Structure elucidation and occurrence of Tc(IV) pyrogallol complexes

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^{99}Tc

- Fission product of uranium-235
- β - emitter
- **Long half-life: 2.13 x 10^5 y**
- High yield in radio-active waste (6% of all fission products !)
- **Potential migration upon storage**
- **Potential association with HS**

^{99}Tc behaviour in natural systems

Organic matter

(Maes *et* al., 2003;2004)

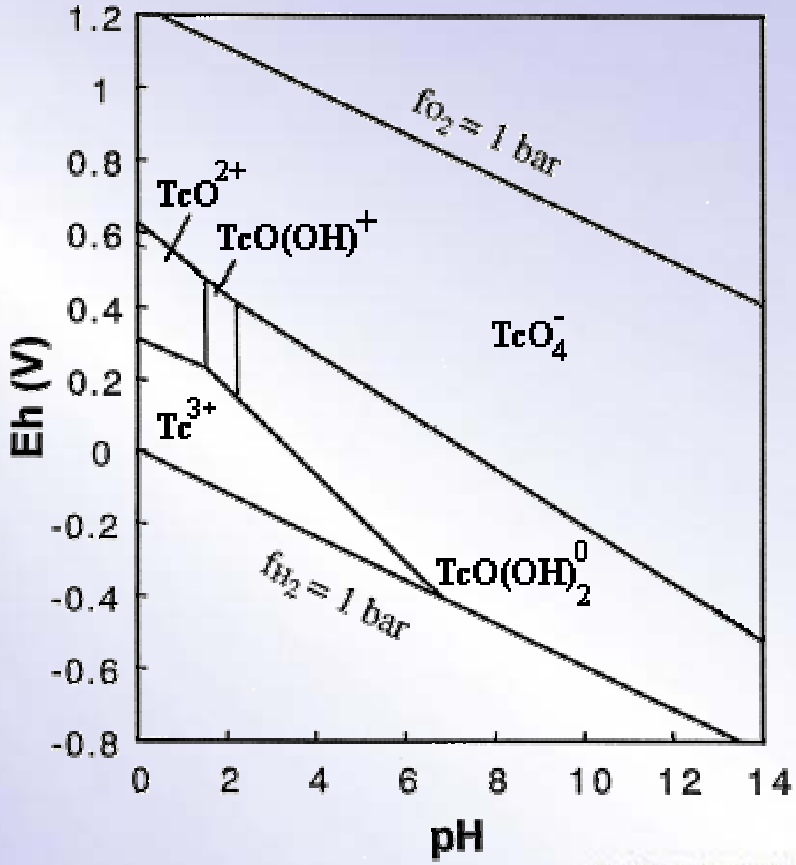
TcO_4^- —reduction / Gorleben, Boom Clay→ **Tc(IV)-HS**

First sight contradiction

$TcO_{2,el.red.}$ —migration test / Boom Clay→ ~~**Tc(IV)-HS**~~

(Baston *et* al., 2002)

~~**Organic matter**~~



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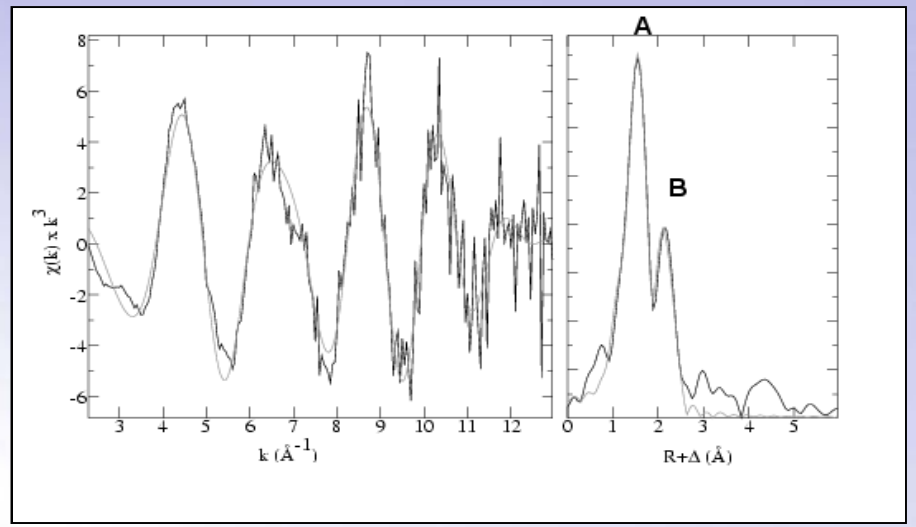
Tc(IV) - HS

Identity ?

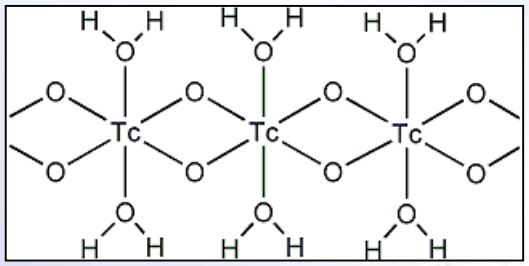
- **Colloid association Tc(IV) eigencolloids and HS**
- **Hydrophobic interaction**



Proof ?

- **XANES, EXAFS**
- **SEC**
- **Modelling BC batch SHUBERT approach**

Tc-O			Tc-Tc		
C.N.	R	σ^2	C.N.	R	σ^2
6	2.03	0.006	1.5	2.56	0.005



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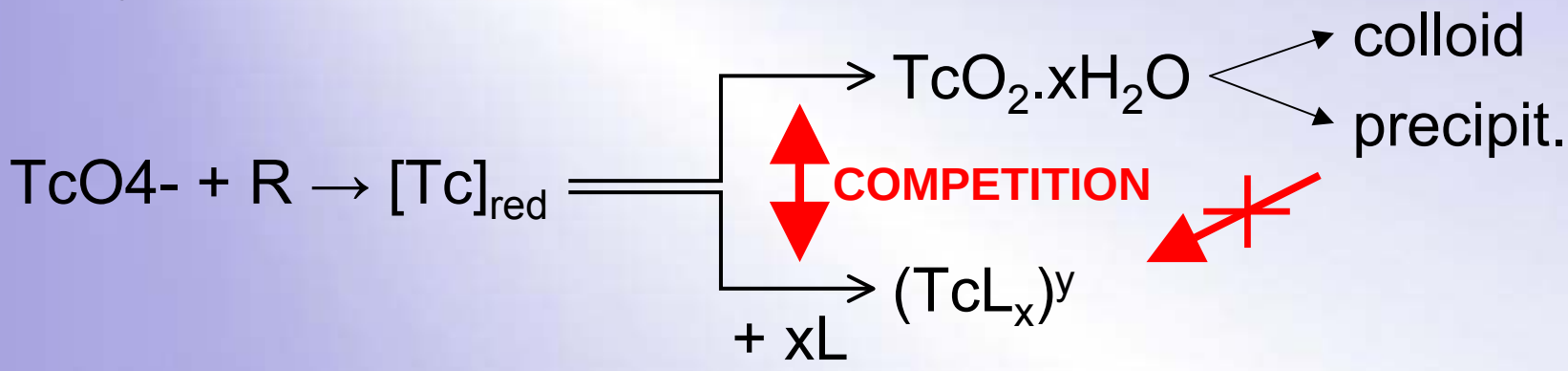
Tc(IV)-HS Complexation ?

- **Possible ?**
- **Nuclear medicine**

  range of synthetic Tc(IV) complexes e.g. EDTA, cysteïne, …



- **High pH (2M NAOH) Tc(IV) complex stability series (Lukens *et* al., 2002)**

$(OCH_2O)_4Tc_2(\mu\text{-}O)^{4-}$ > $TcO_2.xH_2O$ > $(H2EDTA)_2Tc_2(\mu\text{-}O)_2^{2}$

DIOL

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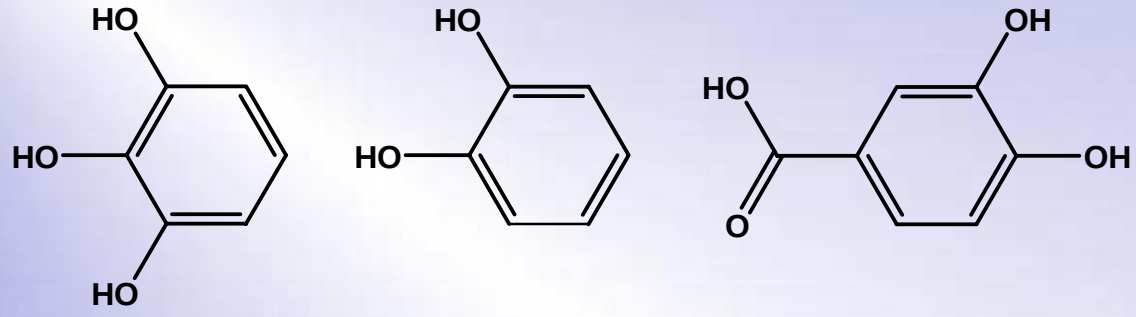
Simple HS-like ligands

- **Intermediates of wood degradation process**



PYROGALLOL CATECHOL PROTOCATECHUIC ACID

- **High pH Tc(IV) species stability**

diol > oxide > aminopolycarboxylic

- **Choice : pyrogallol**
- **Phenolic, model building block of HS**
- **Probably highest stability versus oxide**

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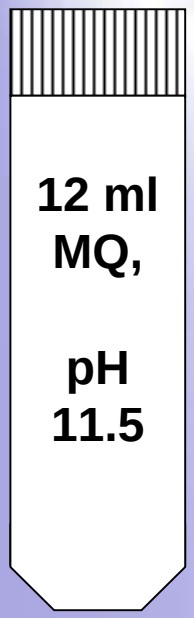
Tc(IV)-pyrogallol solutions



Daily, 12d

+

-1ml pyrogallol 1.25E-2M
-1ml $N_2H_6SO_4$ 1.5E-3M or
dithionite 6.2E-3M
- 50µl 6.2E-2M NH_4TcO_4

- **sample preparation in glovebox (N2/H2 95/5) (< 1 ppm O_2)**
- **2 weeks equilibrium**
- **8 ml samples, titration to pH 11, 8, 5, 2**
- **another 2 weeks equilibrium**

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XAS Sample Preparation & Measurement

- **8 ml sample, concentrated to 2 ml**
- **vac. distillation, 25°C, liquid N_2 trap**
- **sample container sealed in 2 PE bags**
- **transport to ESRF in steel container under N_2 atmosphere**
- **Measurement:**
  - **ROBL beamline (BM20)**
  - **Transmission mode, 21 → 22.5 keV**
  - **Mo foil standard, energy recalibration**

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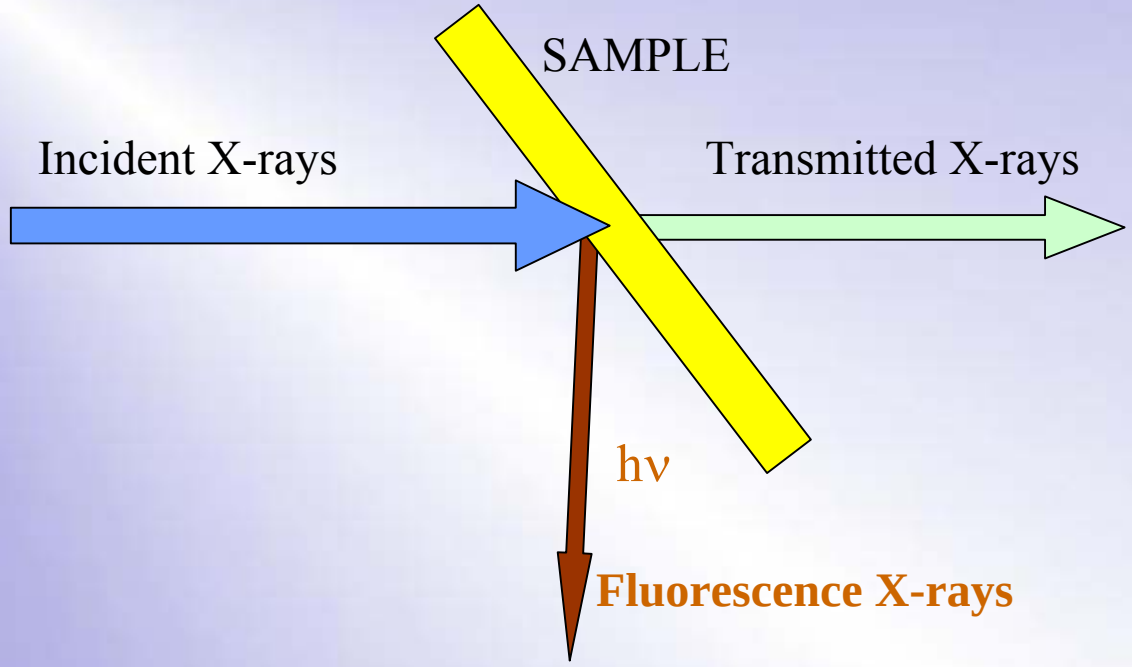
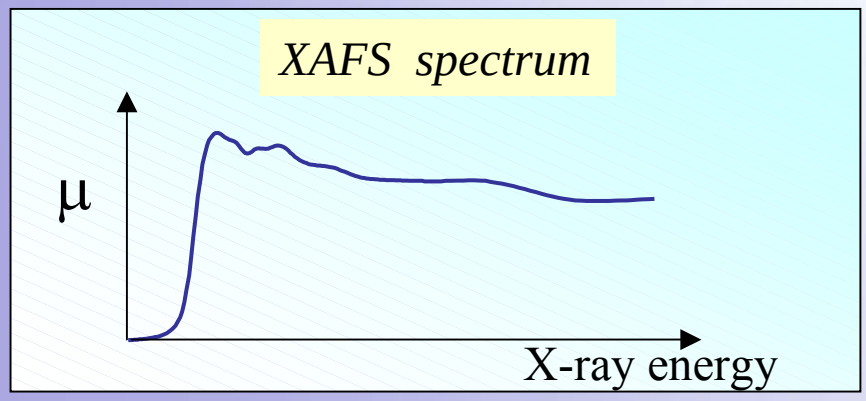
XAFS measurements





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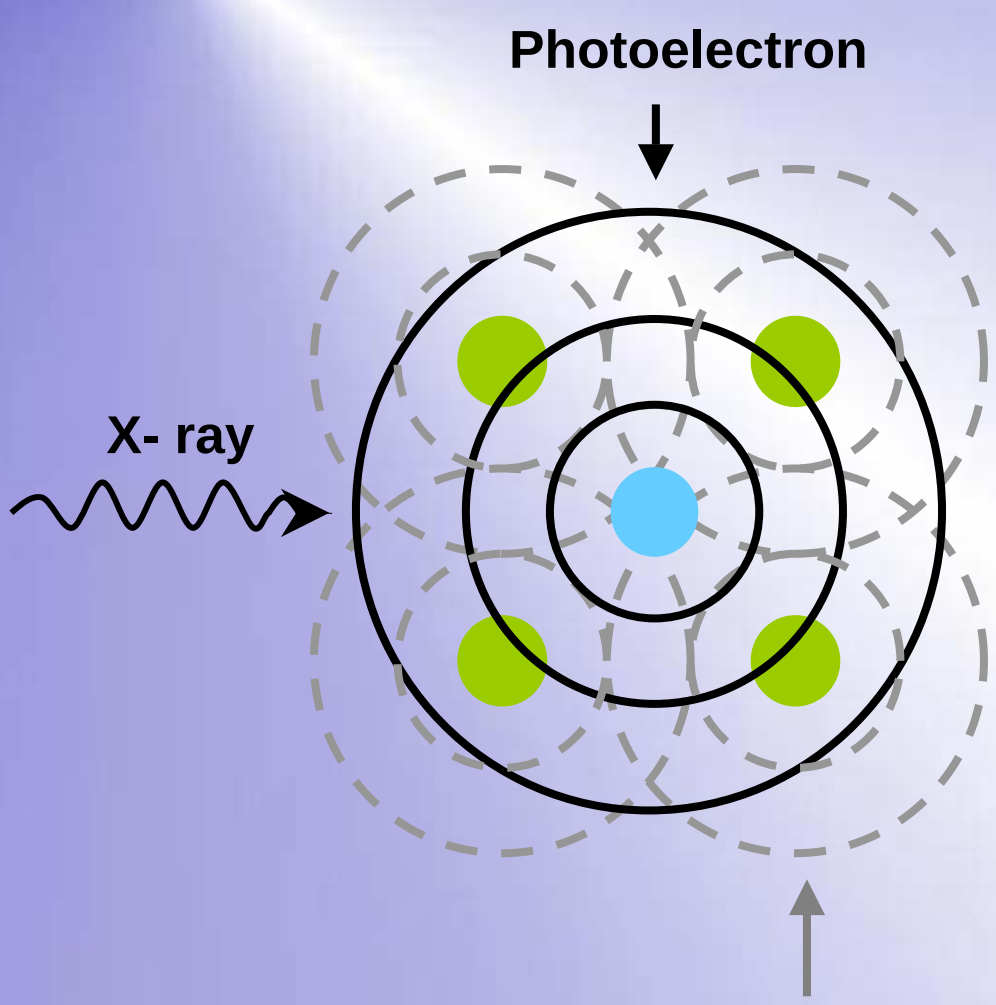
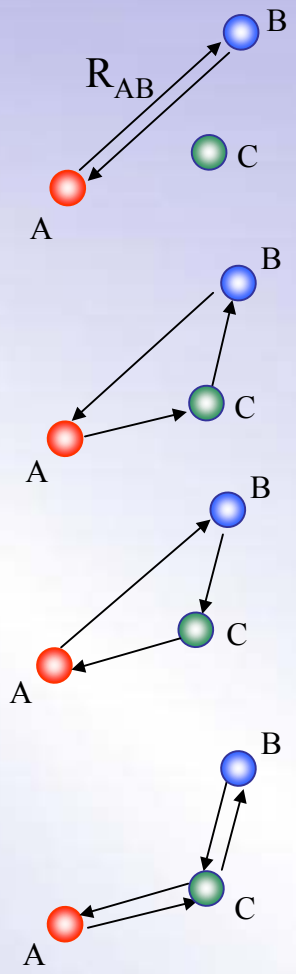
EXAFS phenomenon





Single scattering
‘ 2 legs ’

Double scattering
‘ 3 legs ’

Double scattering
‘ 3 legs ’

Triple scattering
‘ 4 legs ’

Angular info

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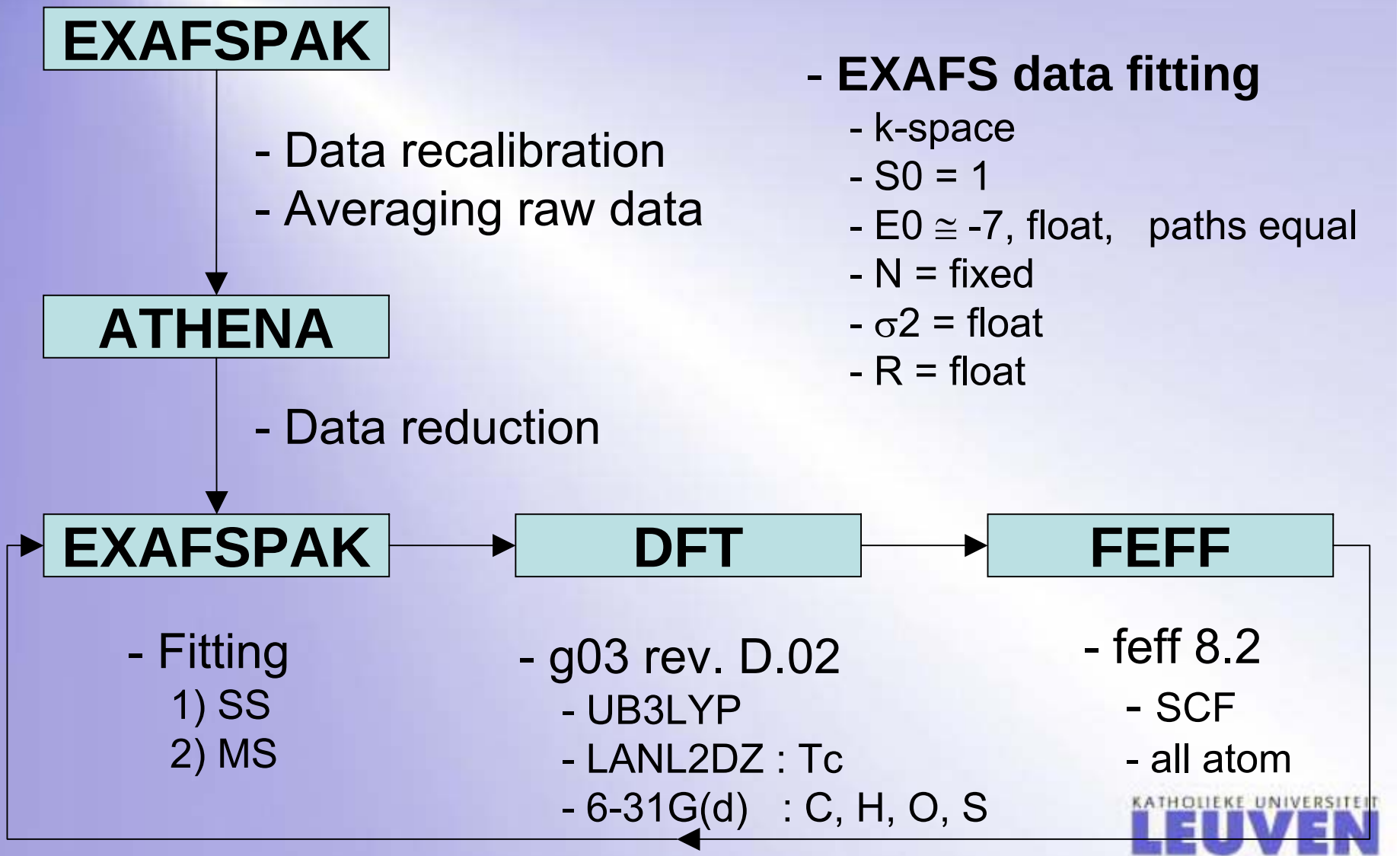
XAS data analysis



- **EXAFS data fitting**
  - k-space
  - S0 = 1
  - E0 ≅ -7, float, paths equal
  - N = fixed
  - $\sigma 2$ = float
  - R = float

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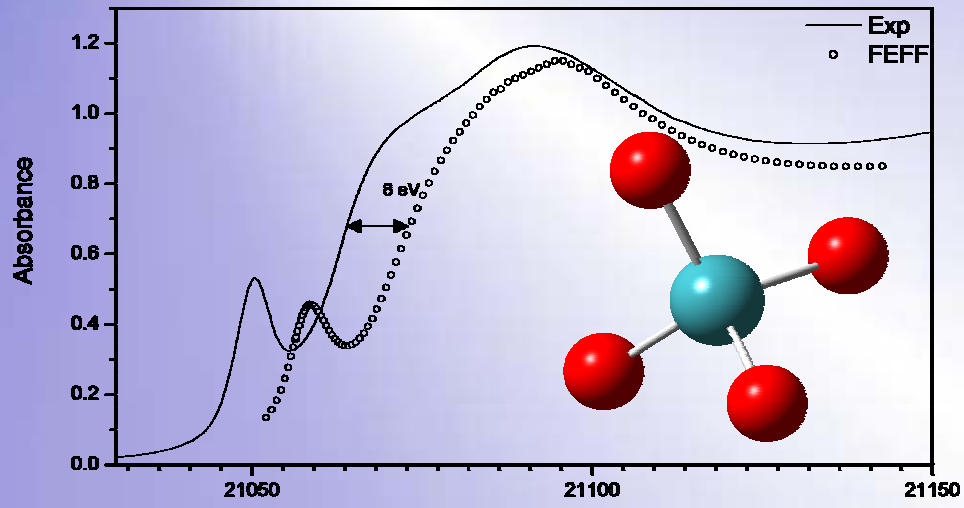
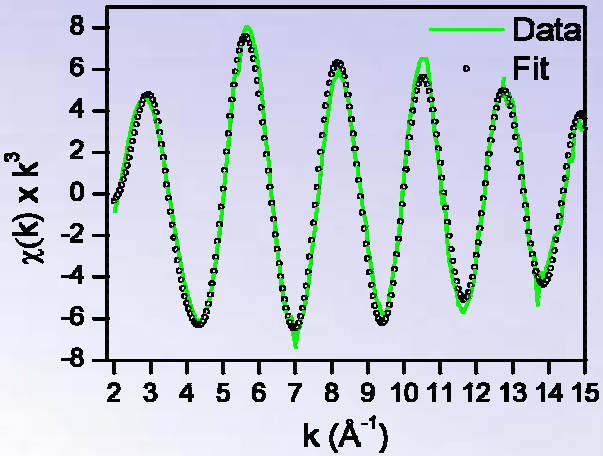
Software Test TcO_4^-





	DFT	EXAFS		
	d(Tc-O) (Å)	N	R (Å)	σ^2
SS: Tc-O	1.75561	4	1.725	0.00164
MS: Tc-O-O		12	3.191	0.00577

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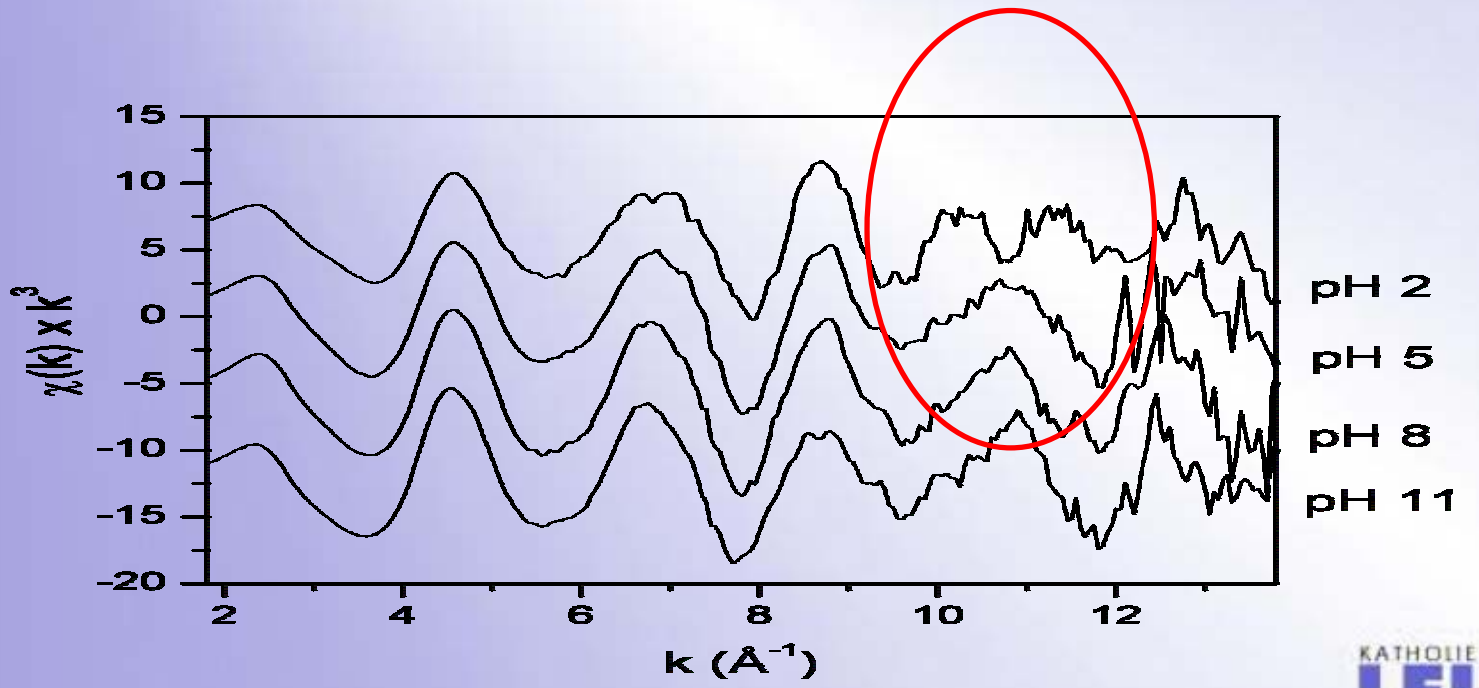
Tc(IV)-pyrogallol (N_2H_4)

- **amplitude difference**
- **pH 2 <> pH 5, 8, 11**



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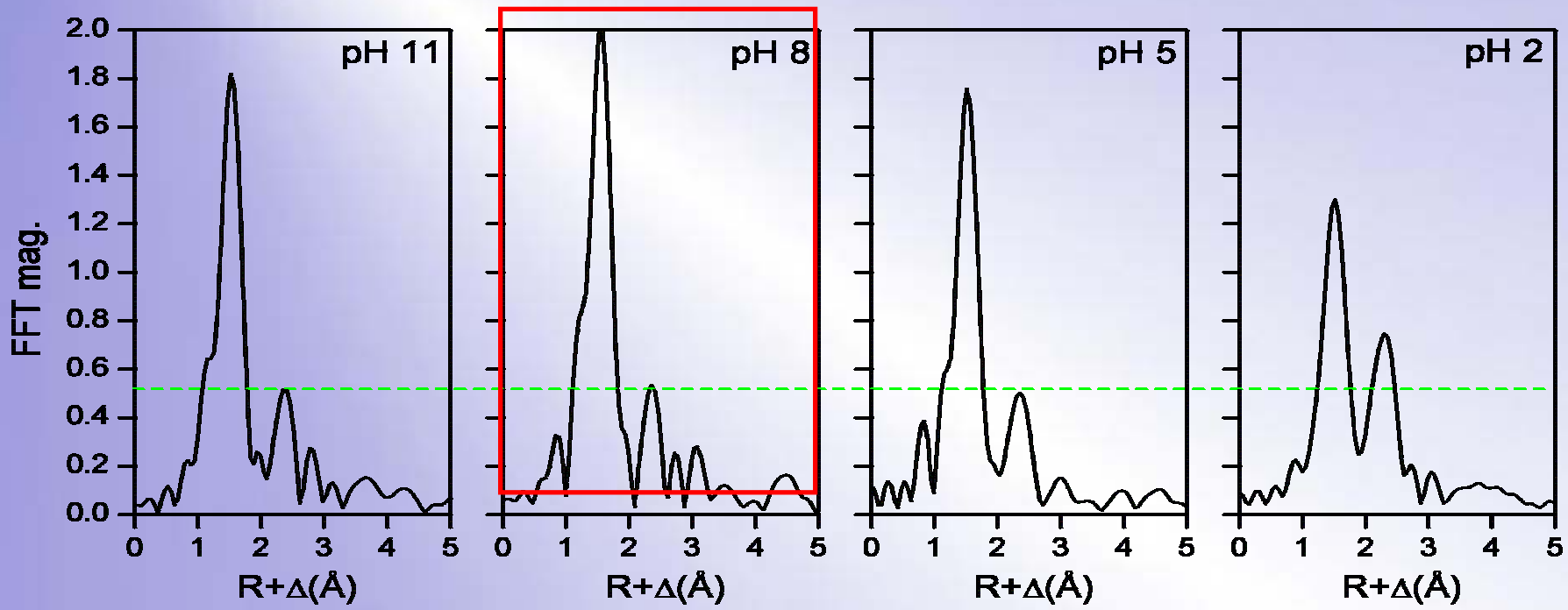
Tc(IV)-pyrogallol (N_2H_4)



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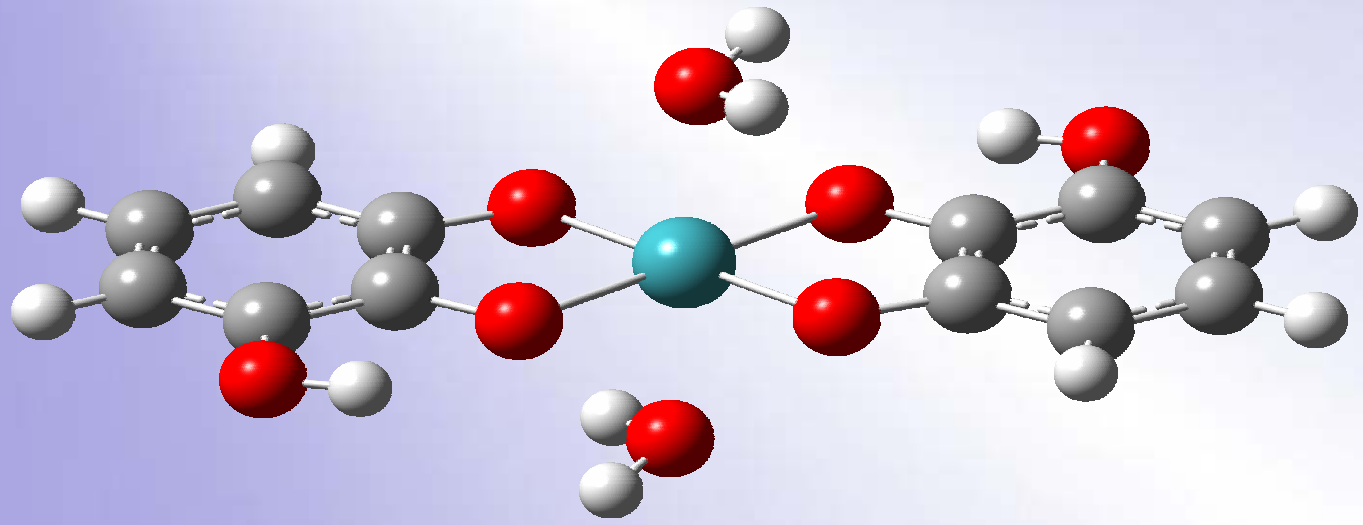
Tc(IV)-pyro (N_2H_4) – pH 8



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pH 8 – EXAFS FIT

bond	DFT	EXAFS	σ^2
Tc - O_eq	2.003	1.995	0.00093
Tc - O_ax	2.186	2.109	0.00130
Tc - C1	2.827	2.805	0.00157
Tc - C2	4.188	4.065	0.00208
Tc - O_pyr	4.788	4.79	0.00253

MS path	R	σ^2
Tc – O_eq – C1	3.09	0.00255
Tc – O – Tc – O	4.01; 4.10	0.00521
Tc – C1 – C2	4.19	0.00817
Tc – O_eq – O_pyr	4.81	0.00506

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Tc(IV)-pyro (N_2H_4) – pH 8

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