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Three-dimensional modeling of EXAFS spectral mixtures by combining Monte-Carlo Simulations and Target Transformation Factor Analysis

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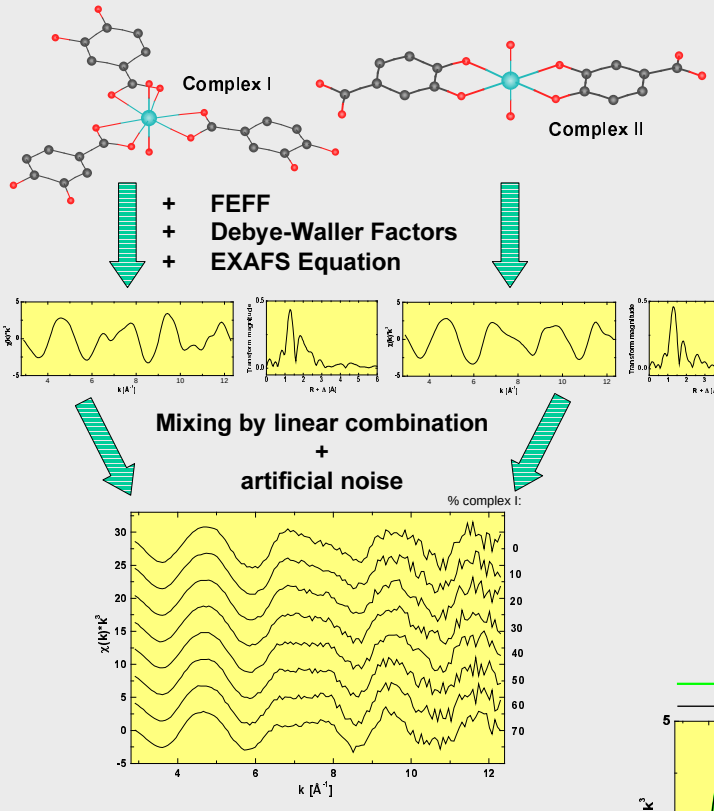
Introduction

- EXAFS spectroscopy is the method of choice to determine the structure of aqueous metal species. However, the method depends on the preparation of a sample with only the target species (either for shell fitting or to derive the spectral reference for linear combination fits).
- Actinide aqueous chemistry is very complex, preventing often the preparation of a sample, which contains only one species. This means one can measure only EXAFS spectral mixtures.
- Iterative target test factor analysis (ITFA) is able to extract the spectra of each of the species only, if the speciation, i.e. the relative concentrations of the species, can be derived from thermodynamic calculations or from other spectroscopic techniques.[1]
- We developped a novel approach, which is solely based on an estimate of the ligand structure. Using this combination of Monte-Carlo simulation and ITFA, we are able to derive a refined structure of the species from the mixture.[2]
- Here we investigate the reliablity of this approach using a well-understood model system, U(VI) protocatechuic acid.

Theoretical EXAFS spectral mixtures of two U(VI) protocatechuic acid (PA) complexes



Objective:

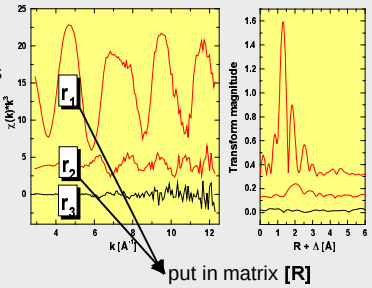
Isolation of the structure of the U(VI)-PCA **complex I** under ill-defined conditions (mixtures, large noise, short k-range: 3.1-12.4 Å^{-1}).

Conclusions

- Even under ill-defined conditions MCTFA is able to isolate the structure and the spectra of the pure complexes from the EXAFS spectral mixtures.
- For diluted samples (noisy spectra), i.e. for most environmentally relevant systems, the prediction of the structure is restricted up to 4–5 Å radial distance.

Steps of MCTFA:

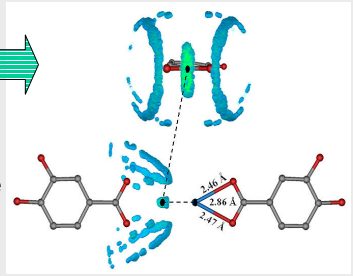
- **Principal component analysis** to determine the number of complexes (red – important eigenvectors):
- take the ligand structure of PA and calculate the theoretical EXAFS spectra x_{test} for random U-positions



put in matrix **[R]**

- **Target transfomation**[3] of x_{test} : $x_{test}^{\#} = [R] * [\Lambda]^{-1} * [R]' * x_{test}$
- Calculate the error (**RET**) in x_{test} by using $x_{test}^{\#}$

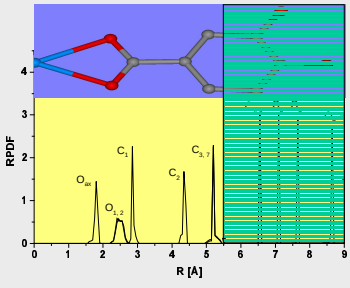
RET distribution for U(VI) around the PA ligand
(green balls indicate best fits, blue balls bad fits, black dot – lowest RET ⇒ best U-position)



- Replicate the estimated complex structure to get a statistical ensemble of molecules
- Move each ligand atom ⇒ statistical **simulation of structural disorder + refinement of the complex structure**

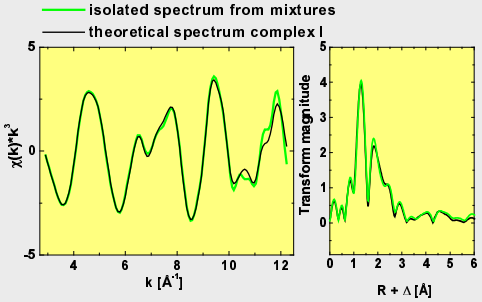
Result of MCTFA:

Isolated radial pair distribution functions for complex I, yellow box – reliable, green box - not reliable



Derived and theoretical radial distances for complex I, green box - not reliable

Atom	R [Å] determined	R [Å] theorie
O_{axial}	1.797	1.797
O_2	2.480	2.469
O_1	2.490	2.470
C_1	2.864	2.860
MS O_{axial}	3.593	3.594
C_2	4.360	4.360
C_7	5.201	5.187
C_3	5.209	5.206
C_6	6.529	6.536
C_4	6.529	6.561
C_5	7.107	7.144
O_3	7.659	7.556
O_4	8.624	8.486



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/2/ Rossberg A., Scheinost A.C., *Physica Scripta*, (2005) in press

/3/ Malinowski, E. R., Anal. Chim. Acta, **103**, 339-354 (1978)

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