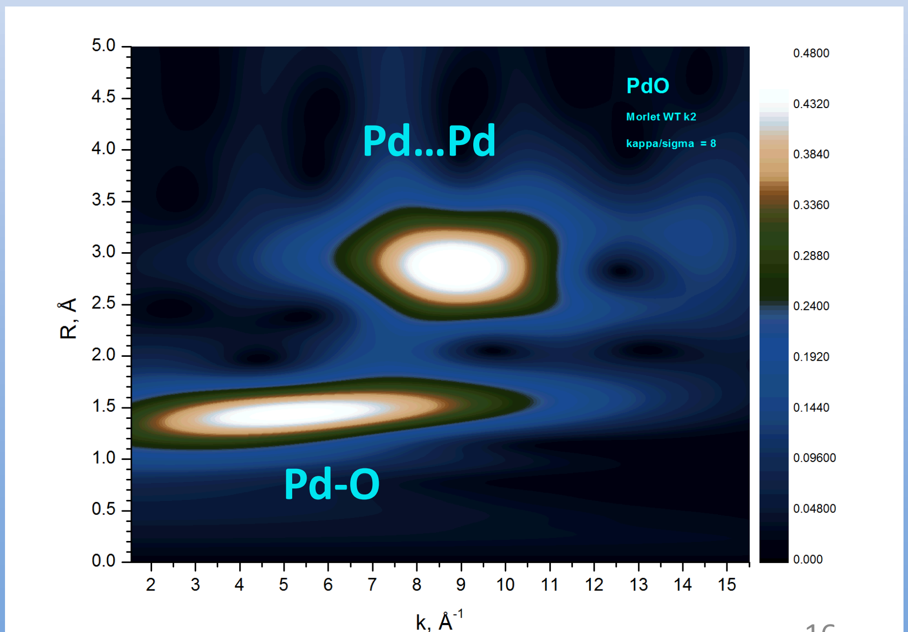
12 Pd-Pd

PdO

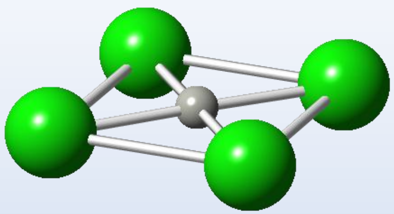


4 Pd-O
12 Pd…Pd



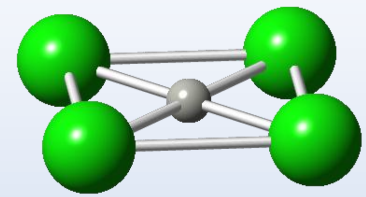


$PdCl_2$

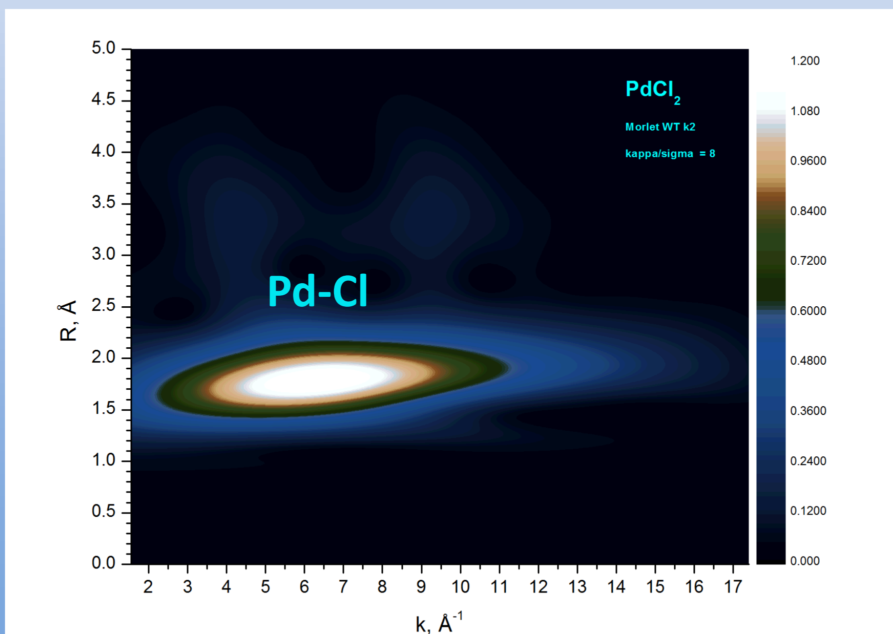


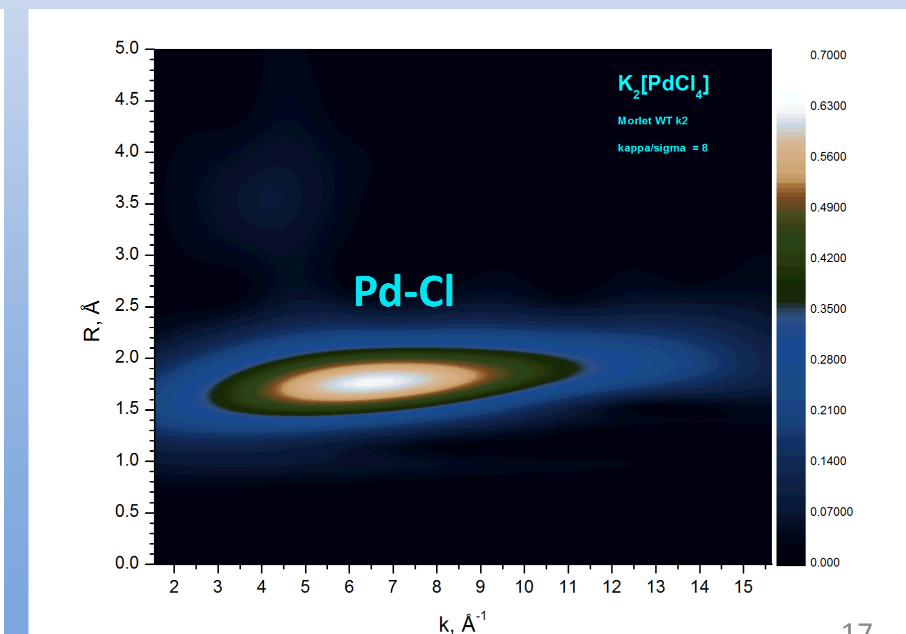
4 Pd-Cl

$K_2[PdCl_4]$

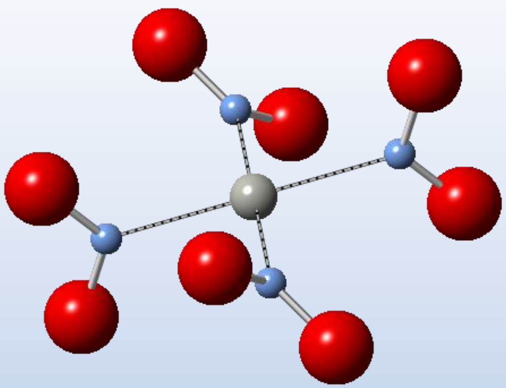


4 Pd-Cl

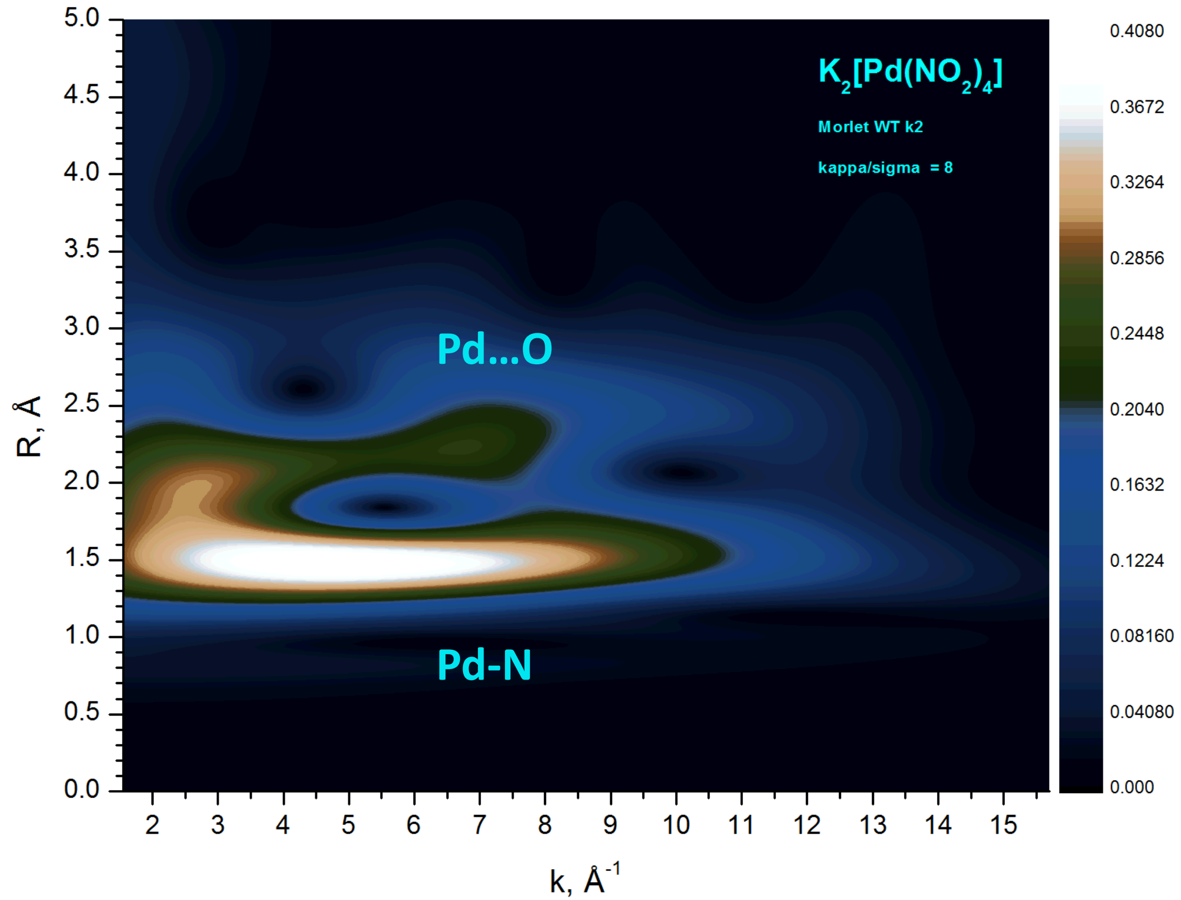




$K_2[Pd(NO_2)_4]$

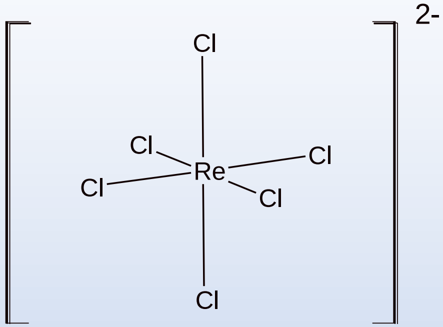


4 Pd-N
8 Pd…O



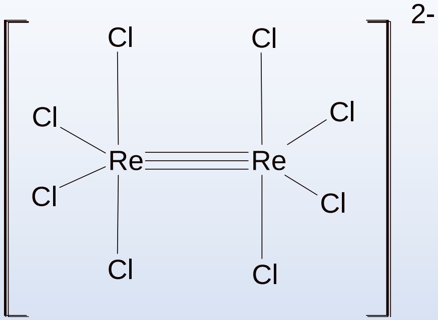
Polynuclear Re complexes

$(PyH)_2[ReCl_6]$

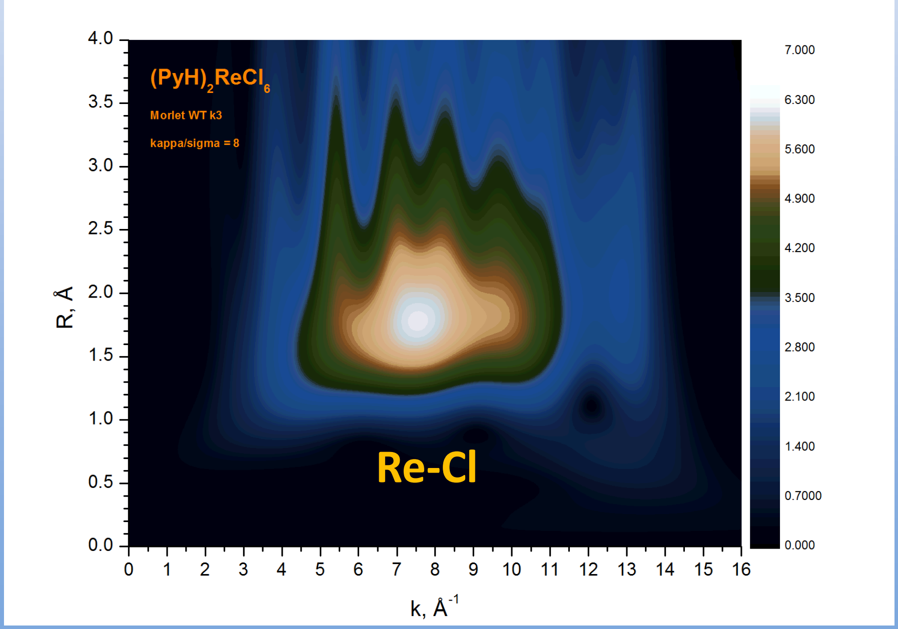


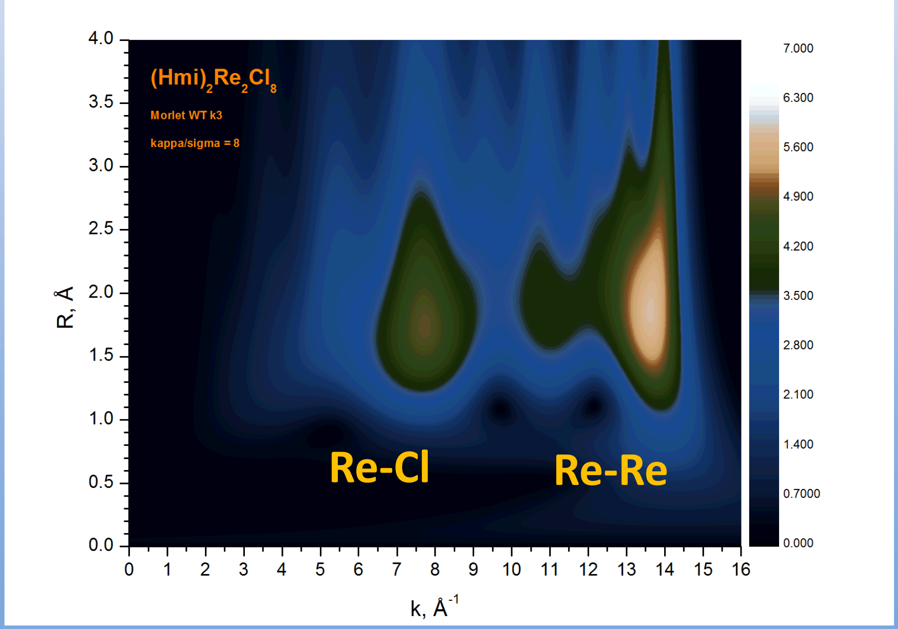
6 Re-Cl

$(Hmi)_2[Re_2Cl_8]$



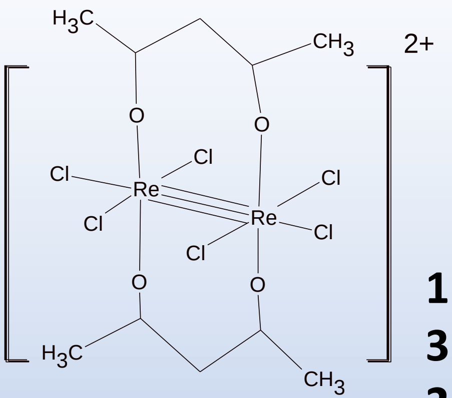
1 Re-Re
4 Re-Cl





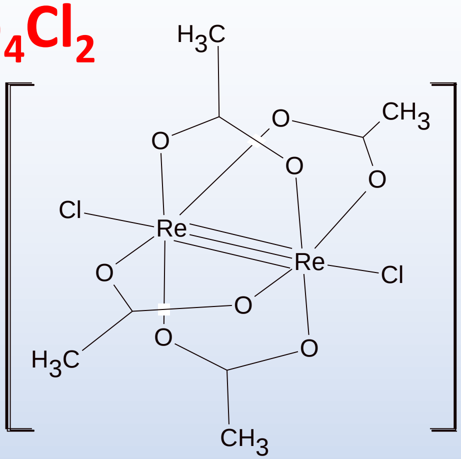
Polynuclear Re complexes

$(AcAc)_2Re_2Cl_8$

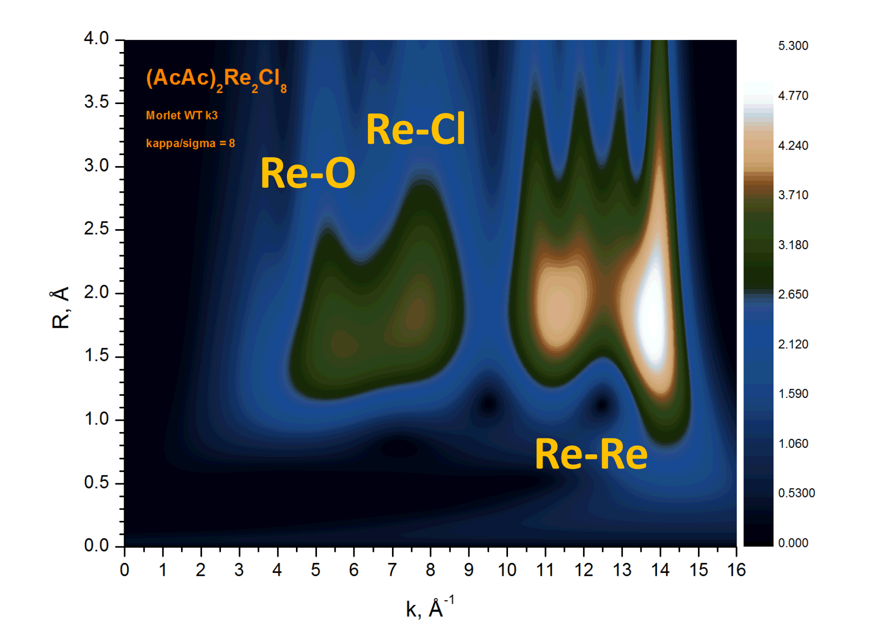


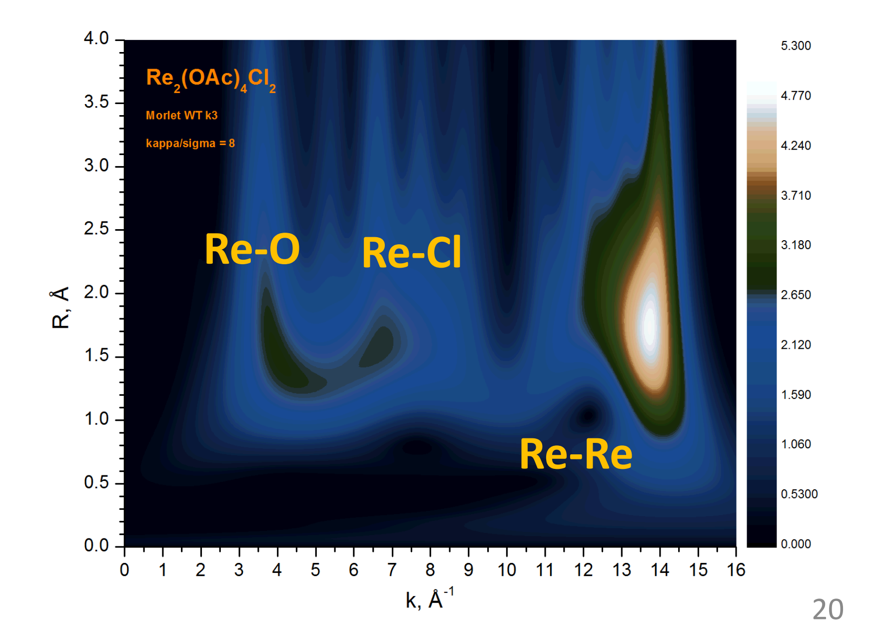
1 Re-Re
3 Re-Cl
2 Re-O

$Re_2(OAc)_4Cl_2$



1 Re-Re
1 Re-Cl
4 Re-O





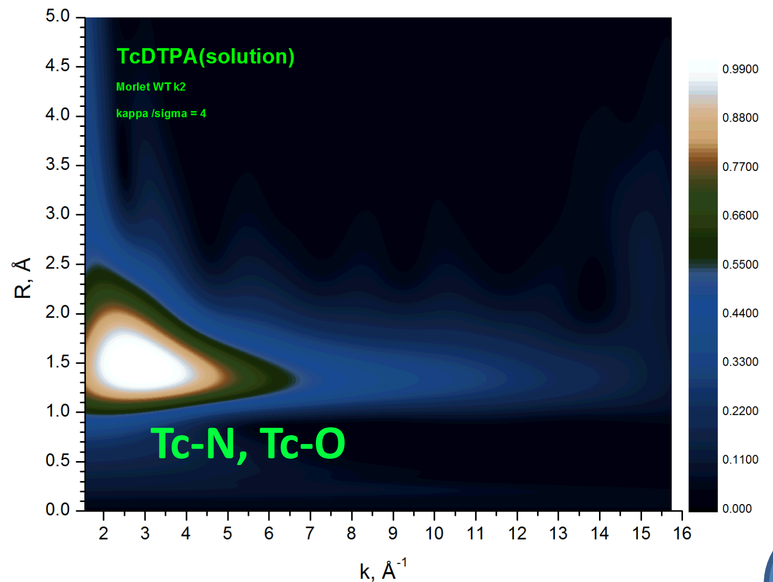
Tc-DTPA precipitation

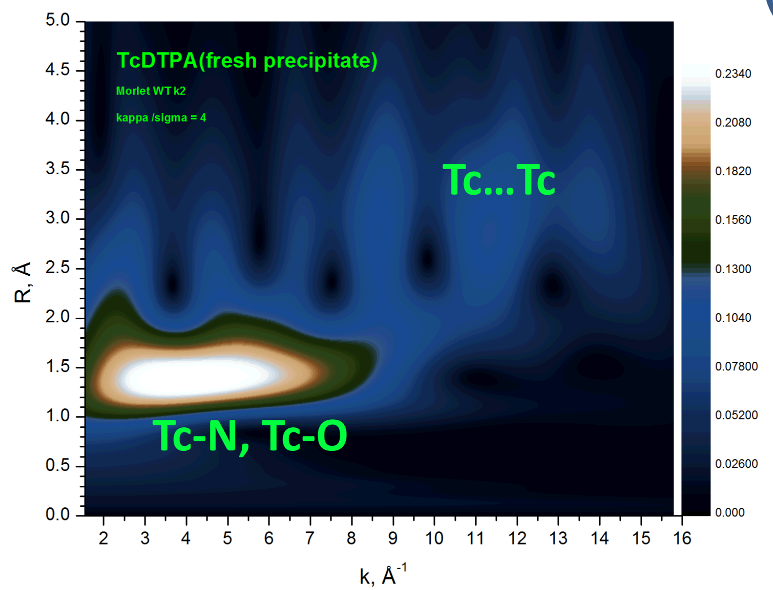
$NH_4TcO_4 + N_2H_4 + HNO_3 + DTPA$

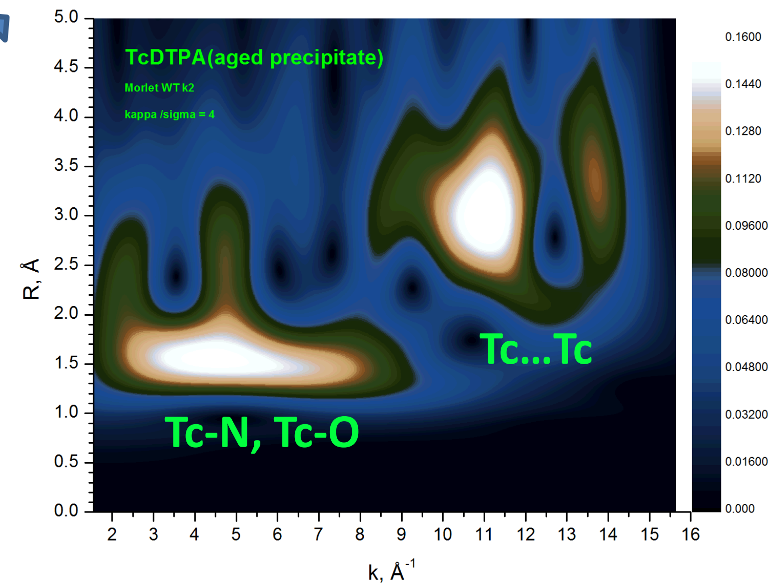
Solution

Fresh precipitate

Aged precipitate





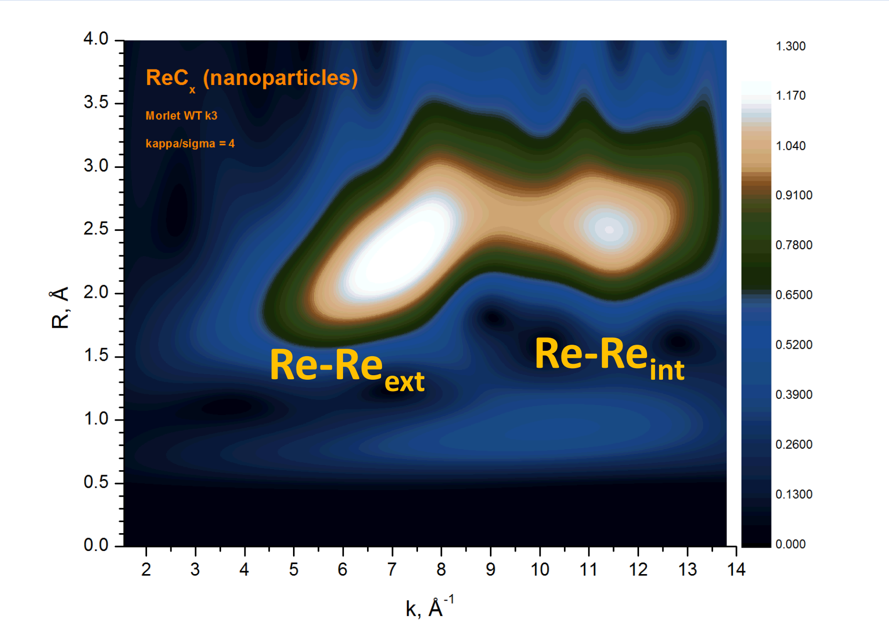


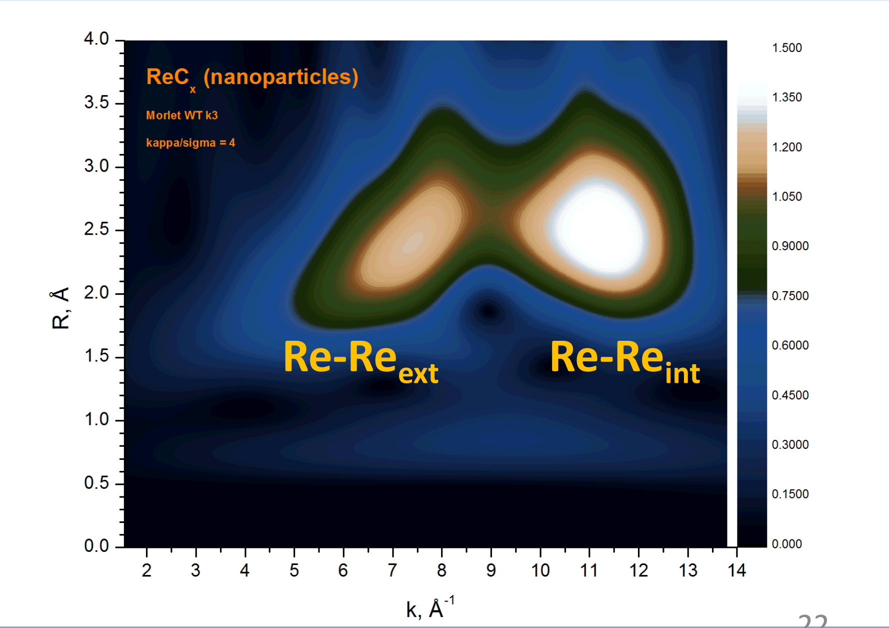
Re nanoparticles from polynuclear complexes

Thermal decomposition of triphenylguanidinium tetraoxorhenate hemihydrate in inert atmosphere.

r=16 nm (SAXS data).

Thermal decomposition of triphenylguanidinium tetraoxorhenate hemihydrate in H_2 atmosphere.

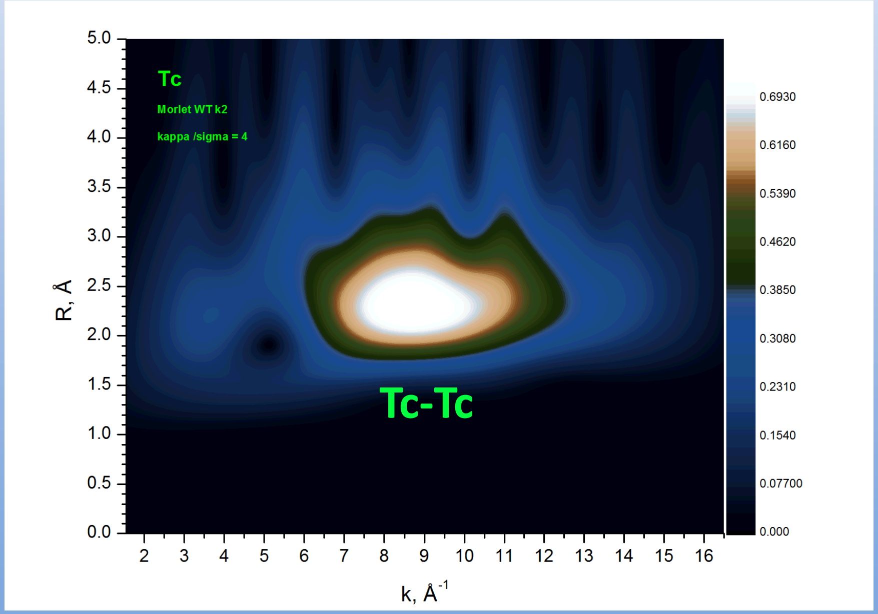


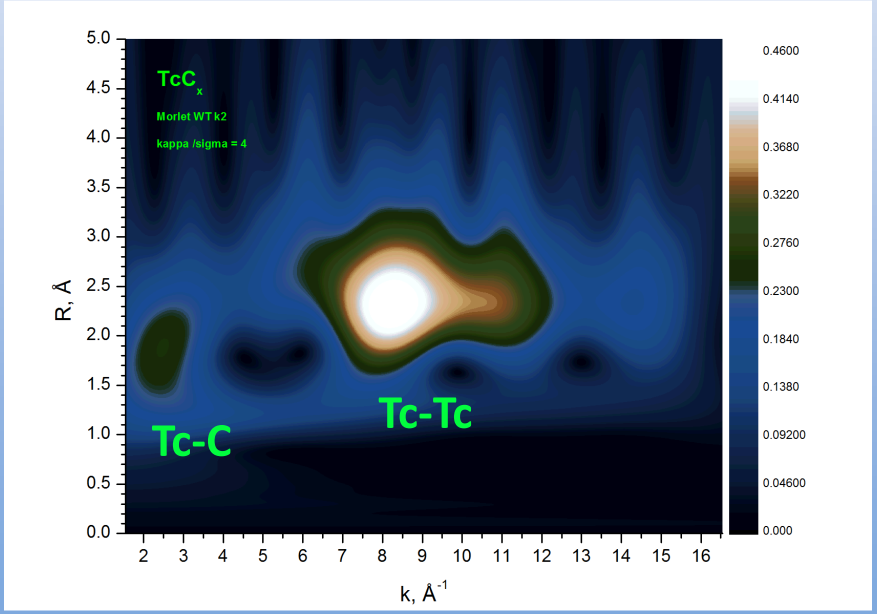


Tc & TcC_x

Thermal decomposition of $(TMA)TcO_4$ at 1000°C in H_2.

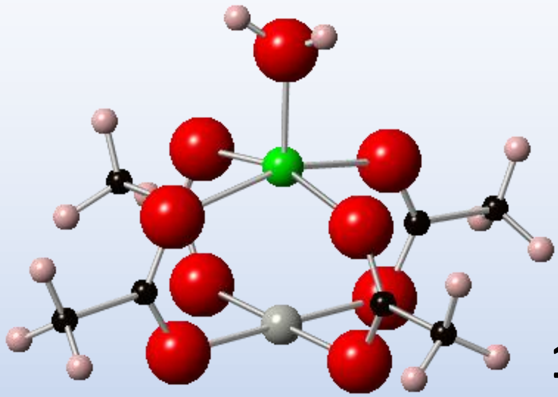
Tc metal → 1000°C, carbon → Tc + 17%(at.) C

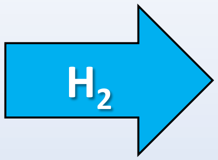




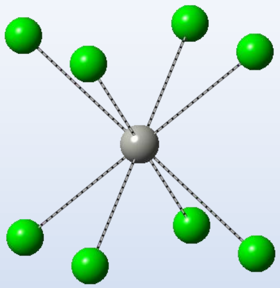
PdZn nanoparticles from $PdZn(OAc)_4 \cdot H_2O$

$PdZn(OAc)_4 \cdot H_2O$



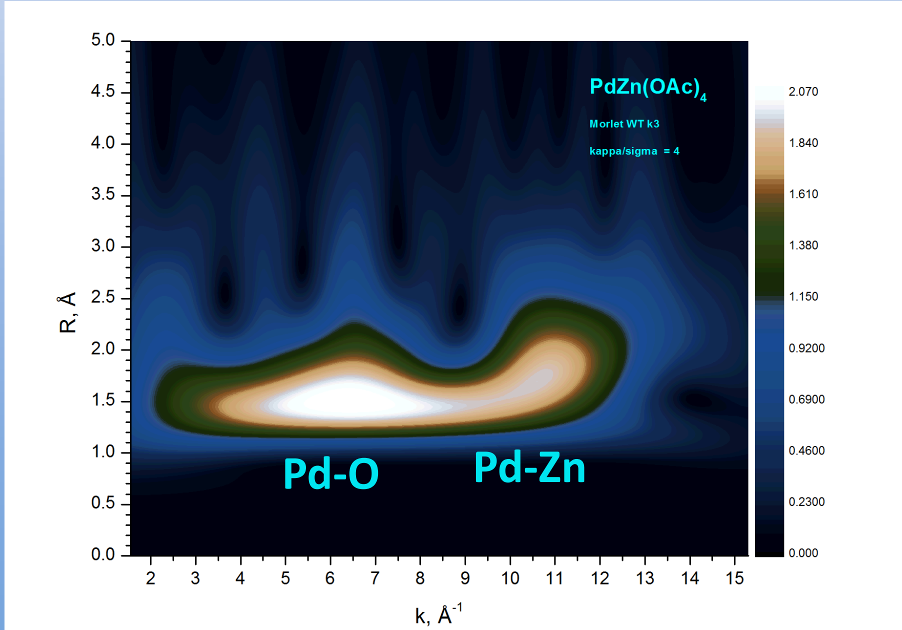


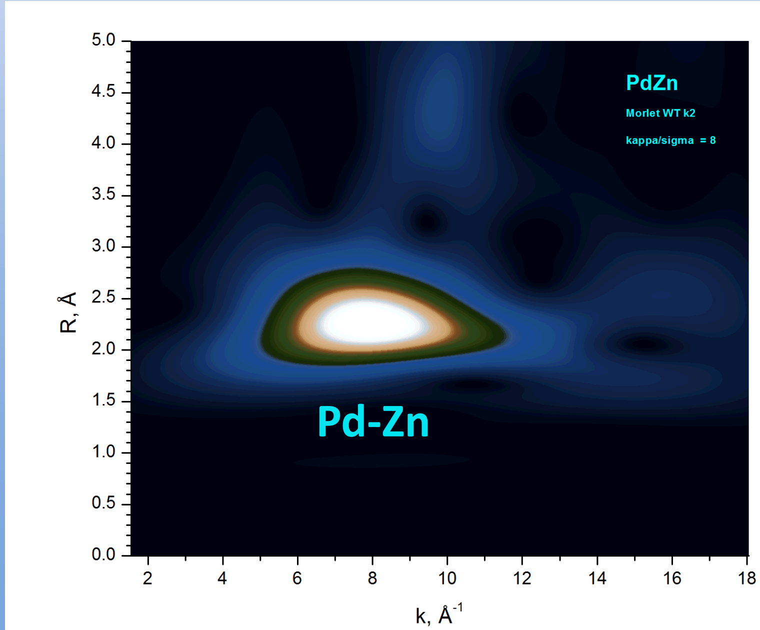
PdZn



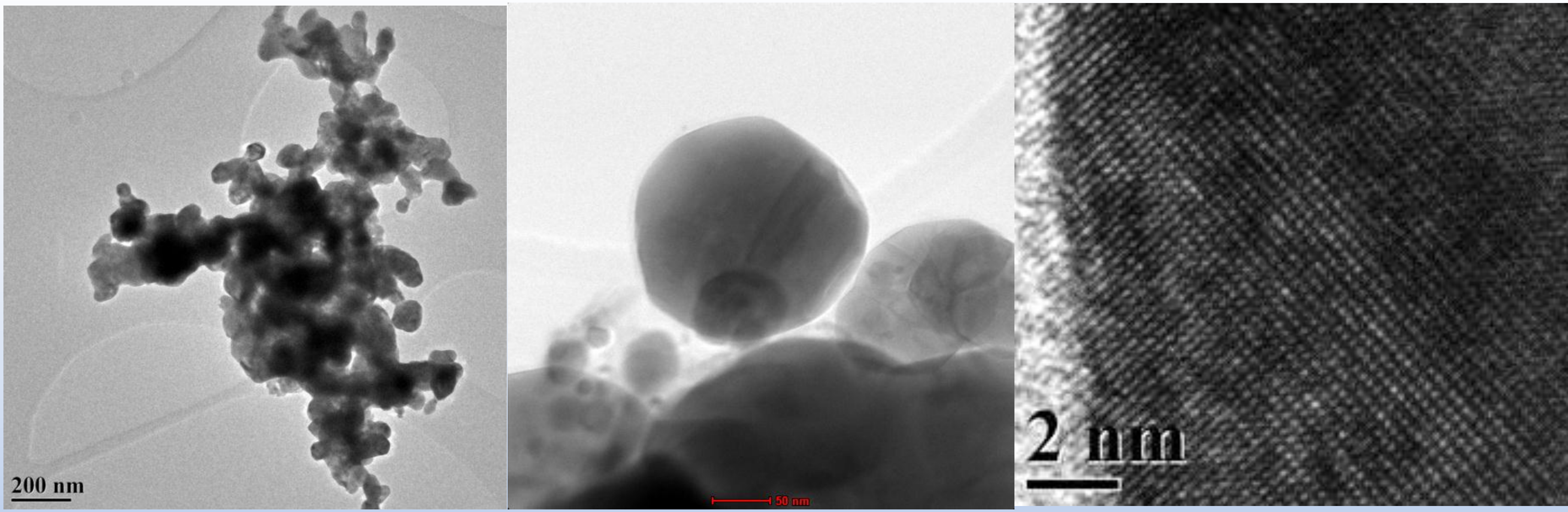
1 Pd-Zn
4 Pd-O

8 Pd-Zn

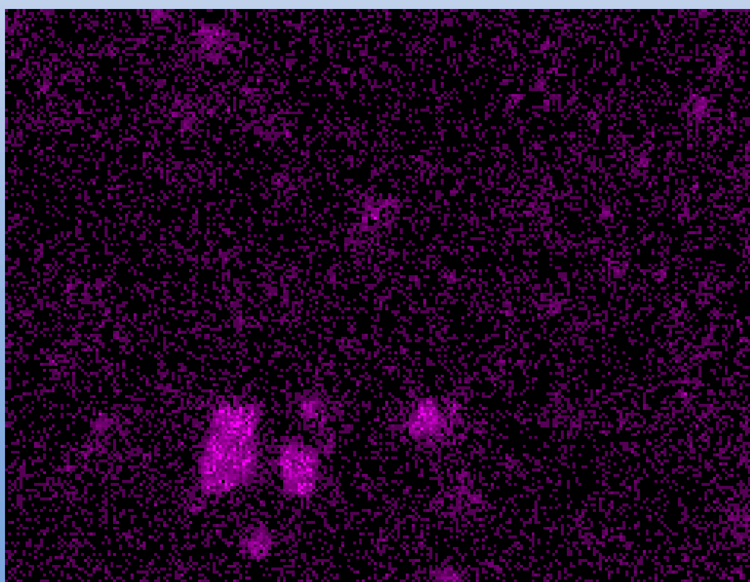




TEM results

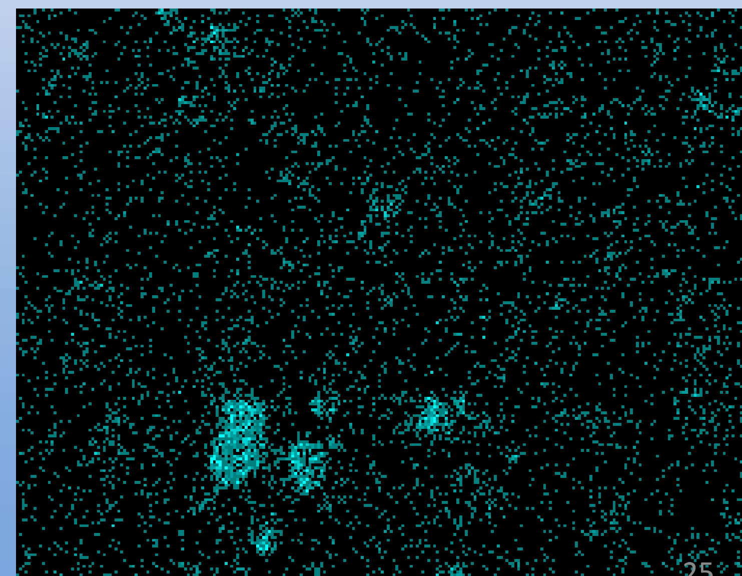


EDAX

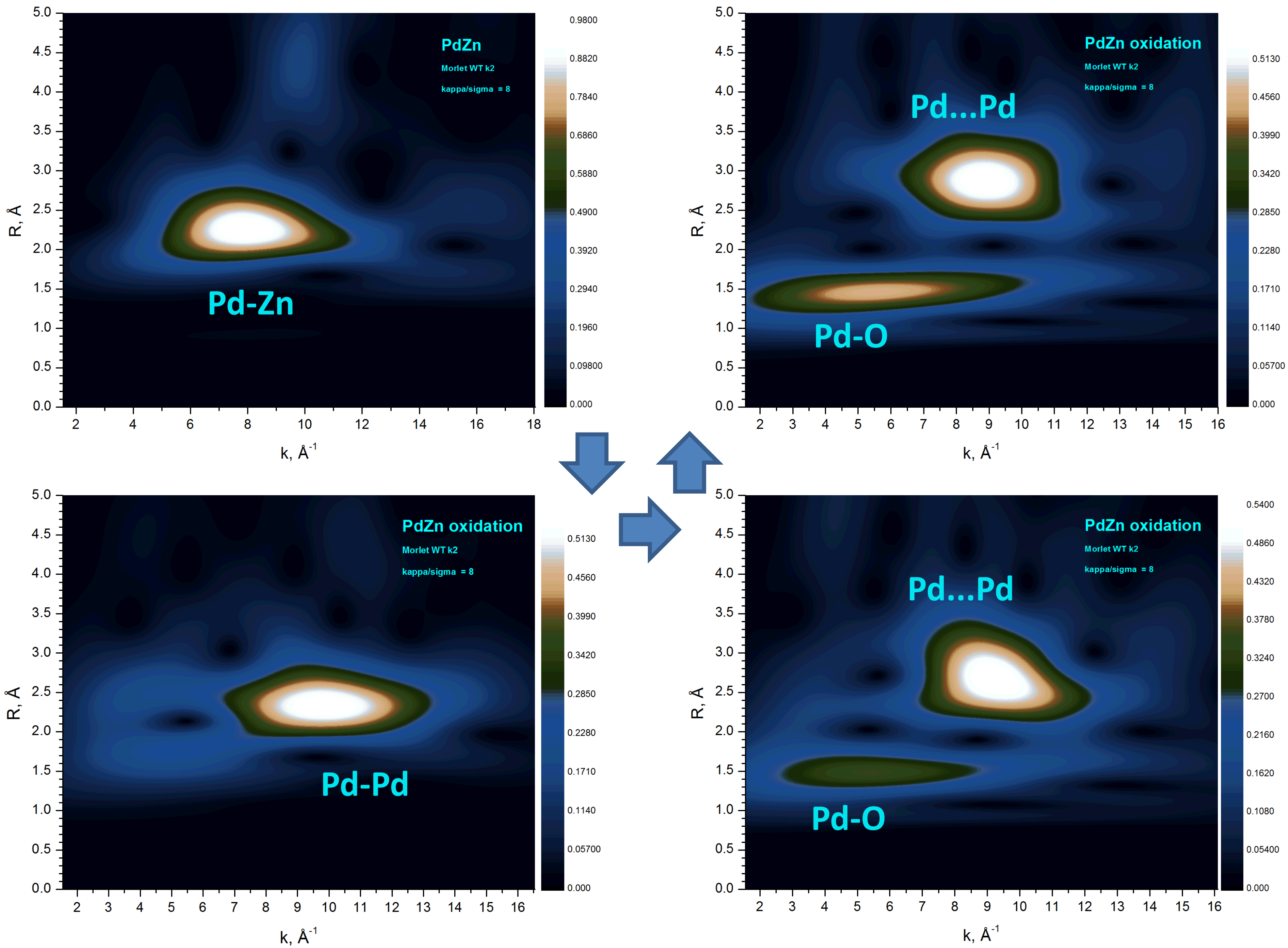


Pd

Zn



Oxidation of PdZn nanoparticles



Conclusions

The examples shown above clearly demonstrate that the WT is indeed a quite informative and instructive way to represent EXAFS spectra prior to more thorough model-based quantitative analysis.

Elements with different atomic numbers Z (typically, from different rows of the Periodic system) are characterized by clearly distinguishable positions along the k axis of the wavelet maps.

The wavelet representation is especially useful for complex and nanostructured materials with mixed-ligand coordination of metal atoms.

Thank you for your attention!