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Wavelet analysis of EXAFS data

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Why wavelets for EXAFS ?

- Simultaneous visualisation of the r and k dependency of backscattering effects.
- Wavelet analysis eases differentiation between heavier and lighter back scatterers, even if they are at the same distance from the central atom.
- Especially in the 2nd and higher shells, this discrimination is often not possible, if solely based on Fourier transformation (FT). Wavelet transformation (WT) gives in such cases a unique answer.
- WT is able to detect (unexpected) co-species, e.g. hydrolysis species containing heavier elements.

The wavelet transform

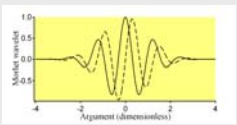
- **Wavelets** as kernels of an integral transform built a wide class of functions.
- **WT** is a complete transformation.
- **Advantage of the WT:** The wavevector-distance window is flexible and adapts in such way that there is always the same number of periods in the k-window.
- **Disadvantage of the FT:** If the signal changes at one time moment, the FT changes everywhere.

	FT	WT
Function	$\cos(x),\ \sin(x)$	$\int_{-\infty}^{+\infty}\psi(x)dx=0,\ \psi(x)\in l^2$
Transform	$\hat{\chi}(r)=\int_{-\infty}^{+\infty}\chi(k)e^{2irk}\,dk$	$W_f^{\psi}(r,k)=\sqrt{2r}\int_{-\infty}^{+\infty}\chi(k')\psi^*\left(2r(k'-k)\right)dk'$
Inversion	$\chi(k)=\frac{1}{C_{FT}}\int_{-\infty}^{+\infty}\hat{\chi}(r)e^{-2irk}\,dr$	$\chi(k)=\frac{1}{C_{\psi}}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}W_{\chi}^{\psi}(r,k')2r\psi\left(2r(k'-k)\right)drdk'$
Scaling	$C_{FT}=2\pi$	$C_{\psi}=\int_0^{\infty}\lvert\hat{\psi}(\omega)\rvert^2\,\omega^{-1}d\omega<\infty$

The Morlet wavelet

$$\psi(x)=\frac{1}{\sqrt{2\pi}\sigma}\exp(i\kappa x)\cdot\exp\left(\frac{-x^2}{2\sigma^2}\right)$$

- Analogy to the Fourier treatment
- Similarity to an EXAFS spectrum
- Complex wavelet



Real (full) and imaginary (dashed) part of the Morlet wavelet (κ=5, σ=1)

The choise of the Morlet parameters κ and σ allows to vary the resolution:

Overview wavelet: $\kappa\cdot\sigma \geq 15$

Detail wavelet: $\kappa\cdot\sigma \approx 2r_{opt}$

The detail wavelet optimizes the resolution of k for the distance of interest r_{opt} (see examples).

Uncertainty (Heisenberg) Box of the Morlet wavelet

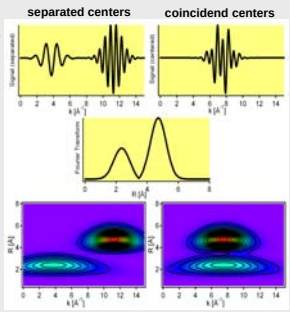
$$\left[k-\frac{\kappa\sigma}{\sqrt{2}r},k+\frac{\kappa\sigma}{\sqrt{2}r}\right]\times\left[r-\frac{r}{\sqrt{2}\kappa\sigma},r+\frac{r}{\sqrt{2}\kappa\sigma}\right]$$

Model example: k-dependence of a signal

Two sine waves, enveloped by Gaussians.

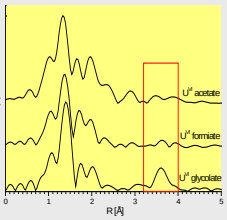
Both test functions generate the same FT (Modulus).

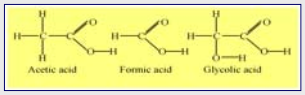
The WT resolves distance **and** position of the two signal components.

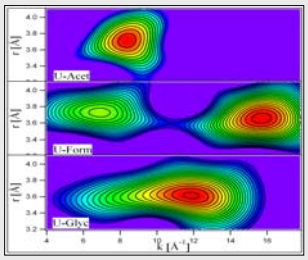


Application 1

Objective:
The EXAFS spectra of aqueous U(VI) complexes with acetate, formiate and glycolate have a FT peak at R≈ 3.7 Å in common.
Where does this peak come from?







Detail wavelet plots of the three uranyl complexes

Result :
The peaks at ≈ 3.7 Å may be interpreted as:

U-acetate:
1 WT peak due to C atoms
⇒ MS interactions along the carboxylate group, i.e. formation of a bidentate complex [Rossberg],

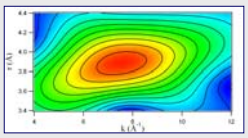
U-formiate:
2 WT peaks, due to C and U atoms
⇒ **both uranyl formiate and hydrolysis species are present** at ph=4.5.

U-glycolate:
1 WT peak due to U atoms
⇒ The k-dependence shows an additional contribution from U atoms, i.e. formation of a polynuclear, bidentate complex [Moll].

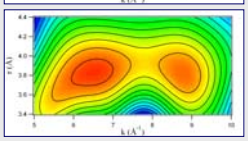
Application 2

Objective
In EXAFS spectra of solid uranyl carbonate complexes, the U-C-O MS resonances and backscattering from alkaline cations overlap.

Overview wavelet
Morlet parameter:
κ=15, σ=1
The ordinate shows an analog to the FT.



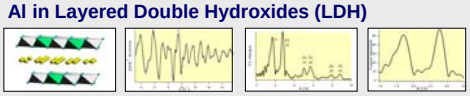
Detail wavelet
Morlet parameter:
κ=7, σ=1
The wavelet ridge at r≈ 3.8Å is resolved and shows two peaks at different k.



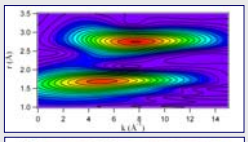
Result:
With WT the two contributions can be resolved (example: strontium uranyl carbonate)
Next step: Application to aqueous uranyl carbonate complexes

Application 3

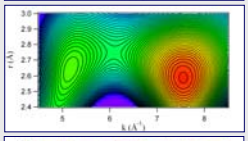
Objective :
Verification of the replacement of 3d metals by Al in Layered Double Hydroxides (LDH)



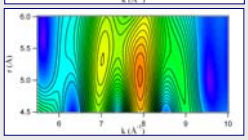
Overview wavelet
Morlet parameter: κ=15, σ=1
The ordinate is analogous to the FT.



Detail wavelet
Morlet parameter:
κ=5.5, σ=1
The wavelet ridge at r≈ 2.8Å is resolved and shows two peaks at different k.



Detail wavelet
Morlet parameter:
κ=9.9, σ=0.47
The MS ridge at r≈ 5.5 Å is resolved and shows two peaks at different k.



Result :
Al and Zn in the first metal shell are clearly discriminated, which is impossible with other methods.
The focused MS paths at r≈ 6 Å show both Zn and Al.

Open questions

- **Are other wavelets even better suited for EXAFS data analysis?**
- **Quantitative investigation of the resolution properties**
- **Influence of the k-weighting of the spectra, etc.**

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References, related links and Download of the EXAFS-wavelet program:
www.esrf.fr/exp_facilities/BM20/Software/Wavelets.html

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