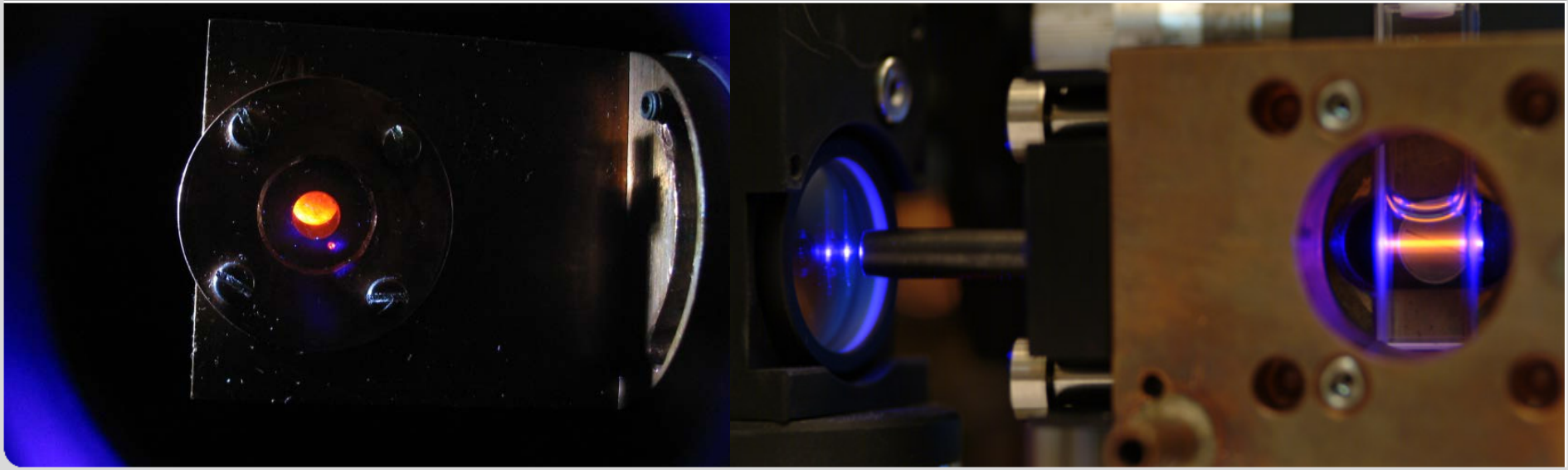
Karlsruhe Institute of Technology

Time Resolved Laser Fluorescence Spectroscopy (TRLFS)

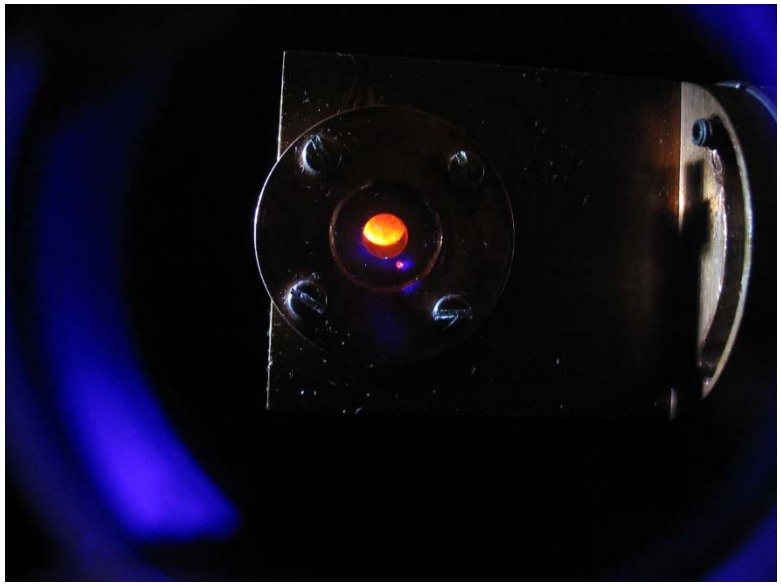
Thomas Rabung

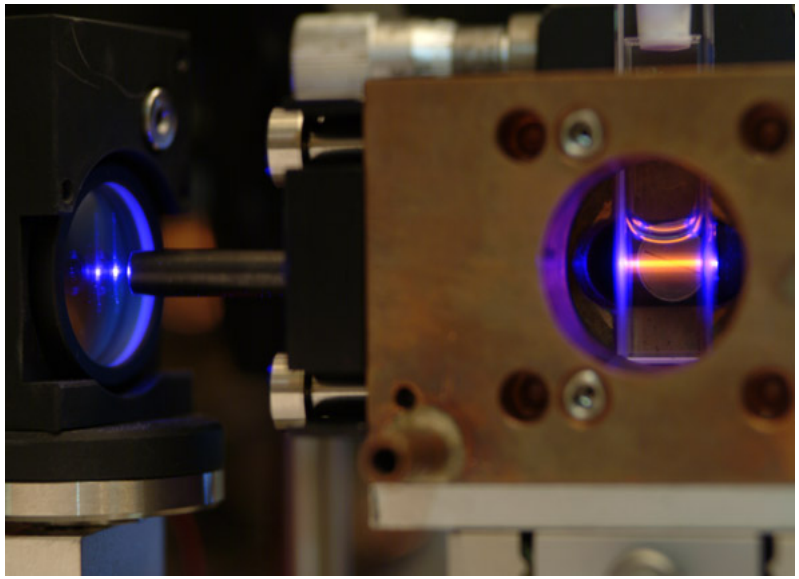
INSTITUTE FOR NUCLEAR WASTE DISPOSAL (INE)



Time Resolved Laser Fluorescence Spectroscopy (TRLFS)

- For metal ion speciation
- mechanistic understanding of aqueous complexation, surface sorption, incorporation
- model validation
- high sensitivity, in–situ experiments





TRLFS – what is necessary:

- **Laser system** (tunable: with variable emission wavelength)
  - Nd:YAG or Excimer pumped Dye-laser
  - OPO (optical parametric oscillator)

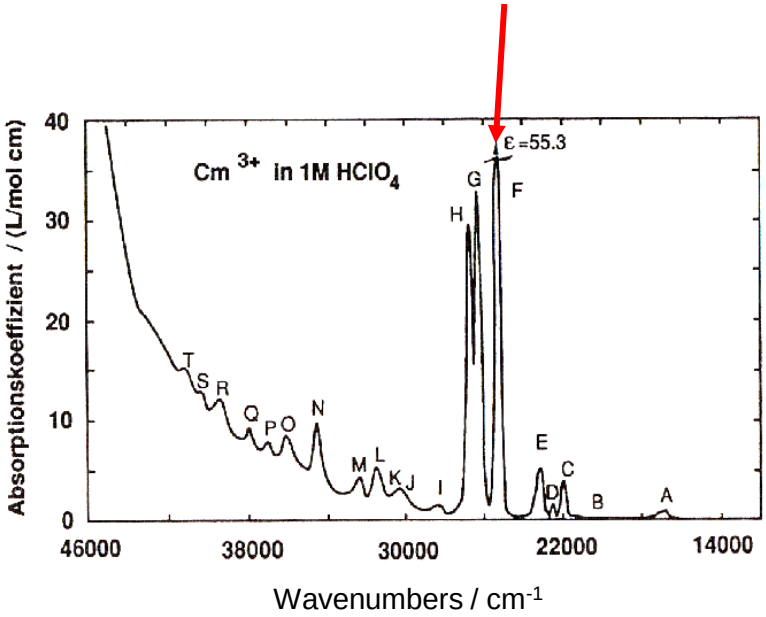
- **Fluorescent Probe**:
  - U(VI)
  - Am(III)
  - Eu(III) (inactive)
  - **Cm(III)** - highest sensitivity, „easiest“ spectra
    - mainly ^{248}Cm: $T_{1/2}$ = 350.000 years

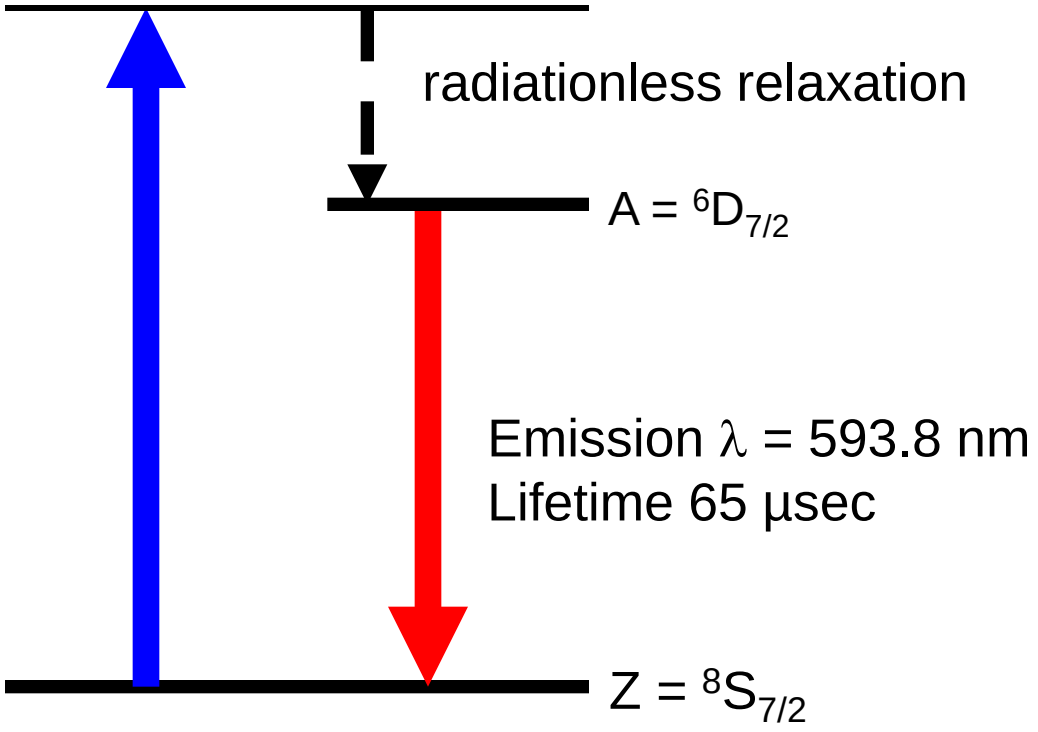
- **Detection system**: e.g. monochromator + ICCD-Camera

Cm(III)-Fluorescence Process

for Cm^{3+}_{aq} (low pH)

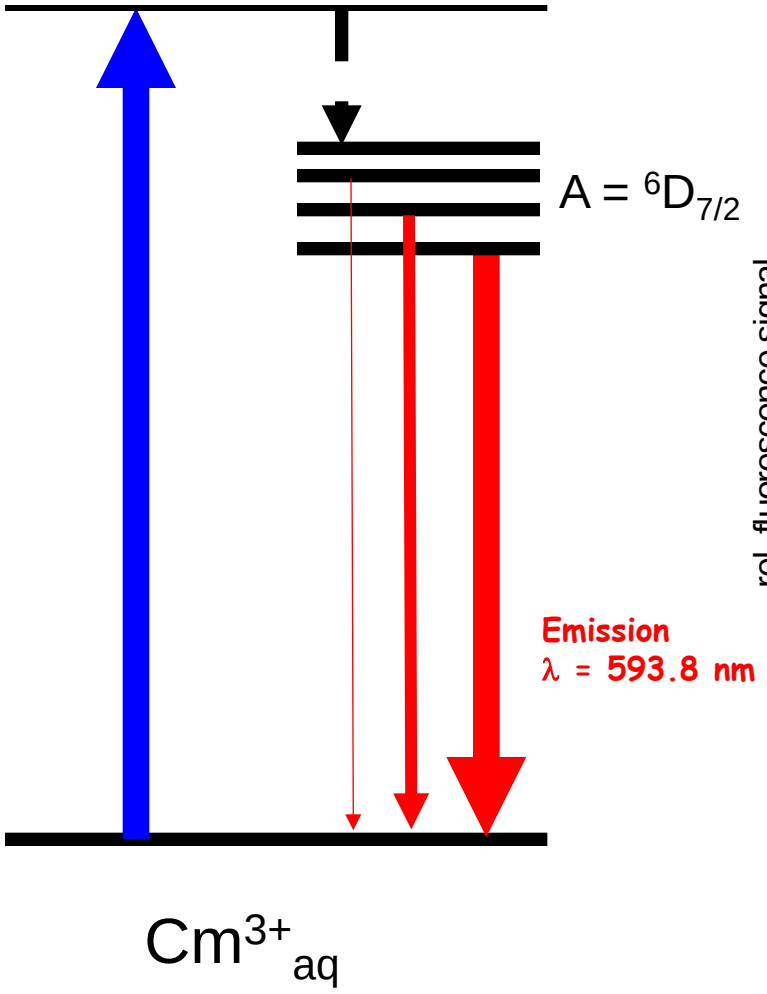
Excitation λ = 396.6 nm

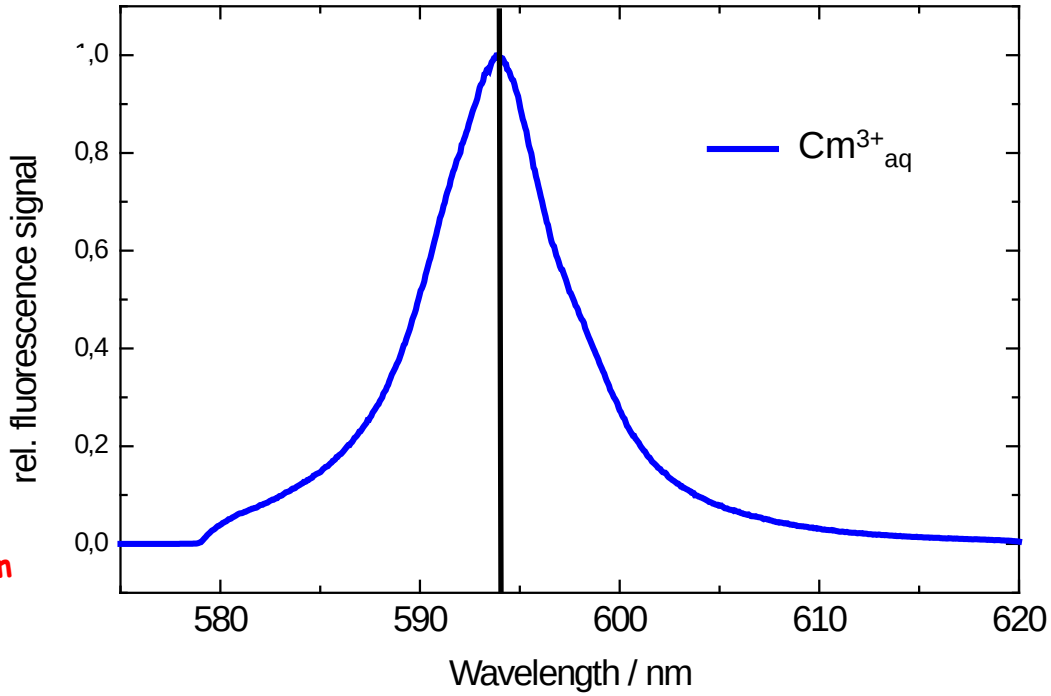




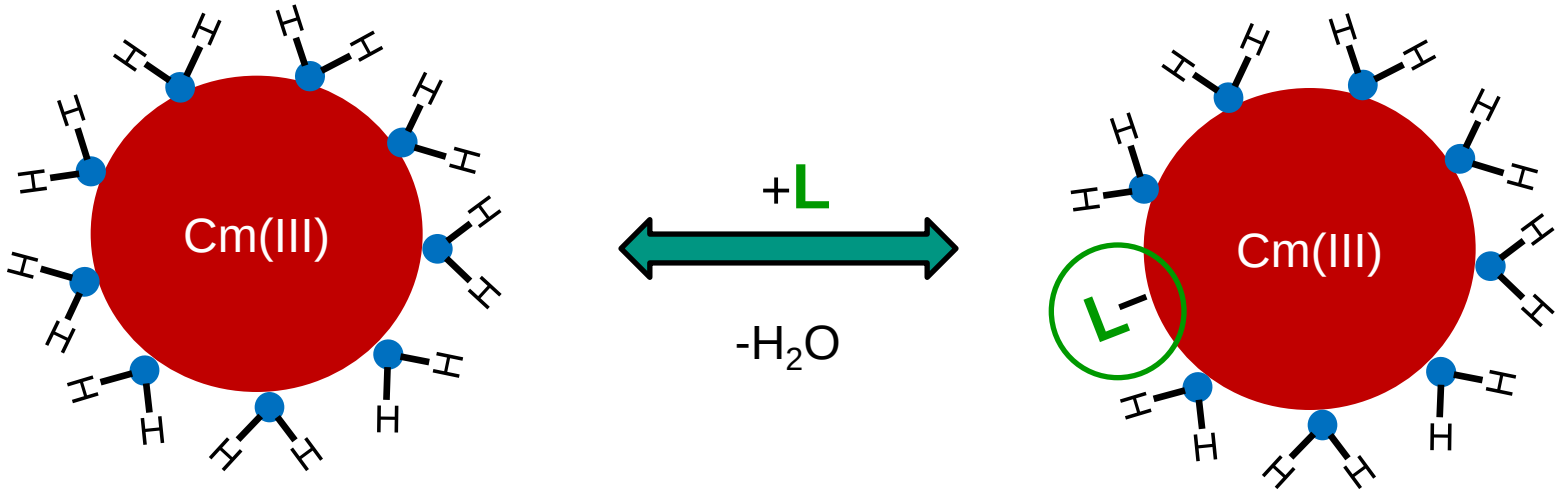
Cm(III)-Fluorescence Process

for Cm^{3+}_{aq} (low pH)





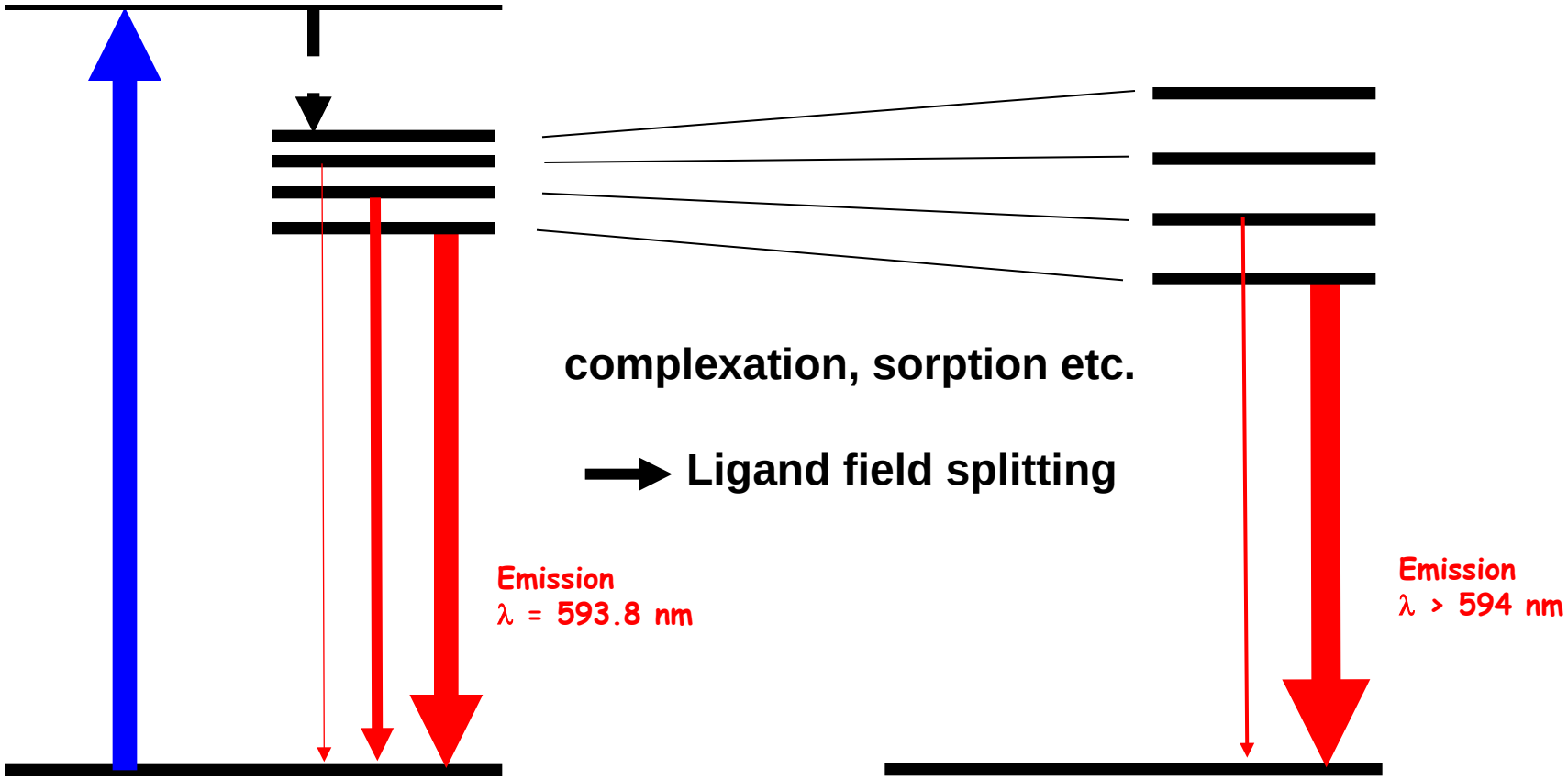
Cm(III)-Fluorescence Process



9 fold coordination with H_2O

8 fold coordination with H_2O
+ 1coordination to ligand L

Cm(III)-Fluorescence Process



Cm^{3+}_{aq}

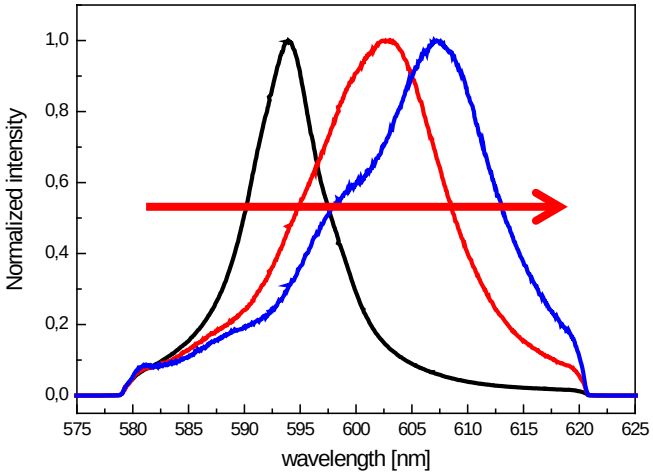
→ **red-shift of fluorescence spectra**

Cm(III)-Fluorescence Process

- The stronger the ligand ⇒ the stronger the peak shift
  (compared to the aquo ion)

- The more ligands are bound ⇒ the stronger the peak shift

⇒ **Chemical information (speciation) from the peak position**



Cm(III)-Fluorescence Process

The isolated Cm^{3+} ion (without surrounding water molecules) has a fluorescence lifetime of ~1300 µsec.

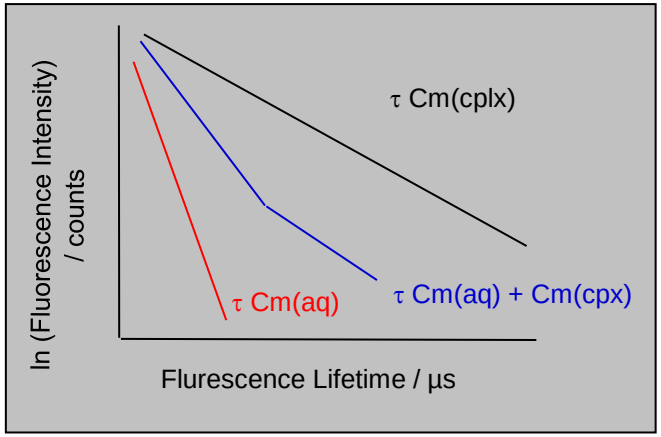
BUT:

In the presence of coordinating water/OH^- ligands radiationless energy transitions from the first excited Cm state to vibronic states of these ligands

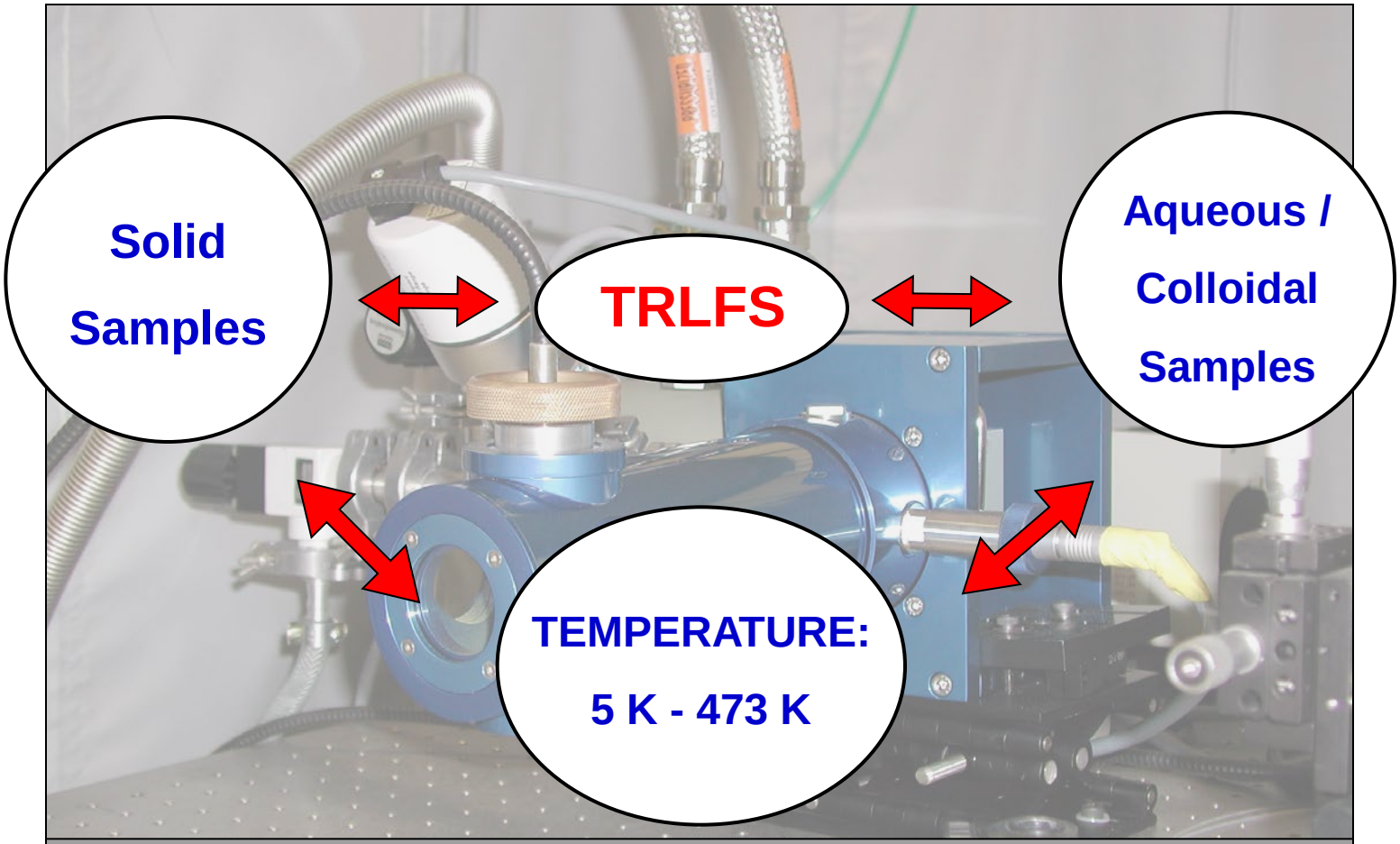
⇒ shorter lifetimes

⇒ number of coordinated water/OH^- ligands can be estimated from fluorescence lifetime.

⇒ **Chemical information (speciation) from fluorescence lifetime**



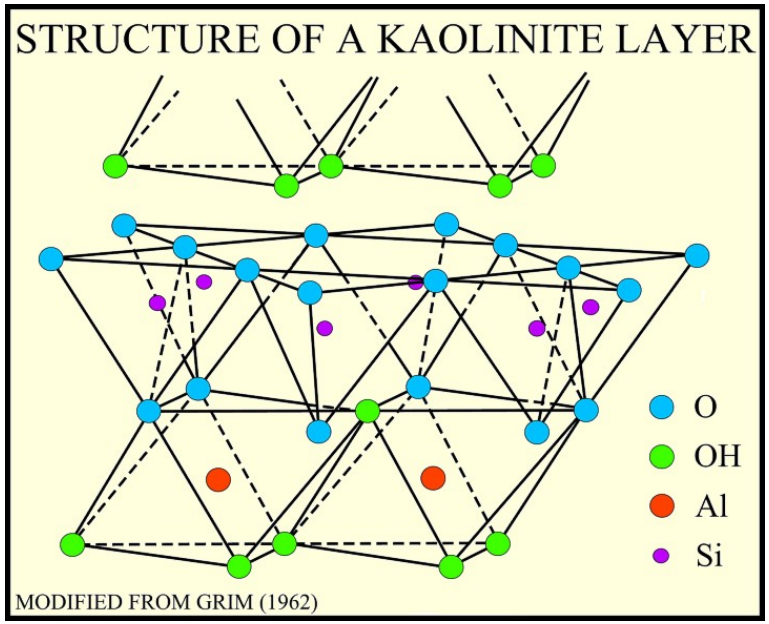
Potential of Cm(III)-TRLFS

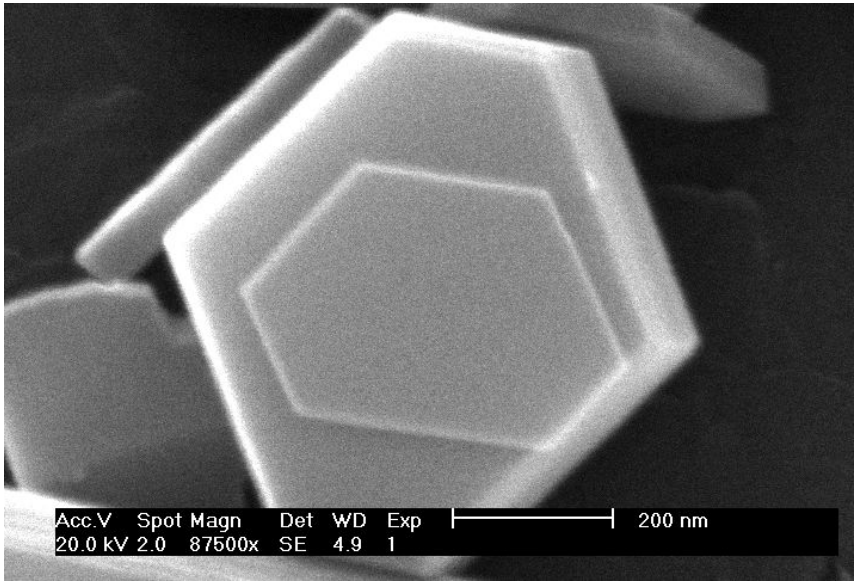


High Sensitivity: Cm(III) concentration: 10^{-7} - 10^{-9} mol/L
10^{-11} - 10^{-14} mol/cm^2

Example:

Cm(III) Sorption onto Kaolinite*

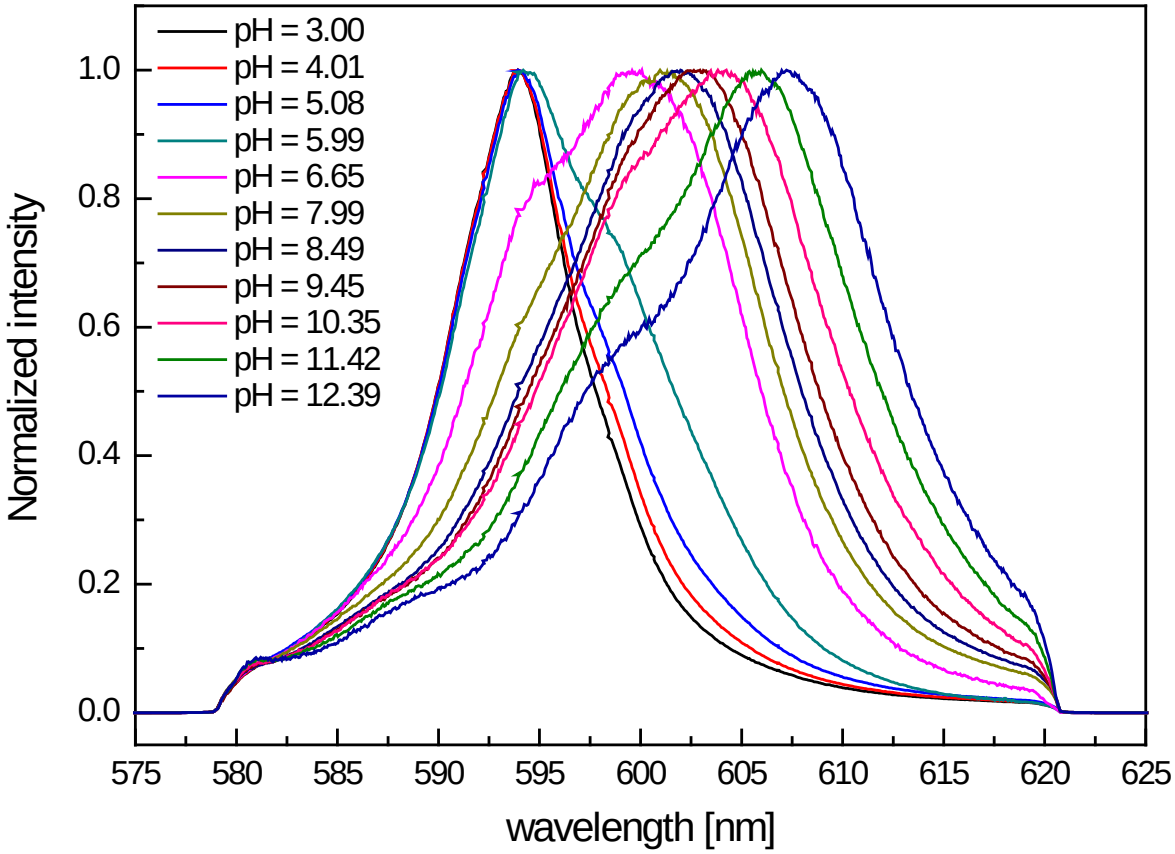




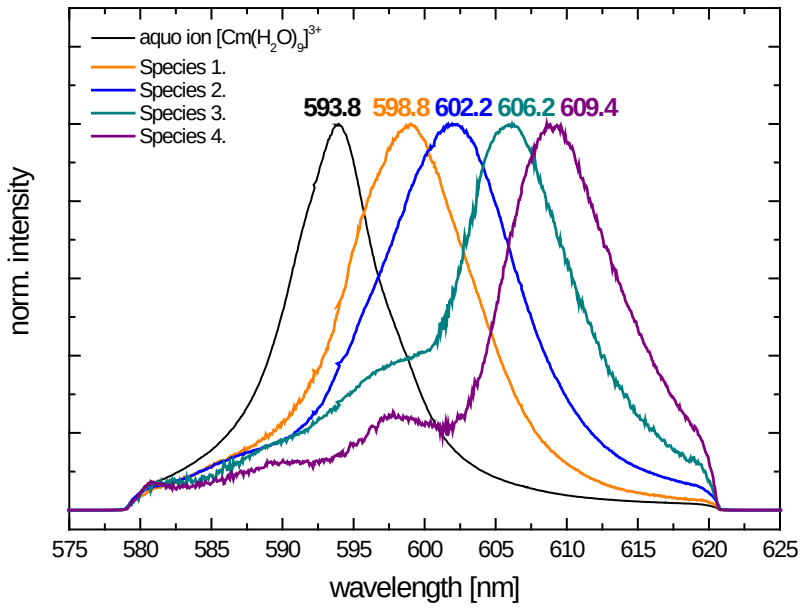
*Huittinen et al., Radiochim Acta 98 (2010)
*Huittinen et al., Geochim. Cosmochim. Acta 99 (2012)

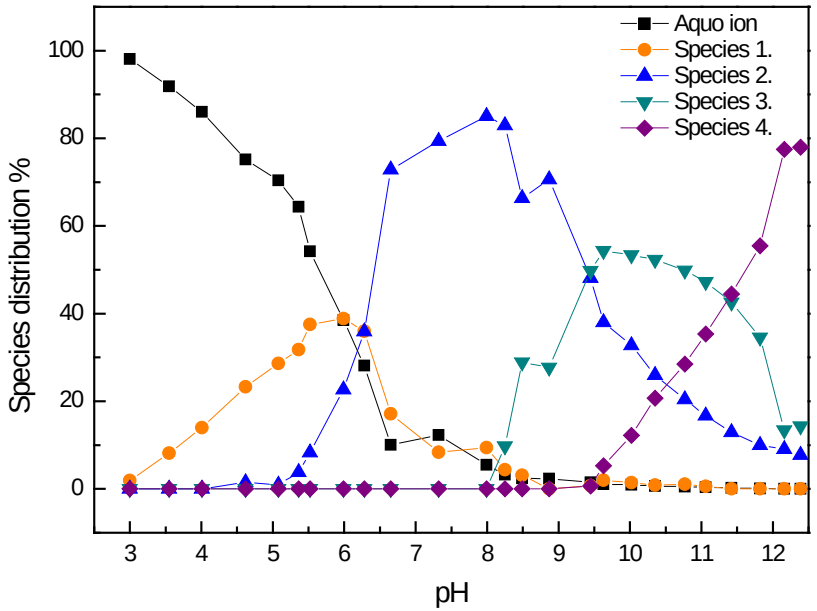
Kaolinite – Cm(III) emission spectra

2E-7 mol/L Cm(III), 0.25g/L Kaolinite (St. Austill), 1mM $NaClO_4$



Kaolinite – species distribution





Ca-exchanged Montmorillonite* 599.1 nm, 603.2 nm, 607.1 nm, 5<pH<12

Na-exchanged illite* 598.8 nm, 602.3 nm, 605.5 nm , 4<pH<12

Species 1 $\equiv S\text{-}O\text{-}Cm^{(2+)}(H_2O)_5$

Species 2 $\equiv S\text{-}O\text{-}Cm(OH)^{(+)}(H_2O)_4$

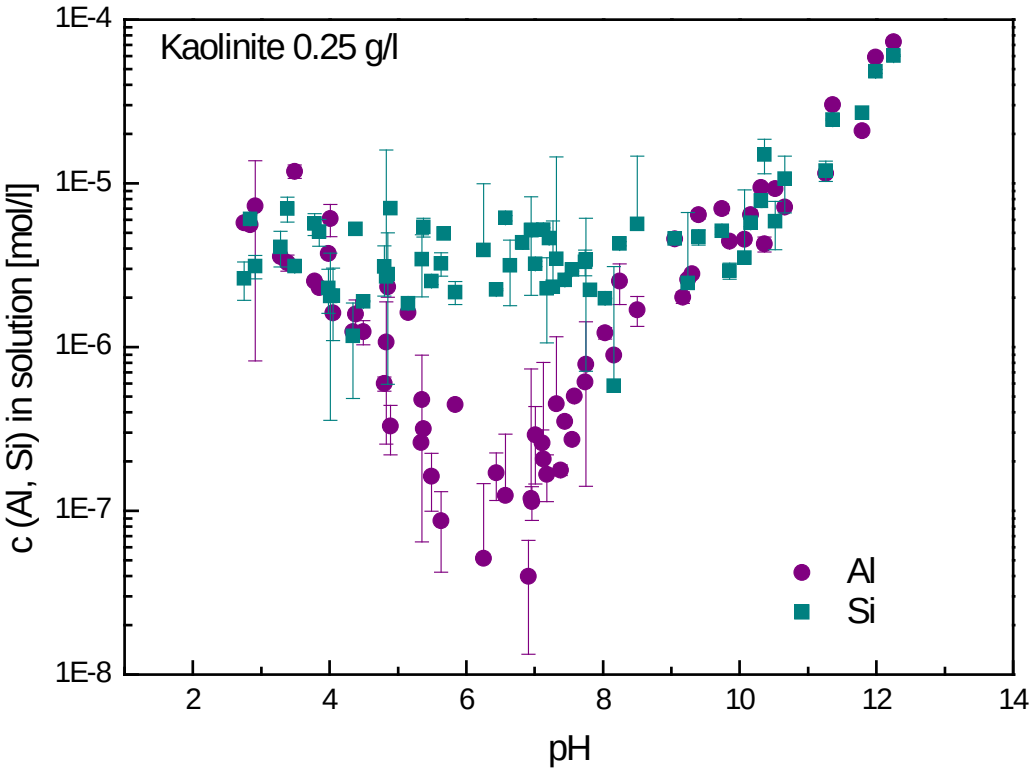
Species 3 $\equiv S\text{-}O\text{-}Cm(OH)_2^{(0)}(H_2O)_3$

Species 4 ?

** Rabung et al., Geochim. Cosmochim. Acta 69 (2005)*

Kaolinite – species 4?

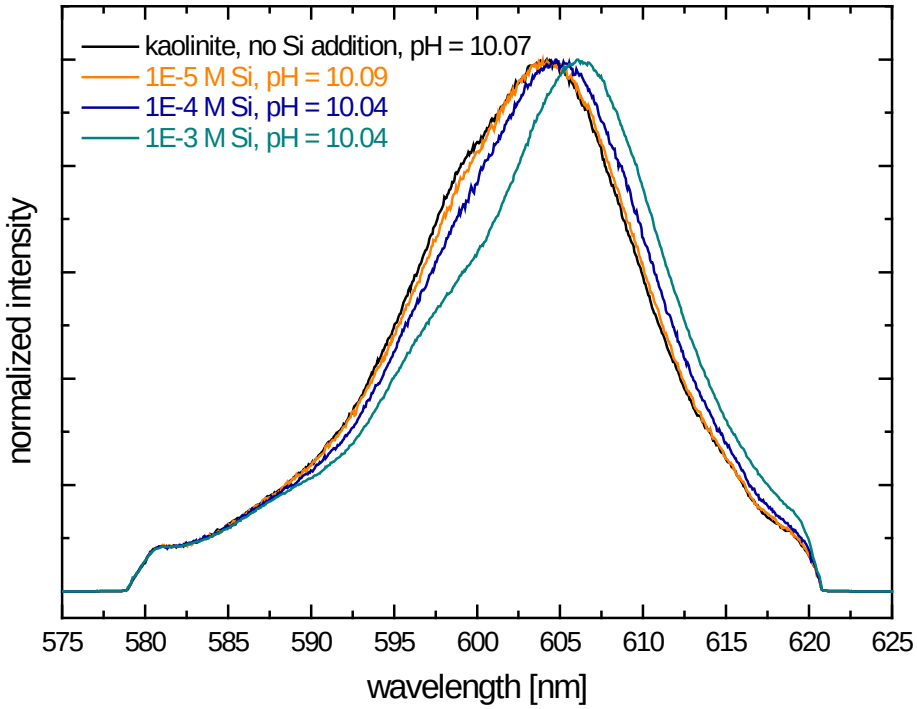
- Al, Si or Al/Si effect?
- Precipitation of alumosilicates or surface complexation with aluminate or silicate?

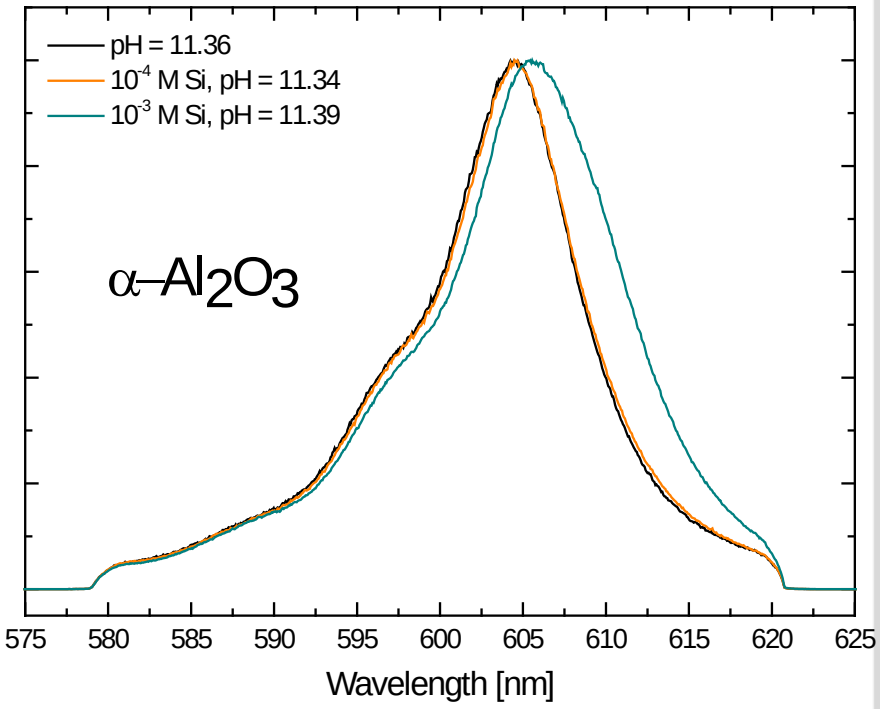


***Panak et al., Colloids Surf., A 227 (2003)*

Kaolinite – oversaturation experiments

Addition of Si



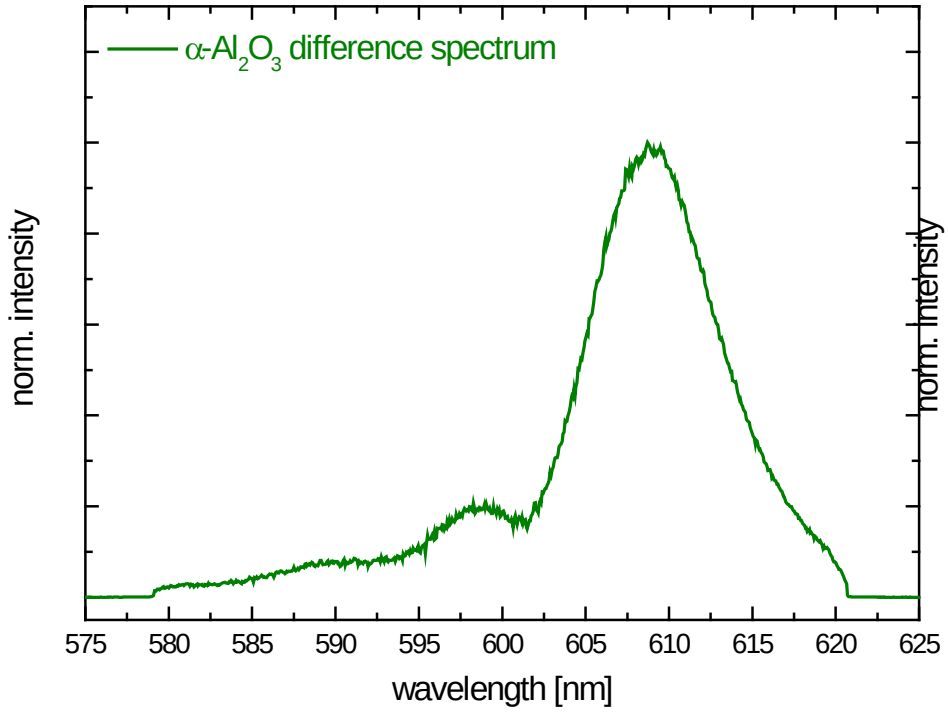


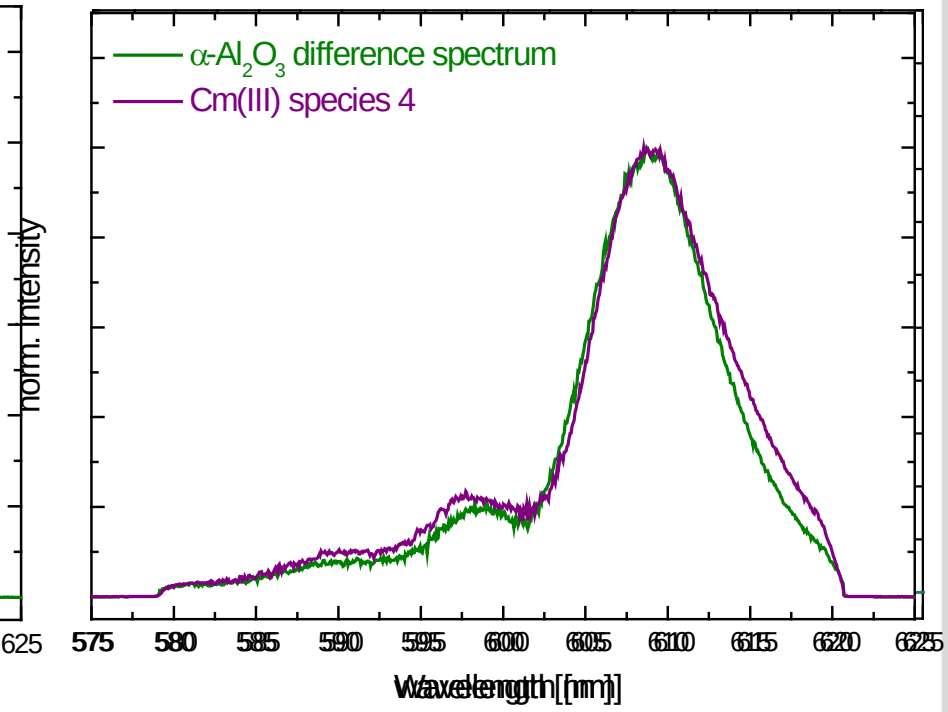
Silicate effect on Cm speciation

$$\equiv S\text{-}O\text{-}Cm(OH)_x\,(Si(OH)_3)_y^{(2-x-y)}(H_2O)_{5-x-y}$$

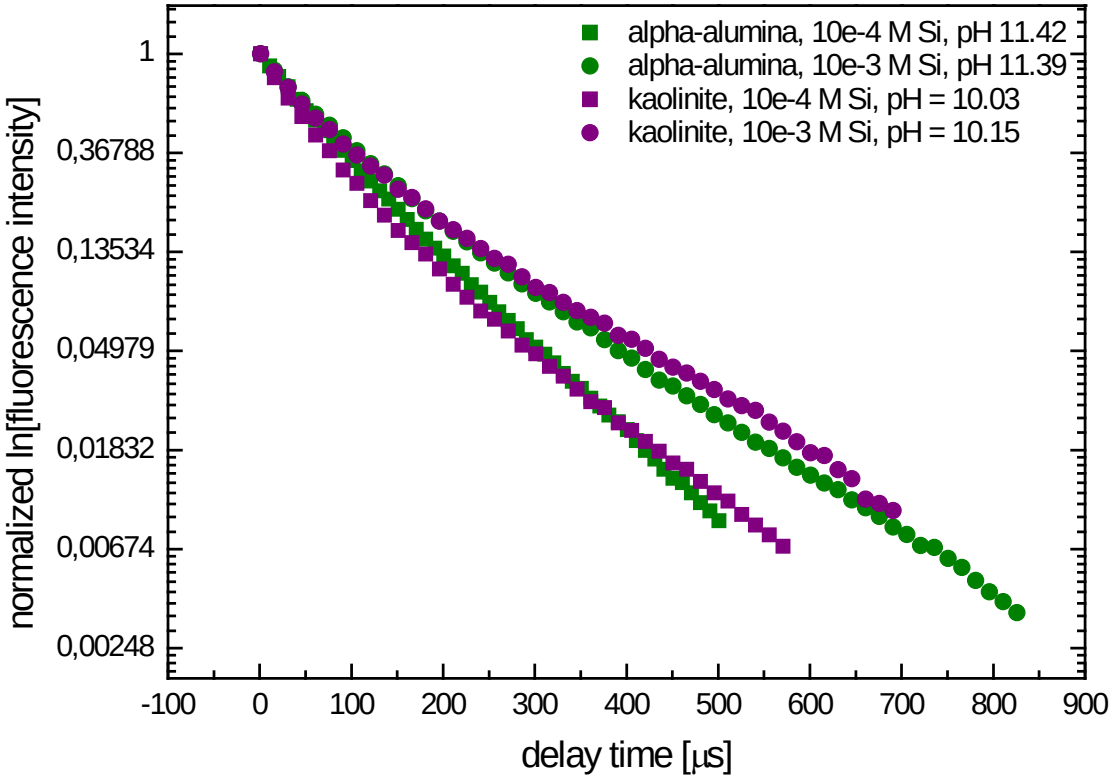
Kaolinite – oversaturation experiments

Addition of Si





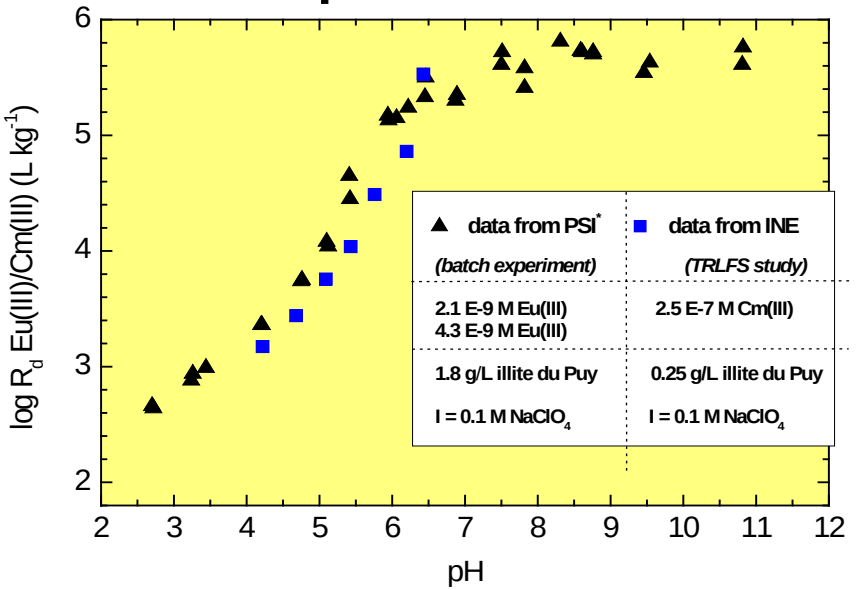
Si addition to Kaolinite and α-Al_2O_3



$\equiv S\text{-}O\text{-}Cm(OH)_x\,(Si(OH)_3)_y^{(2-x-y)}(H_2O)_{5-x-y}$

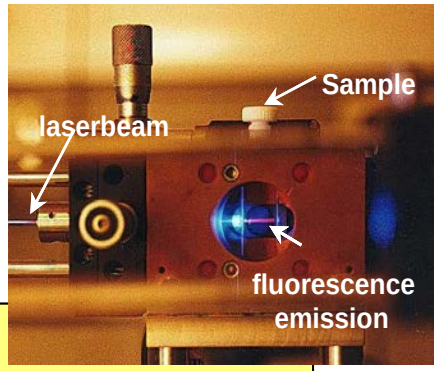
Cm(III)/Eu(III) sorption onto Na-exchanged illite-IdP-1

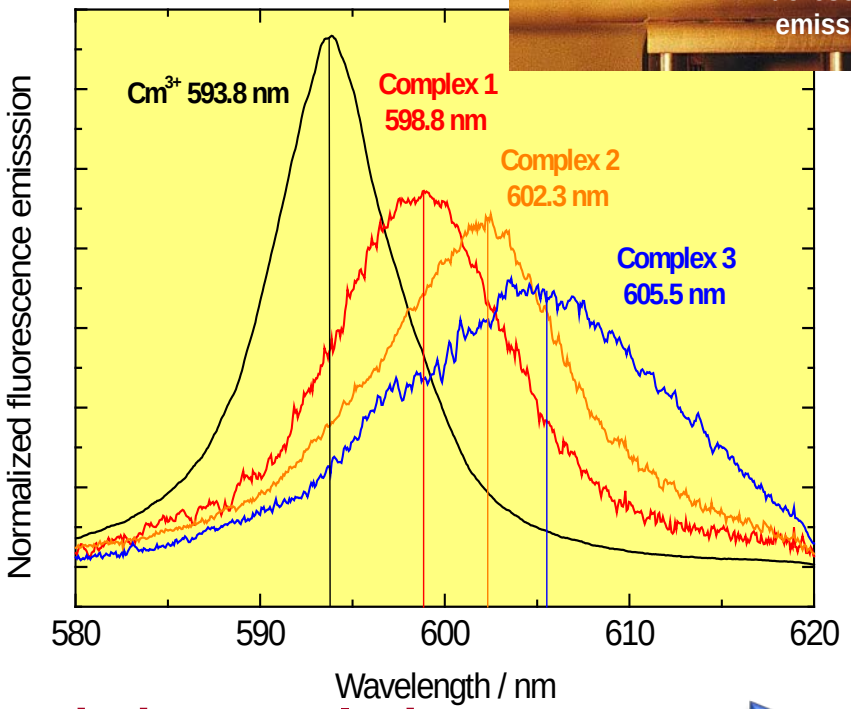
Batch sorption data



*Poinssot, C., Baeyens, B., Bradbury, M.H.: PSI Bericht Nr. 99-06

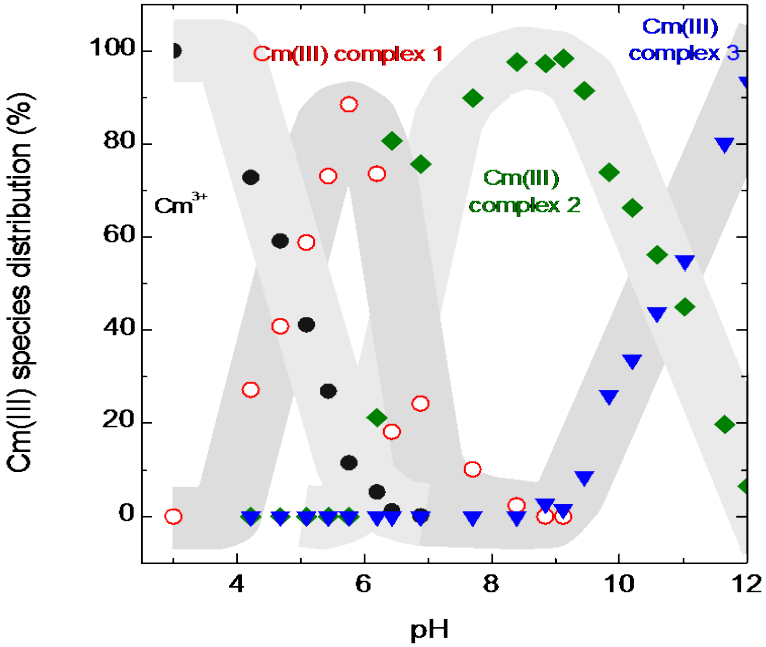
TRLFS



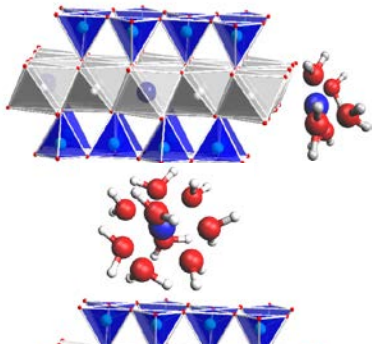


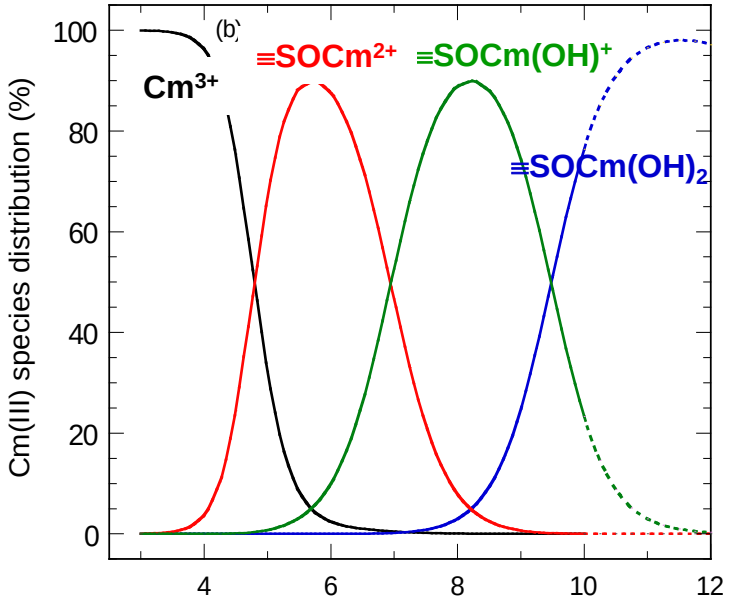
Peak deconvolution

Comparison of species distribution from TRLFS and modeling



- **TRLFS**





- **Modeling** (new hydrolysis constants and small variation of surface complexation constants)

Hydrolysis species	Log stability constants	selected values
$AnOH^{2+}$	-7.2 ± 0.5	-6.7
$AnOH_2^{+}$	-15.1 ± 0.7	-15.8
$AnOH_3^{0}$	-26.2 ± 0.5	-26.7

Good congruence, reduction of uncertainty concerning thermodynamic data implemented in transport models for long-term predictions.

Summary

TRLFS very helpful and sensitive method for:

Molecular process understanding

Metal ion speciation