Final Report

Project¹:
“Interaction and transport of actinides in natural clay systems in the presence of humic substances and clay organic matter”

Subproject²:
“Spectroscopic investigations for an improved process understanding in binary and ternary Systems of humic substances – clay – lanthanides: thermodynamic and kinetic parameters”


University of Potsdam, Institute of Chemistry, Physical Chemistry

Karl-Liebknecht-Str. 24-25, 14476 Potsdam-Golm

#kumke@uni-potsdam.de

¹Deutscher Titel: Wechselwirkung und Transport von Actiniden im natürlichen Tongestein unter Berücksichtigung von Huminstoffen und Tonorganika

²Deutscher Titel: Spektroskopische Untersuchungen zum erweiterten Prozessverständnis in binären und ternären Huminstoff – Tongestein – Lanthanoid Systemen: Thermodynamische und kinetische Kenngrößen

Das Forschungsvorhaben war ein Teilprojekt im Forschungsverbund „Wechselwirkung und Transport von Actiniden im natürlichen Tongestein unter Berücksichtigung von Huminstoffen und Tonorganika“ und erfolgte in Kooperation mit folgenden Institutionen:

- Forschungszentrum Dresden-Rossendorf, Institut für Radiochemie (FZD-IRC)
- Forschungszentrum Karlsruhe, Institut für Nukleare Entsorgung (FZK-INE)
- Institut für Interdisziplinäre Isotopenforschung Leipzig (IIF)
- Johannes Gutenberg-Universität Mainz, Institut für Kernchemie (UM-IKC)
- Universität des Saarlandes, Institut für Anorganische und Analytische Chemie und Radiochemie (UdS-IAARC)
- Technische Universität Dresden, Sachgebiet Strahlenschutz, Professur Radiochemie (TUD)
- Technische Universität München, Fachgebiet Theoretische Chemie (TUM-TC)
Abstract

Within the project “Spectroscopic investigations for an improved process understanding in binary and ternary Systems of humic substances – clay – lanthanides: thermodynamic and kinetic parameters” an in-depth analysis of europium- and terbium-related luminescence was performed using steady-state and time-resolved spectroscopy. With respect to system complexity the full scale from well-defined organic model ligands to highly complex and heterogeneous matrices like natural organic matter (e.g., humic substance) was investigated. Binary as well as ternary systems containing clay minerals were investigated in the temperature range 5 K < T < 333 K and up to ionic strength I > 4.

In high-resolution luminescence experiments at ultra-low temperature STARK level resolved spectra were recorded, which were evaluated with respect to the complex geometry, the binding conditions (e.g., first vs. second coordination sphere influences, mono- vs. bidentate binding), number of water molecules or bond covalency. From the spectra the crystal field strength parameters were extracted. Moreover, due to the outstanding spectral resolution of those measurements it was possible to characterize the equilibrium between eight- and nine-fold coordinated aquo species of Eu(III). This equilibrium was further utilized to monitor even weak influence of counter ions as well as the overall ionic strength of the medium. From species-selective excitation and emission spectra inner- and outer-sphere binding were monitored and shifts in the equilibrium between the two aquo species were measured.

Time-resolved luminescence experiments revealed the importance of ligand-specific quenching contributions to the overall photophysics. Although by organic ligands the influence of OH-related quenching should be reduced with increasing number of organic ligands in the first coordination sphere of the lanthanide (Ln(III)) ion, for a certain group of organic ligands a further reduction in the luminescence decay time was observed. It could be shown that the activation energy connected to this quenching process is very similar for this group of ligands. A prominent member in this group, which showed a particular distinct ligand-specific quenching, is salicylic acid (2HB). Transient absorptions spectroscopy was used to further investigate the molecular processes involved. It was shown that in complexes with Eu(III) the triplet state of 2HB is fully quenched, the same is true for the solvated electron, which is seen for 2HB solutions under moderate laser irradiation. Instead a novel transient absorption signal was found, which was attributed to metal-to-ligand charge transfer transition. This MLCT transient absorption was only seen for metal ions, which were capable of accepting an electron (such as copper). In contrast, Tb(III) did quench the triplet state absorption of 2HB but no novel transient absorptions was observed.

Finally, the interlanthanide resonance energy transfer was used to investigate distances between Ln(III) ions when bound to (natural) polymers as well as to clay mineral surfaces. Using Eu(III) (or Tb(III)) as energy donor and Nd(III) as an acceptor, interionic distance up to 1.2 nm could be addressed, which is – so far – not accessible with other spatial-resolution techniques.
1. Introduction

For the risk assessment of nuclear waste repositories a sound understanding of the fundamental processes defining the fate of radionuclides in the natural environment on a molecular level is indispensible. In this context also novel analytical techniques are required and existing technologies are needed to be further improved to reach the next level in process understanding.

For long term safety handling the speciation of radionuclides in possible underground repositories is of utmost importance for their mobility in case of leakage from the primary technical safety compartment. Depending on the layout of the underground repository the presence of possible reaction partners (molecules in solutions, mineral surfaces, and the combination of both) can significantly affect the speciation and subsequently the mobility as well as bioavailability of the radionuclides. In the near but especially in the far field of the repository humic substances (HS) are key players with respect to speciation of metal ions in general (and of radionuclides in particular). HS are a major component in the aqueous and soil environment. Since these macromolecules are degradation products of plant and animal tissue, the structure of HS depends on the point of their origin. Hence, the exact structure of HS is not known. For the further development in understanding the binding interactions between HS and metal ions a sound approach is the usage of suitable model compounds.

Here, small organic compounds containing the major binding motifs of HS are frequently used as proxies for HS. Ligands such as phthalic acid or salicylic acid are often considered as basic units of HS with respect to metal binding. Such small organic compounds are further important because they are major components of the clay-organic matrix and are therefore key players in clay systems with respect to complexation of metal ions.

Lanthanide ions such as terbium (Tb(III)) and europium (Eu(III)) are frequently used as natural analogs for actinides (An) in environmental studies. In addition to a comparable chemical reactivity to An(III), Tb(III) and Eu(III) show an intrinsic luminescence in aqueous solutions. Spectral and time-resolved luminescence data can be used in speciation analysis. The luminescence characteristics of the two ions are dependent on their coordination environment. Especially, Eu(III) is a luminescence probe with outstanding luminescence properties. Spectroscopic parameters such as the decay time \( \tau \), the asymmetry ratio \( r \) and the spectral position of the \( ^{5}D_{0} \rightarrow ^{7}F_{0} \) transition can be used for a speciation analysis and consequently.

The interaction between molecules and/or ions happens on distances on a nanometer scale. The measurement of these short distances is a challenging task. A number of methods are available to resolve distances on this distance scale. Very often X-ray based methods are applied. But some of these methods can also be applied to solid state (like X-ray crystal structure analysis) or require special facilities (like synchrotron sources). A different approach is to use visible light as tool. Using light at wavelengths in the visible region eases instrumentation. Light can be absorbed by certain ions and molecules. After the absorption process, the ions are in an excited state. The transition back into the ground state requires losing energy. This can be achieved by radiative or non-radiative processes. One non-
radiative process is the transfer of energy from the excited molecule/ion to a second molecule/ion in the ground state. The efficiency of this energy transfer depends on the distance between the molecules/ions involved.

In the research project molecular processes of lanthanide ions (as natural analogues for actinides, Ln(III)) in binary and ternary systems consisting of organic ligands (covering the full spectrum from small, simple organic ligands via model polymers to complex humic substances) and mineral surfaces were investigated using luminescence spectroscopy as sophisticated analytical tool. Especially time-resolved laser spectroscopy and measurements at ultra-low temperature (T ~ 5 K) were applied to elucidate the speciation of Ln(III) and to shed light on the intra- and intermolecular interaction processes on a molecular level. Based on an in depth analysis of the set of different spectroscopic parameters (e.g., ligand field strength parameter, asymmetry ratio, luminescence decay time, interlanthanide energy transfer efficiency) conclusions on the speciation of the Ln(III) ion under specific medium conditions are drawn. Especially, the ionic strength and the influence of the temperature were considered in this context.

2. Experimental details

2.1 General experimental details

As model compounds for binding sites in HS, different (hydroxy)benzoic acids and aliphatic acids were investigated. The relative positions of the hydroxyl- and/or carboxyl group were systematically varied, in order to study the effect of complex formation and of the ligand structure on the luminescence spectra of Eu(III). All reagents were of analytical grade. Cyclohexanecarboxylic acid was obtained from SAFC supply solutions, 2-Hydroxyacyclohexanecarboxylic acid was obtained from ABCR GmbH & Co. KG and 2-hydroxybenzoic acid was purchased from VEB Jenapharm. Other chemicals were ordered from Sigma-Aldrich with the highest purity available. As background electrolyte 0.1 M sodium perchlorate solution was applied. All solutions were stored in the dark at room temperature.

From speciation analysis based on stability constants taken from literature it was calculated that only a very minor concentration of the “free” Eu$_{aq}$ion is present at a the highest Ln:ligand ratio.

To avoid formation of hydroxyl and carbonate complexes the pH was adjusted to five with sodium hydroxide and hydrochloric acid. Each solution was equilibrated for approximately 10 days prior to the luminescence measurements. In-between measurements, the samples were stored in the dark at room temperature.

2.2 Influence of ionic strength and counter ions

Aqueous Eu(III) samples were prepared from EuCl$_3$ 6H$_2$O. Further samples without any chloride ions were made by dissolving Eu$_2$O$_3$ in the appropriate amount of 70% HClO$_4$; the
final perchlorate ion concentration was 0.1 M. All samples were prepared in deionized water and contained 0.2 M Eu(III). Two sets of samples with pH = 2 and pH = 5 were prepared using HCl, HClO₄ or NaOH as required. Samples in D₂O were prepared in a glove box using dry EuCl₃ and NaClO₄. The pH of the solution was also adjusted to 5, using DCl, DClO₄ and NaOD. All chemicals were purchased from Aldrich with the highest purity available and used as received.

2.3 Luminescence measurements

(i) Luminescence measurements at ambient and higher temperature: Time-resolved laser luminescence spectroscopy measurements were performed using a pulsed Nd-YAG Laser (Spectra Physics) combined with an optical parametric oscillator (GWU Lasertechnik). The luminescence emission was detected with an iCCD-camera coupled to a spectrograph (Andor Technology). For the Eu(III) complexes the emission spectra were recorded in the spectral range of 575 nm < λ_em < 635 nm, the emission spectra of the Tb(III) complexes were recorded in the range of 475 nm < λ_em < 675 nm. For the measurements at room temperature (T = 290 K) the excitation wavelength was 394 nm to excite directly the Eu(III) ion according to the electronic 7F₀ → 5L₆-transition. For the investigation of Tb(III) complexes a wavelength of 377 nm was chosen according to the 7F₆ → 5G₅-transition. In the time-gated detection scheme, the initial delay time after the laser flash (δt) was varied between 0.4 µs < δt < 30.4 µs (depending on the temperature) in order to minimize interference originating from the luminescence of the 5D₁ → 7F₀ transition. The time dependence of the Eu(III) and Tb(III) luminescence was analysed using a box car technique. A Eu(III) luminescence spectrum was measured at different δt using an integration time of 50 µs. For a typical emission spectrum at a particular δt, 100 laser pulses were accumulated. To record a full luminescence decay, between 120 and 130 luminescence spectra were measured at increasing δt. The Tb(III) luminescence spectra were recorded in the same way.

In addition, emission spectra and decay times between 278 K < T < 338 K were also recorded using a Fluoromax 4 spectrofluorometer (HoribaJobinYvon) in the phosphorescence mode. Here, a pulsed Xe lamp was applied for excitation. Spectra as well as decay measurements were performed in a box car mode (vide supra). In order to maintain the desired temperature, a thermostat system was used (LAUDA, Proline RP 845 C).

(ii) Fluorescence line narrowing (FLN) spectroscopy: For FLN spectroscopy, sample solutions were transferred to quartz tubes (40 mm length x 4 mm o.d. x 2 mm i.d.; volume ca. 100 µL), and sealed with rubber septums. Samples were cooled to ~5 K in a lab-built sample holder, mounted on a closed-cycle helium refrigerator (SRDK-205 cryostat; Janis Research Company, Wilmington, MA, USA). The samples were excited using a dye laser (LPD 3002; Lambda Physics, Göttingen, Germany) pumped by a XeCl excimer laser (LPX 110i; Lambda Physics, Göttingen, Germany). Coumarin 153 (Radiant Laser Dyes & Accessories GmbH, Wermelskirchen, Germany) was used as laser dye. The laser was operated at 20 Hz with a pulse width of 10 ns. The Eu(III) emission was collected at a 90° angle relative to the
excitation light by two 10 cm F/4 quartz lenses and focused on the entrance slit of a triple monochromator (Spex 1877; Edison, NJ, USA). For detection an intensified charged-coupled device (iCCD) camera (iStar DH720-25U-03; Andor Technologies, Belfast; Northern Ireland) was used in the gated mode. In order to obtain adequate stray light suppression, delay and gate width of the iCCD were set to 1 µs and 10 ms, respectively. The achieved spectral resolution in the emission dimension was 0.1 nm (3 cm⁻¹) in a total spectral detection window of 37 nm. Each emission spectrum was accumulated for 1 s to 5 s, comprising 20 to 100 laser pulses. The excitation wavelength was varied with a scan rate ranging from 0.001 nm/s to 0.05 nm/s, yielding a resolution in the excitation dimension between 0.03 cm⁻¹ and 1.5 cm⁻¹. The decay curves were extracted from time series of emission spectra (delay 1 µs, gate width 10 ms) of 200 spectra. For each sample several decay series were recorded, at each excitation wavelength λ_{exc} corresponding to a separate species in the TLS.

2.4 Data analysis

Luminescence decays: In case the luminescence decay curves were monoexponential, they were evaluated according to Eq. (1)

\[ y = y_0 + B \cdot \exp\left(-\frac{t}{\tau}\right) \]  

(1)

\( y \) is the measured luminescence intensity at time \( t \) after the laser flash, \( B \) is the luminescence intensity at \( t = 0 \), \( \tau \) is the luminescence decay time, and \( y_0 \) accounts for residual background signal.

From the in-depth analysis of the Eu(III) luminescence, especially when recorded at kryogenic conditions, a wealth of information can be obtained:

\(^5\text{D}_0 \rightarrow \text{^7F}_0\) transition energy: The \(^5\text{D}_0 \leftrightarrow \text{^7F}_0\) transition is extremely weak because of parity forbiddance. It gains intensity in cases in which the symmetry of the Eu(III) complex is lowered, for instance due to the formation of non-centrosymmetric complexes or due to vibrational motion of the ligands. For being non-degenerate the \(^5\text{D}_0 \leftrightarrow \text{^7F}_0\) transition is a powerful indicator for the presence of different coexisting complexes in a sample. Moreover, its energy is very sensitive to specific parameters characterizing the complex. Two partly contradicting effects determine the energy of the \(^5\text{D}_0 \leftrightarrow \text{^7F}_0\) transition: i) the nephelauxetic effect and ii) the splitting of the \(^7F_1\) transition, which is dependent on the crystal field exerted by the ligands.

STARK splitting, crystal field strength parameter and jackstraws plots: The \(^7F_1\) state is further split into three STARK levels \((^7F_{1-1}, ^7F_{1-2}, ^7F_{1-3})\) and the effective crystal field can be quantified by the crystal field strength parameter \(N_v(B_{2g})\). For weak crystal fields the crystal field strength parameter \(N_v(B_{2g})\) can be calculated based on this energy difference:

\[ N_v(B_{2g}) = \sqrt{\frac{\pi(2 + \alpha^2)}{0.3}} \Delta E \]  

(2)
with \[ \alpha = \frac{E_b - E_c}{\Delta E/2} \]

where \( E_b \) is the barycentre (mean energy) of the \( ^7F_1 \) multiplet and \( E_c \) is the energy of the central level \( (^7F_{1/2}) \). The reduction in inhomogeneous broadening in the FLN spectra enables a precise determination of \( \Delta E \) (or \( N_v(B_{2g}) \)). A plot of the excitation energy vs. the energy difference \( \Delta E \) (or the crystal field strength parameter \( N_v(B_{2g}) \)) results in a straight line of which the length, position and slope are characteristic for the particular species (jackstraws plot).

**Point symmetry group:** Under site-selective excitation conditions the number of Stark levels in the \( 5D_0\rightarrow^7F_1 \) and \( 5D_0\rightarrow^7F_2 \) transitions can be used to determine the point symmetry group of the coordination polyhedron.

**Asymmetry ratio \( r \):** The integrated intensity of the \( 5D_0\rightarrow^7F_2 \) transition is especially sensitive to the complex symmetry. The more the local complex symmetry deviates from inversion symmetry the more the parity forbiddance is relaxed. In contrast, the integrated \( 5D_0\rightarrow^7F_1 \) emission is not affected and can therefore be used as an internal reference. A change of the “asymmetry ratio \( r \)” (Equation 3) indicates an alteration of the complex symmetry. In general, an increasing deformation of the coordination polyhedron following the exchange of water molecules by other ligands results in a larger \( r \) value according to:

\[
r = \frac{I(5D_0\rightarrow^7F_2)}{I(5D_0\rightarrow^7F_1)}
\]  

(3)

The asymmetry ratio \( r \) depends on several other parameters, such as i) the polarizability of the ligands, ii) the complex-related concentration of the ligands, and iii) the dielectric constant of the solvent. Nonetheless, for samples containing the same or very similar ligands, investigated under identical experimental conditions, \( r \) may be used as a discriminator for different species present in the sample.

**Number of water molecules in the first coordination sphere:** A major radiationless deactivation pathway of Eu(III) is related to the OH groups present in the first, but also (to a minor extent) in the second coordination sphere of the complex. It has been established that the number of water molecules \( n_{H_2O} \) in the first coordination sphere of Eu(III) can be determined from luminescence decay time measurements \( \tau_{obs} \). The well-known empirical equations of Horrocks et al. and Kimura et al. have been extended to account for additional quenching contributions from other ligands and from OH groups in the second coordination sphere with the terms 0.25 and 0.4 \( n_{OH} \), respectively.

\[
n_{H_2O} = 1.2 \left( \frac{1}{\tau_{obs}} - 0.58 - 0.25 - n_{OH} \cdot 0.4 \right)
\]  

(4)
This formula was derived at room temperature conditions. Since no influence of temperature on the fluorescence decay time was observed ($\tau_{Ea(OH)} = 100 \pm 10 \, \mu s$ at 298.15 K and $106 \pm 10 \, \mu s$ at 4.7 K) it is concluded that the quenching efficiency of OH vibrations is not altered with temperature and thus Equation (4) can also be used at 4.7 K.

### 2.5 Energy transfer

Non-radiative energy transfer can take place according processes proposed by Dexter and Förster. The Dexter mechanism – also known as exchange mechanism – happens on relatively short distances as electrons have to be exchanged between these two molecules/ions. This requires an overlap of the orbitals involved. According Förster’s theory a different energy transfer can happen at longer – on the Nanometer to Sub-nanometer region – distances. Here, the energy transfer is based on a dipole-dipole (coulomb) interaction between the molecules/ions. The efficiency of the energy transfer depends on the overlap between the emission spectrum of the donor and the excitation (absorption) spectrum of the acceptor as well as the distance between donor and acceptor. The donor-acceptor distance, at which the efficiency $\eta$ reaches 50 percent, is called the Förster distance $R_0$. The value of $R_0$ is given by spectral properties of the donor-acceptor pair according the following equation (1)

$$R_0 = \frac{9n^2(10)e^4\Phi_D}{128\pi^6N_A\varepsilon^2}$$

(5)

with luminescence quantum yield $\Phi_D$ of the donor, Avogadro’s number $N_A$, refractive index $n$ of the surrounding medium, the overlap integral $J$ and the orientation factor $\kappa^2$ between the transition dipole moments of the donor and the acceptor. It is given by

$$J = \int \frac{F(\lambda)g(\lambda)\kappa^2 d\lambda}{\int F(\lambda)g(\lambda) d\lambda}.$$  

(6)

Here, $F(\lambda)$ reflects the emission spectrum of the donor, $g(\lambda)$ is the wavelength dependent extinction coefficient and $\lambda$ the wavelength. The efficiency of the energy transfer decreases with the sixth power of the distance $R$ between donor and acceptor

$$\eta = \frac{R_0^6}{R^6 + R_0^6}.$$  

(7)

As a result of a transfer of energy, the luminescence decay time of the donor is quenched. By knowing the donor’s luminescence decay time in absence $\tau_D$ and presence of an acceptor $\tau_{DA}$ the efficiency of the energy transfer can be calculated

$$\eta = 1 - \frac{\tau_{DA}}{\tau_D}.$$  

(8)
With eq. (7) and (8) the distance between donor and acceptor can be connected to a measured quantity. It can easily be shown, that the luminescence decay time in presence of a suitable donor $\tau_{DA}$ depends on the donor-acceptor distance

$$\frac{1}{\tau_{DA}} = \frac{1}{\tau_D} + \frac{1}{\tau_D} \left( \frac{2\sigma}{\bar{R}} \right)^6.$$  \hspace{1cm} (9)

Taking eq. (9) into account, the donor’s luminescence decay in presence of an acceptor is given by

$$I(t) = I_0 \exp \left( -\frac{t}{\tau_{DA}} \right) = I_0 \exp \left[ -\frac{t}{\tau_D} - \frac{t}{\tau_D} \left( \frac{2\sigma}{\bar{R}} \right)^6 \right].$$  \hspace{1cm} (10)

So far a donor-acceptor pair with a certain distance was considered. In more complex systems, like natural occurring polymers, it is more likely to assume a distribution of possible distances. This can be achieved, if eq. (6) is extended by a distribution function like a Gaussian function $P(R)$

$$P(R) = \frac{1}{\sigma \sqrt{2\pi}} \exp \left[ -\frac{1}{2} \left( \frac{R - \bar{R}}{\sigma} \right)^2 \right].$$  \hspace{1cm} (11)

In eq. (11) $\sigma$ reflects the width of the distance distribution and $\bar{R}$ is the mean distance between donor and acceptor. Now, both parameters ($\sigma$ and $\bar{R}$) describing the distribution of distances can be deduced from the decay of the donor luminescence in presence of suitable acceptors using the following equation.

$$I(t) = I_0 \int_{R=0}^{\infty} P(R) \exp \left[ -\frac{t}{\tau_D} - \frac{t}{\tau_D} \left( \frac{2\sigma}{\bar{R}} \right)^6 \right] dR$$  \hspace{1cm} (12)
3. Results

3.1 Structure-interaction relationship of Eu(III) and small organic ligands probed by luminescence spectroscopy at room and elevated temperature

Spectral and time-resolved luminescence data of different Eu(III)-complexes with model ligands were investigated in detail. Since the chemical structure of the model ligands is fully known, many problems arising from the uncertainty in structure of HS are circumvented. This is important for the development of a fundamental understanding of the relationship between (electronic) structure of the ligands and observed luminescence response, because spectroscopic techniques are major tools in the investigation of molecular processes in natural systems. The model compounds show only moderate binding constants and in the samples investigated often a mixture of different complexes with respect to number of model ligands coordinated to the Ln(III) ion is observed. In the present study the influence of temperature on the photophysical properties of the Ln(III) complexes was used to further evaluate the intramolecular deactivation processes and to conclude on structure-related processes in the corresponding complexes.

Luminescence measurements at room temperature

Asymmetry ratio \( r \)

An useful spectroscopic parameter which is sensitive to the Eu(III) coordination environment is the asymmetry ratio \( r \). For the Eu(III)\textsubscript{aq} ion the asymmetry ratio is \( r = 0.6 \). Due to complexation the symmetry of the complex is changed and the asymmetry ratio is altered as well. Figure 1a shows luminescence spectra of Eu(III) complexes with 2-hydroxyphenylacetic acid. With an increasing ligand concentration the concentration of complexes is also increased. As a consequence the symmetry of the complex is affected and consequently the intensity of the hypersensitive \( ^5\text{D}_0 \rightarrow ^7\text{F}_2 \) transition may be increased. The parameter \( r \) is a good indicator to monitor the complex formation. Moreover, from the time dependence of \( r \) the presence of different species in the samples can be deduced. Hence, the evaluation of \( r(t) \) can assist the interpretation of complex luminescence decay data. Figure 1b) is an example representative for the small organic ligands investigated in the present chapter. For those ligands \( r \) is independent of time indicating that only one (or only very similar) type of complex is present in the sample and/or that no excited state reaction like dissociation of the complex is operative during the luminescence decay of the sample.
Figure 1: Luminescence spectra a) of Eu(III) complexes in 0.1 M NaClO₄ (…), with 2-hydroxyphenylacetic acid at a molar ratio of 1:1 (- - -), 1:3 (straight line) and 1:6 (line dot line) and b) the time-resolved asymmetry ratio of Eu(III)ₐq in 0.1 M NaClO₄ and in complexes with 2-hydroxyphenylacetic acid at a molar ratio of 1:1, 1:3, and 1:6, respectively (λₑₓ= 394 nm, δt= 17.3 µs).

Figure 2 shows that the determined asymmetry ratio is dependent on the molar fraction of ligand. With increasing concentration of ligand the asymmetry ratio r also increases. Since the asymmetry ratio is r > 0.6 in the presence of any organic compound investigated, all potential ligands form complexes with Eu(III). Reasons for the different increase in r depending on the ligand could be different charge density, different symmetries of the complexes due to the specific properties of the ligand as well as mono and bidentate binding capabilities.

**Decay times τ of the ⁵D₀-state of Eu(III) complexes**

In water the Eu(III)ₐq ion is surrounded by 8-9 water molecules (*vide infra*). Since the vibration state of these OH-oscillators is near the emitting state of the Eu(III) ion (⁵D₀ state), the water molecules act as quencher and the decay time is only 0.11 ms. When a ligand like glycolic acid enters the coordination sphere, quenching water molecules are displaced and the decay time of Eu(III) increases. In Figure 3 the luminescence decay curves of Eu(III) complexes with different model ligands (and at different molar fraction of ligand) are shown. Depending on the luminescence decay time of Eu(III) in the different complexes, these were (at this point) operationally divided into three groups (A, B and C).
Figure 2: Asymmetry ratio $r$ for different molar fractions of ligand: phtalic acid($\bullet$), glycolic acid($\square$), 2-hydroxyphenylacetic acid ($\Delta$), cyclohexanecarboxylic acid ($\Delta$), 2-methoxybenzoic acid ($\blacktriangle$), anthranilic acid ($\triangle$), 2-hydroxybenzoic acid ($\star$), 2-hydroxy cyclohexanecarboxylic acid($\star$), 4-hydroxybenzoic acid($\Box$), tropic acid ($\bigcirc$) ($\lambda_{ex} = 394$ nm)

*Group A:* The decay times of Eu(III) complexes with group A ligands are about 0.130 ms at a molar fraction of 0.5. This increase in the luminescence decay time is expected since water molecules are displaced by the coordinated ligand. With increasing molar fraction of ligand the decay time is also increasing as more complexes are formed.

*Group B:* Ligands like 2-methoxybenzoic acid or 4-hydroxybenzoic acid only have a small influence on the luminescence decay time $\tau$. For complexes with a molar fraction of 0.5 a decay time of only 0.12 ms (or less) is determined. As the ligand concentration is increased only a slight increase in the decay time was observed.

*Group C:* Ligands attributed to this group show a non-typical behaviour of the luminescence decay time. At a molar fraction of 0.5 the decay time is only about 0.1 ms (or smaller) similar to the decay time of the Eu(III)$_{aquo}$ ion. This suggests that no complexes with Eu(III) were formed in solution. But from the asymmetry ratio of these complexes it can be concluded that the coordination sphere of the Eu(III) ion is changing with increasing ligand concentration (see Figure 2). Moreover, increasing the ligand concentration the luminescence decay time is even further decreased, which points towards a ligand-specific quenching.
Figure 3: Decay times of the $^5D_0$ state dependent on the molar fraction of ligand of all investigated Eu(III) complexes with phtalic acid (○), glycolic acid (■), 2-hydroxyphenylacetic acid (▲), cyclohexanecarboxylic acid (△), 2-methoxybenzoic acid (◀), anthranilic acid (◄), 2-hydroxybenzoic acid (★), 2-hydroxycyclohexanecarboxylic acid (☆), 2-mercaptobenzoic acid (►), 4-hydroxybenzoic acid (□), tropic acid (○) and at molar fraction of zero the Eu(aquo) ion (sphere) is shown ($\lambda_{ex} = 394$ nm)

Decay times $\tau$ of the $^5D_4$-state of Tb(III) complexes

To further investigate the ligand-specific quenching of ligands (group C), the luminescence decay time of Tb(III) complexes was determined. The Tb(III) ion was chosen because it differs in its electronic properties compared to the Eu(III) ion: i) the emitting $^5D_4$ state of the Tb(III) ion has an energy of 20500 cm$^{-1}$, which is 3233 cm$^{-1}$ above the emitting state of the Eu(III) ion and ii) Eu(III) can be reduced to Eu(II) at moderate oxidation potentials. In water a luminescence decay time for Tb(III)$_{\text{aq}}$ ion of 0.4 ms is found. In Figure 4 the observed luminescence decay times for Tb(III) complexes with the different model compounds are compiled. Alike in the case of Eu(III) the ligands could again tentatively divided into three groups.

Group A: The decay time increased (e.g., for phtalic acid or glycolic acid at a molar ratio of 0.5, a luminescence decay time of 0.46 ms $< \tau < 0.49$ ms was found). Like for the Eu(III) complexes, the decay time of Tb(III) complexes with ligands of group A is increased with increasing molar fraction of ligand.

Group B: Complexes with 2-methoxybenzoic acid, 4-hydroxybenzoic acid and tropic acid show almost no influence on the luminescence decay time of Tb(III). In that group, only a slight increase with increasing ligand concentration was observed.
**Group C:** The decay time of Tb(III) complexes with 2-aminobenzoic acid and 2-hydroxybenzoic acid shows an opposite trend to the Tb(III) complexes attributed to group A. Like in the case of Eu(III) complexes of group C, the luminescence decay time is decreasing with increasing ligand concentration.

**Figure 4:** Decay times of the $^5D_4$ state dependent on the molar fraction of ligand of all investigated Tb(III) complexes with phtalic acid($\bullet$), glycolic acid($\blacksquare$), 2-methoxybenzoic acid (◀), anthranilic acid (◀), 2-hydroxybenzoic acid (★), 4-hydroxybenzoic acid($\square$) and tropic acid ($\bigcirc$) ($\lambda_{ex}=377$nm)

**Luminescence measurements at elevated temperatures in the range of $278 \, K < T < 340 \, K$**

**Asymmetry ratio $r$**
In Figure 5 the determined asymmetry ratios depending on the temperature for Eu(III) complexes with different ligands are shown. For all Eu(III) complexes investigated an increase of $r$ with increasing temperature was observed, which could be attributed to the fact that usually the stability constants also increase with increasing temperature. The asymmetry ratio of the Eu(III) complexes with glycolic acid and 2-hydroxybenzoic acid is also increasing with increasing temperature, which is unusual because according to literature an opposite trend was expected, because complex formation with such ligands should be exothermic. The spectroscopic parameter $r$ depends on different parameters and a possible reason for the observed increase of $r$ in that particular cases may be a shift of the
equilibrium towards a higher stoichiometry, e.g., 1:2 complexes. When with increasing temperature more 1:2 complexes are formed, the asymmetry ratio $r$ increases because of alterations in symmetry of the complexes.

**Figure 5:** Determined asymmetry ratio of Eu(III) complexes with phtalic acid (●), glycolic acid (■), 2-methoxybenzoic acid (▲), 4-hydroxybenzoic acid (□), tropic acid (○), 2-hydroxybenzoic acid (★) and 2-hydroxyphenylacetic acid (▼) at different temperatures

**Luminescence decay times of Eu(III) complexes in the temperature range of 278 K < T < 340 K**

To further elucidate the ligand-specific quenching processes luminescence measurements at elevated temperatures were performed. Figure 6 shows the measured luminescence decay times of the different Eu(III) complexes of groups A - C for the temperature range of 278 K < T < 340 K.
Figure 6: Decay times of Eu(III) complexes with phtalic acid (●), glycolic acid (■), 2-methoxybenzoic acid (▲), 4-hydroxybenzoic acid (▲), tropic acid (○), 2-hydroxybenzoic acid (★), 2-mercaptobenzoic acid (▽) and 2-hydroxyphenylacetic acid (▲) at different temperatures.

*Group A:* Here, complexes show slightly different trends in the temperature dependence of the luminescence decay time. The increase in the temperature seems to have no influence on the decay time of Eu(III) complexes with phtalic acid. But for the Eu(III) complex with glycolic acid a decrease in the decay time was observed. Here, a possible explanation for the decrease of the luminescence decay time may be a decrease in the complex formation with increasing temperature.

*Group B:* Like for group A, no clear trend is found, in the case of complexes with 2-methoxybenzoic acid and 3-hydroxy-2-phenylpropionic acid almost no temperature dependence of the luminescence decay time was observed. On the other hand, for the Eu(III) complex with 4-hydroxybenzoic acid the decay time decreases distinctly with increasing temperature.

*Group C:* For that group of ligands a clear trend was found: the luminescence decay time decreased with increasing temperature and it seems that ligand-specific quenching mechanisms become more efficient.

In Figure 7 a data analysis according to Arrhenius for the group C ligands is shown. From the slopes of the lines it can readily concluded that the activation energy for the ligand-specific quenching process is not very different for the investigated compounds. In Table 1 the calculated activation energies for three compounds of group C are summarized.
Figure 7: Evaluation of the luminescence decay times of the Eu(III) complexes of group C with 2-hydroxybenzoic acid (★), 2-hydroxyphenylacetic acid (▲) and 2-mercaptobenzoic (▽) acid according to Arrhenius.

The model ligands were tentatively grouped into three groups based on the spectroscopic parameters $r$ and $\tau$. While for groups A and B the two parameter showed slightly different pronounced trends in both parameters, the trends observed for group C were clear and in good agreement for both photophysical parameters. The observed dependence of $r$ and $\tau$ on the ligand concentration as well as on the temperature show that the interplay between thermodynamics (complex stability, formation of higher complex stoichiometry) and ligand-specific quenching has to be understood for a proper evaluation of the luminescence data.

Table 1: Calculated activation energies $E_A$ for Eu(III) complexes of group C

<table>
<thead>
<tr>
<th>Eu(III):Ligand</th>
<th>$E_A$ [cm$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-hydroxybenzoic acid</td>
<td>2100</td>
</tr>
<tr>
<td>2-hydroxyphenylacetic acid</td>
<td>2100</td>
</tr>
<tr>
<td>2-mercaptobenzoic acid</td>
<td>2800</td>
</tr>
</tbody>
</table>
Transient absorption spectroscopy

Especially the ligand-specific quenching needs to be further evaluated. Often the formation of charge-transfer states is discussed as a possible source for the observed alterations in the photophysical properties of Eu(III) complexes. However, in the regular UV/Vis absorption no (or only very faint) changes are found, leaving the contribution of intra-complex charge transfer states as an explanation for the observed effects unclear.

In order to further improve the understanding of the ligand-specific quenching and to elucidate the possible contribution of a transient state, pump-and-probe experiments with 2-hydroxy benzoic acid and different Ln(III) ions were carried out. In Figure 8 the decay kinetics of the triplet state absorption of 2-hydroxy benzoic acid is shown in absence and presence of different Eu(III) concentrations. At low Eu(III) concentrations the decay of the transient absorption is quenched. Here, only a minor part of the Eu(III) is bound in a complex. A Stern-Volmer evaluation of the triplet-state related decay time showed that the corresponding quenching reaction is diffusion limited. Upon increasing the Eu(III) concentration the kinetics of the transient signal is distinctly altered. A rise of the transient signal is followed by slow decrease.

![Figure 8: Transient absorption decay of 2-hydroxy benzoic acid in the absence and presence of different Eu(III) concentrations (λ_{ex} = 290 nm, λ_{abs} = 455 nm).](image)

In Figure 9 the transient absorption spectra of 2-hydroxy benzoic acid in the absence and presence of La(III) and Eu(III) are depicted. A Ln(III) concentrations of 5*10^{-2} M ensure that the ligand is completely bound in a complex. In the absence of Ln(III) the spectrum shows the transient absorption of the phenoxy radical (λ ~ 390 nm), the triplet state (λ ~ 450 nm)

---

and of the solvated electron (\( \lambda \sim 690 \text{ nm} \)), respectively. The addition of La(III) does not change the spectrum and all three transient species are present. In contrast, upon addition of Eu(III) only the transient signal of the phenoxy radical is left. In addition in Figure 9 the transient spectrum of 2-hydroxy benzoic acid in the presence of Eu(III) at a time delay of 50 \( \mu \text{s} \) after the laser pulse is shown.

\[ \begin{align*}
\text{Figure 9: Transient absorption spectra of 2-hydroxy benzoic acid in the absence and presence of La(III) and Eu(III), respectively. The Ln(III) concentrations of } & 5 \times 10^{-2} \text{ M ensure that the ligand is completely bound in a complex.}
\end{align*} \]

It can be seen that a new absorption band occurs in the spectrum at \( \lambda \sim 420 \text{ nm} \), which was not present in the other samples investigated. The observed rise (see Figure 8) in the transient absorption kinetics and the changed decay can be attributed to the occurrence of this new species. Since such transient signals were only found in the present of metal ions which are able to participate in a redox-related step (e.g., similar results were also found in the presence of copper), it is tempting to attribute the observed signal to a charge transfer (CT) state. This CT state is formed in complexes with ligands of group C and opens an additional deactivation pathway, which finally decreases the luminescence decay time of the corresponding Eu(III) complex. In case of Tb(III), which is not know for the formation of a \(+II\) state, different mechanisms such as energy back transfer, may be the cause for the observed effects.
3.2 Fluorescence line narrowing (FLN) spectroscopy of Eu(III) in complexes with small organic ligands$^{4,5,6}$

The total luminescence spectrum (TLS) measured at 4.7 K contains a wealth of information, which is especially valuable for the investigation of samples containing mixtures of Eu(III) complexes. From the width of the $^5D_0\leftrightarrow^7F_0$ transition (excitation spectrum) the degree of inhomogeneity (e.g., small variations in bond lengths, bond angles or water molecules in the second coordination sphere) can be assessed, whereas non-Gaussian shaped excitation spectra point at the occurrence of several distinct "species". As a first step towards FLN analysis of Eu(III) complexes with natural ligands such as humic acids, various small organic ligands (aliphatic and aromatic carboxylic acids) were investigated as model compounds, mimicking possible binding sites in HS.

An in-depth analysis of the FLN spectra is carried out with respect to: i) the number of $^5D_0\leftrightarrow^7F_0$ transitions observable in the excitation spectra, ii) the asymmetry ratio $r$ of the $^5D_0\leftrightarrow^7F_2$ and $^5D_0\leftrightarrow^7F_1$ transitions, and iii) the variation of the excitation energy with the crystal field strength parameter $N_e(B_{2g})$ (referred to as jackstraws plots). Making use of the specific excitation wavelengths corresponding to the observed $^5D_0\leftrightarrow^7F_0$ transitions in the TLS, species-selective luminescence decays were recorded in order to determine the number of water molecules in the first coordination sphere for a particular complex. On the basis of an integrated analysis of the excitation spectra, of the emission spectra and of the luminescence decay times, the number of different complexes coexisting in the sample, their stoichiometry and geometry (e.g., symmetry point group) were deduced.

With respect to the potential binding to Eu(III), the model ligands investigated here can be tentatively divided into two sets: A) ligands that may form chelates due to a hydroxyl group (or a second carboxyl group) and B) ligands that can bind to Eu(III) via one carboxyl group alone. Type A model ligands are: 2-hydroxy benzoic acid (2HB), phthalic acid (PHA), and glycolic acid (GL), while 3-hydroxy benzoic acid (3HB), 4-hydroxy benzoic acid (4HB), 4-methoxy benzoic acid (4MB), benzoic acid (BA), galic acid (GA) and 3-hydroxy propionic acid (3HP) belong to Type B.

---


**Total luminescence spectra**

From the high-resolution TLS, the luminescence excitation and emission spectra can be derived as horizontal and vertical cross-sections, respectively (as shown for Eu(III) : 4HB in Figure 10). The position, width and shape of the excitation band as well as the splitting of the \( ^7F_1 \) multiplet as a function of the excitation wavelength and subsequently the number of different species can be extracted from the TLS.

![Figure 10: Contour plot of the \( ^7F_1 \) multiplet of the Eu\(^{3+} \) and 4-hydroxy benzoic acid at a molar ratio of 1:9 (\( T = 5 \text{ K} \)).](image)

At a series of emission wavelengths (614 nm < \( \lambda_{em} < 620 \text{ nm} \) corresponding to 16287 \( \text{cm}^{-1} \) > \( E_{em} = 16129 \text{ cm}^{-1} \), the spectral positions and the average FWHM of the \( ^5D_0 \leftarrow ^7F_0 \) transitions were obtained from the TLS (see Figure 10, for example). These spectra were also used to select the optimal excitation wavelengths for the species-selective decay time measurements (*vide infra*). For the aromatic ligands 2HB, 4HB and PHA excitation spectra (cross-sections for \( \lambda_{em} = 614 \text{ nm}, E_{em} = 16287 \text{ cm}^{-1}, ^5D_0 \rightarrow ^7F_2 \) transition) are shown in Figure 11. As reported earlier, for the crystals of the reference compound EuCl\(_3\) \( \cdot \) 6H\(_2\)O a very narrow \( ^5D_0 \leftarrow ^7F_0 \) transition was observed (FWHM of 0.2 \( \text{cm}^{-1} \)), indicating a single, well-defined Eu(III) complex. For **TYPE A** ligands such as salicylic acid (2HB) and phthalic acid (PHA), also relatively narrow-banded \( ^5D_0 \leftarrow ^7F_0 \) transitions were found (FWHM = 1.3 and 1.1 \( \text{cm}^{-1} \) respectively). This clearly indicates the formation of well-defined complexes, presumably with a high stability constant and a high degree of symmetry. However, for GL a broadened excitation transition was observed, probably due to the rotational freedom of the possibly chelating OH group. In contrast to 2HB and PHA for **TYPE B** ligands broader, non-GAUSSian shaped peaks already indicate a more inhomogeneous situation and often the presence of more than one species.
Figure 11: Smoothed excitation spectra of the Eu(III) complexes with aromatic carboxylates ($\lambda_{em} = 612$ nm $E_{em} = 16340$ cm$^{-1}$) and Jackstraws plot calculated from the $^5D_0 \rightarrow ^7F_1$ and the $^5D_0 \rightarrow ^7F_0$ transition of the corresponding TLSs (full lines refer to $N_{v}$(B$_{2g}$), dashed lines to $\Delta E$). 3HB and BA are omitted for clarity reasons.

Luminescence decay times
Based on the excitation spectra extracted from the TLS, species-selective excitation conditions were chosen for the cryogenic luminescence decay measurements; these decay times are summarized in Figure 12. For the interpretation of the decay time data it was assumed that the aquo ion of Eu(III) is coordinated by nine water molecules, which can be substituted by nine oxygen containing groups from ligands – which may be considered as an oversimplification because an equilibrium between eight and nine-fold coordinated water species is present (vide infra).

It is striking that especially for TYPE A ligands (chelate formation via carboxyl and/or a hydroxyl group) relatively short luminescence decay times were found also at T = 5 K: around 420 µs for 2HB and GL (vide supra). Considering the decay times obtained for TYPE A ligands, and the fact that very sharp excitation peaks indicate the formation of well-defined complexes, estimating the number of water molecules $n_{H_2O}$ in the first coordination sphere based on the standard approaches of HORROCKS et al. and KIMURA et al. seems should be considered with great care.
Figure 12: Decay times of the Eu(III) complexes of 2HB, 3HB, 4HB, BA, PHA, 3MB, 4MB, GL, 3HP and GA at different excitation wavelengths. The grey bars indicate the variation of decay time due to influence of individual ligand properties and the water molecules of the second coordination sphere. (*of a biexponential fit only the longer lifetime is shown).

For example, in case of 2HB the $\alpha$-hydroxy group can participate in the complexation and subsequently quench the Eu(III) luminescence. Applying Equation (4), in which also quenching contributions from water molecules in the second coordination sphere and ligand-related hydroxyl groups are taken into account, at most one water molecule is left in the first coordination sphere. This interpretation is supported by the absence of quenching from ligand-related OH groups for aromatic carboxylic acids that do not possess an $\alpha$-hydroxy group (3HB, 4HB: $n_{OH}=0$). The overall steric requirements for these ligands should be at least similar to those of 2HB, e.g., a comparable number of water molecules can remain in the first coordination sphere of Eu(III). For these ligands a luminescence decay time of about 750 $\mu$s was found (see Figure 12), which based on Equation (4) corresponds to one water molecule in the first coordination sphere.

In contrast, “pure” benzoic acid (and 4MB) is free of steric constraints caused by substituents and has no additional binding possibilities. In this special case a shorter luminescence decay time of 520 $\mu$s was found, which points to one or two water molecules still present in the first coordination sphere.

For the ligands 3HB, 4HB, 4MB and PHA additional species with luminescence decay times in the range of 150 $\mu$s to 250 $\mu$s were found. Their relative intensities varied with the excitation energies and in general the fraction of these species was rather low (15 % to 30 %). Most probably we are dealing with complexes containing four to six remaining water molecules in the first coordination sphere of Eu(III), indicating complexation by less than three organic ligands.

On the other hand, in the case of one of the phthalate (PHA) complexes an extremely long luminescence decay time of $\tau=1702$ $\mu$s was found, which points to a complex without any water molecule left in the first coordination sphere. It is probably formed by the phthalate...
fraction with both carboxyl groups deprotonated (no remaining OH-groups). Considering the very narrow peaks (FWHM ~ 1 cm⁻¹) in excitation, it can be assumed that this species corresponds to a well-defined complex (see Figure 12). For the other phthalate species identified in the TLS somewhat shorter luminescence decay times were observed, probably due to the presence of a non-deprotonated carboxyl group in the first coordination sphere. Another possible explanation would be a bound water molecule in exchange for the carboxyl OH-group.

Compared to the other aromatic ligands investigated, the short luminescence decay time (τ = 310 µs) found for 3MB indicates that in this complex three water molecules are present in the first coordination sphere. A possible explanation could be the overall larger spatial requirements of the methoxy group, which limits the number of ligands and thus allows additional water molecules to be coordinated via H-bonding. This way the decay time will be shorter than in the case of BA or 4MB. This hypothesis is further supported by the spectral information, such as peak width and excitation energy, pointing to a well-defined complex and suggesting the assignment to a TYPE A ligand. This special coordination would also be possible for 3HB, for which, however, a much longer luminescence decay time was observed. Apparently, an extra 3HB ligand is bound, leaving room for only one water molecule. Here, additional information (e.g., from NMR experiments) is required to test this hypothesis.

In comparison to the aromatic carboxylates the steric requirements for aliphatic ligands are relaxed. Especially for GL chelation formation can be expected. According to the literature because of the small size of GL, even in a 1:3 complex the Eu(III) ion may still be coordinated by about three water molecules. However, in the (ice) crystal GL can act as a bridging ligand and additional water molecules can be removed from the first coordination sphere. Moreover, some of the OH groups may also be binding to the Eu(III). The observed decay time of 420 µs could in principle be explained by four ligand hydroxyl groups and zero water molecules, or by fewer coordinating OH groups and one water molecule. The relatively broad excitation band (vide supra) would support the latter suggestion, in accordance with references.

The total change in entropy upon complexation consists of two fractions: the entropy increase caused by the ligand release and the entropy loss resulting from conformational rearrangement of the ligand to allow complex binding. With regard to 3HP and GA the entropy loss by ligand rearrangement overcompensates the chelate effect making chelate formation less favourable. In solution GA is bound via only one carboxyl group. In crystals the formation of a ligand bridge has been described. Under the experimental conditions applied (e.g., pH 5 and ligand in high excess), both carboxyl groups of GA should be deprotonated but a bidentate binding via only one COO⁻ group is favoured (one remaining water molecule), providing an explanation for the observed luminescence decay times (see Figure 12). Interestingly the luminescence decay time of 3HP is somewhat shorter than that of GA, indicating a minor influence of the ligand hydroxyl group.

**Excitation energy**

The effect of the geometry of the complexes (especially due to ligand-related constraints) and the covalence of the bonds to the Eu(III) ion are key factors for the energy of the $^5D_0 \leftrightarrow ^7F_0$ transition. Also the Stark splitting of the $^7F_1$ levels affects the energy of the $^5D_0 \leftrightarrow ^7F_0$ transition, which makes - due to opposed effects - predicting the shift of this transition for different ligands/complexes very difficult. Good examples are 2HB and PHA: they show the highest $^5D_0 \leftrightarrow ^7F_0$ transition energy among the complexes investigated, although a relatively high degree of covalence and subsequently a red-shift would be expected. However, both
ligands can form chelates and therefore there will be ligand-related geometry constraints. Apparently, the induced STARK splitting out weighs the nephelauxetic effect and an overall blueshift is observed – adding experimental evidence to the theoretically proposed influence of the $^7F_1$ STARK splitting. Therefore, conclusions with respect to bond covalence and/or geometry can only be drawn for very similar ligands and in combination with additional information, such as the spectral width of the $^5D_0 \leftrightarrow ^7F_0$ transition observed under high-resolution conditions. Of course also information from accompanying techniques such as extended X-ray absorption fine structure (EXAFS) spectroscopy could help to identify geometry differences (especially bond length) in the complexes. For 3HB, 4HB, BA (and also for the minor fraction of low-energy PHA species) the excitation spectra are nearly identical (illustrated in Figure 11 for PHA and 4HB), which suggests that the geometries of those complexes are very similar (e.g., with respect to the Eu-O distances and the bond angles). The same holds true for the aliphatic ligands investigated, except for the glycolic acid, which could form chelates.

In contrast to these “inhomogeneously broadened” species (of 3HB, 4HB, BA, low-energy PHA, GA, 3HP, and 4MB, respectively), higher excitation energies are found for the 3MB complex, which is attributed to the stronger influence of the $^7F_1$ STARK splitting on the energy of the $^7F_0$ level (Figure 13, note the high $\Delta E$ and $N_0(B_{2u})$).

Figure 13: Smoothed excitation spectra of the Eu(III) complexes with methoxy benzoates ($\lambda_{em} = 612$ nm ($E_{em} = 16340$ cm$^{-1}$)) and Jackstraws plot calculated from the $^5D_0 \rightarrow ^7F_1$ and the $^5D_0 \rightarrow ^7F_0$ transition of the related TLS (full lines refer to $N_0(B_{2u})$, dashed lines to $\Delta E$).
**Jackstraws plots, \( ^7F_1 \) Stark splitting and crystal field strength parameter**

The TLS of the Eu(III) complexes investigated show relatively narrow, sloping lines instead of broad, oval-shaped peaks. The same was found for the \( ^5D_0 \rightarrow ^7F_2 \) transition. This indicates that within an inhomogeneously broadened band these energies are correlated with the excitation energy \( ^5D_0 \rightarrow ^7F_0 \). A similar dependence has been reported before for the luminescence of Eu(III) in glassy matrices. Applying the data reduction procedure described before, jackstraws plots are obtained from the TLS.

Figures 11 and 13 (left frames) show that for all organic ligands investigated the observed \( N_v(B_{2q}) \) dependence on the excitation energy was significantly different from that of aqueous Eu(III) in NaClO₄ solution, providing an important confirmation of the actual complex formation. As a reference, also the data obtained for EuCl₃·6H₂O crystals are shown.

The energy difference \( \Delta E \) is added as second abscissa. Comparing “both” diagrams it is evident that the mid Stark level has a minor influence on \( N_v(B_{2q}) \), because the latter includes all three \( ^7F_1 \) levels, whereas \( \Delta E \) is only calculated from the highest and the lowest one.

Looking at the jackstraws plots in detail, each line represents the increase in excitation energy with the crystal field strength parameter for one species of the Eu(III) ligand mixture in question. This is to be regarded as a consequence of the correlation of the \( ^7F_1 \)-splitting and the excitation energy (vide supra). Moreover, the slopes of the lines are different. This may be attributed to the individual symmetry of the crystal field influencing the f-orbitals differently. In the procedure of data analysis and reduction it turned out that in Figures 11 and 13 different slopes can be ascribed to different species.

Moreover, comparing all different ligands it is interesting to note that the crystal field strength parameter \( N_v(B_{2q}) \) and the excitation energy seem to be correlated in general: the absolute excitation energy increases with increasing Stark splitting. An analogous correlation was observed by CARLOS et al. for \( N_v(B_{2q}) \) and the excitation energy, although “in principle, no evident correlation between the nephelauxetic effect and \( N_v(B_{2q}) \) is to be expected”.

The large \( \Delta E \) (or \( N_v(B_{2q}) \)) for Eu(III) complexes of 2HB and PHA (see Figure 11) was attributed to the formation of chelates, in which the concentration of negative charges close to the Eu(III) ion is high. As can be expected considering the formation of complexes without any coordinating water molecule for the “sharp” PHA species charge density is highest for this complex species resulting in the highest \( ^7F_1 \) splitting and consequently in the largest blue shift of the excitation spectrum.

**Crystal field parameters**

The crystal field parameters extracted from the TLS provide an important connection to quantum mechanics. In particular, the crystal field parameters \( B_{20} \) and \( B_{22} \) are related to the crystal field strength parameter \( N_v(B_{2q}) \) according to Equation (17). Those two parameters are in turn involved in the quantum mechanical description of the energy states of the crystal field by the Hamilton operator \( \hat{H}_{CF} \) (Equation (18)):

\[
N_v(B_{2q}) = \sqrt{\frac{4\pi}{5}} \left( B_{20}^2 + 2B_{22}^2 \right)
\]

\[
\hat{H}_{CF} = B_{20} C_0^{(2)} + B_{22} (C_{-2}^{(2)} + C_2^{(2)})
\]

\( C_2^{(2)} \) and \( C_{-2}^{(2)} \) are the one-electron tensor operators describing the crystal field. From the energy of the Stark levels \( ^7F_{1-3} \) to \( ^7F_{1-1} \) of the \( ^7F_1 \) multiplet, \( B_{20} \) and \( B_{22} \) are obtained. In the
present case both parameters are negative, ranging from \(-134 \text{ cm}^{-1} > B_{20} > -690 \text{ cm}^{-1}\) and \(-54 \text{ cm}^{-1} > B_{22} > -304 \text{ cm}^{-1}\), respectively. The absolute values of \(B_{20}\) and \(B_{22}\) are proportional to the energy splitting of \(^7\!F_{1,1}\) and the barycentre of \(^7\!F_{1,2}\) and \(^7\!F_{1,3}\), and to the energy splitting of \(^7\!F_{1,2}\) and \(^7\!F_{1,3}\), respectively. Hence, it may be concluded that \(^7\!F_{1,1}\) and the barycentre of \(^7\!F_{1,2}\) and \(^7\!F_{1,3}\) are subject to considerable changes for a particular species itself as well as for all complexes together, whereas the energy splitting between \(^7\!F_{1,2}\) and \(^7\!F_{1,3}\) does not vary significantly, except for the high energy PHA species.

**Point symmetry group**

The luminescence spectra of the \(^{5}\!D_{0}→^{7}\!F_{1}\) and the \(^{5}\!D_{0}→^{7}\!F_{2}\) transitions of the different species for each model ligand were evaluated with respect to the number of STARK levels visible in the spectrum. It was found that the number of observed STARK levels is dependent on the specific ligand, indicating the formation of complexes with different symmetries and/or number of ligands (species), respectively. For a particular ligand, different complex symmetries were found depending on the species at hand (e.g., a \(D_{2}\) or \(C_{2v}\) symmetry for 2HB).

For the ligands investigated the highest symmetry found is \(D_{2}\), concerning the chelate PHA and 2HB species as well as the solid EuCl\(_3\)⋅6H\(_2\)O. Here, the \(^7\!F_{1,1}\)-level is split into three peaks, which means that the unit cell has orthorhombic, monoclinic or triclinic symmetry. For further refinement one has to consider the splitting of the \(^{5}\!D_{0}→^{7}\!F_{2}\) transition, showing three lines.

**Asymmetry ratio \(r\)**

Complexation is also evident from the high asymmetry ratio \(r\) for all Eu(III) ligand mixtures except for Eu(III) in water. The relatively small value for the solid EuCl\(_3\)⋅6H\(_2\)O confirms the high symmetry deduced from the emission spectrum (symmetry point group: \(D_{2}\)). In contrast, the \(r\) values for complexes with organic ligands are considerably higher due to distortions of the coordination sphere caused by the ligands. Examination of the asymmetry ratio clearly supports the presence of several species.
3.3 Direct spectroscopic evidence of eight- and nine-fold coordinated aquo Eu(III) species in H₂O and D₂O

In aqueous solutions an equilibrium exists between an eight- and a nine-fold coordinated Eu(III)(aq) species.

\[ [\text{Eu(H}_2\text{O)}_9]^{3+} \rightleftharpoons [\text{Eu(H}_2\text{O)}_8]^{3+} + \text{H}_2\text{O} \]

At \( T = 5 \) K, any interchange reaction between potential Eu(III)(aq) species can be ruled out and a reduction of inhomogeneous spectral line-broadening is achieved. From the total luminescence spectra (TLS, excitation vs. emission wavelength) and the luminescence decay matrices (time vs. emission wavelength), fundamental species-selective spectroscopic parameters are determined: excitation wavelength \( \lambda_{\text{exc}} \), decay time \( \tau \), crystal field energy splitting \( \Delta E \) (crystal field strength parameter \( N_c(B_{2g}) \), crystal field parameters \( B_{2g} \) and \( B_{2g} \), asymmetry ratio \( r \), and point symmetry group. The spectroscopic findings were analyzed with respect to the presence of different Eu(III) aquo species. To check the possible influence of the counter ion to inner-sphere coordination, samples were prepared with different counter ions (Cl⁻, ClO₄⁻) and at different pH (2 and 5).

In Figure 14 the \( ^5D_0 \rightarrow ^7F_1 \) low-temperature TLS of Eu(III) in water at \( pH = 5 \) is shown for the excitation wavelength range of 578.8 nm < \( \lambda_{\text{exc}} \) < 579.8 nm, which corresponds to the non-degenerate \( ^5D_0 \rightarrow ^7F_0 \) transition of Eu(III). Therefore, in case of a single Eu(III) aquo species one expects the excitation spectra (horizontal cross-sections, see top spectrum in Fig. 14) to show only one peak and the corresponding high resolution emission spectrum (\( ^7D_0 \rightarrow ^7F_1 \), transition with \( J = 1 \); vertical cross-section of the TLS), should exhibit at most three STARK levels. However, two distinct peaks are visible in the excitation spectrum. Moreover, in the emission spectrum shown on the right of Fig. 1 (extracted from the TLS at \( \lambda_{\text{exc}} = 579.26 \) nm), four clearly resolved peaks are observed. Closer inspection of the TLS (Fig.14, middle) reveals even six peaks. Especially the high-energy emission bands around 590 nm are clearly different, as indicated by the two separate slanted "islands" for the two excitation wavelengths. Thus, from the excitation and emission spectra the presence of two different Eu(III) aquo species, such as \([\text{Eu(H}_2\text{O)}_9]^{3+}\) and \([\text{Eu(H}_2\text{O)}_8]^{3+}\), was already deduced. Very similar spectral (see Table 2) and also temporal (vide infra) features were found at \( pH 2 \) or in the presence of different anions, which excludes the formation of hydroxyl complexes or any inner sphere complexation of the counterions.

From the high-resolution TLS, the crystal field splitting energy \( \Delta E \) of the \( ^7F_1 \) multiplet and the crystal field strength parameter \( N_c(B_{2g}) \) was extracted. For \( \Delta E \) (\( N_c(B_{2g}) \)) values of (142±4) cm⁻¹ ((656±16) cm⁻¹) and (124±4) cm⁻¹ ((568±17) cm⁻¹) were determined for the different species (see Table 2). For \([\text{Eu(H}_2\text{O)}_9]^{3+}\) it is expected that water ligands can approach the central ion more closely and subsequently a stronger crystal field is exerted on the Eu(III), which is reflected in a larger \( \Delta E \) (\( N_c(B_{2g}) \)). This expectation is also supported by crystal field calculations, according to which the crystal field splitting would be significantly larger for the eightfold coordinated species than for the nine-fold coordinated. Therefore, species 1 with its excitation maximum at \( \lambda_{\text{exc1}} = 579.43 \) nm is assigned to an eightfold coordinated

---

europium aquo ion. This species shows the strongest splitting of the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition (larger $\Delta E(N_{\text{v}}(B_{2g}))$), as can be seen in Fig. 14 and 15.

Figure 14: TLS of a 0.2 M solution of EuCl$_3$ in water at pH = 5; T = 5 K. The top spectrum shows the excitation cross-section at $\lambda_{\text{em}} = 590$ nm, while the graph on the right hand side shows the emission spectrum applying non-selective excitation at $\lambda_{\text{exc}} = 579.26$ nm (white lines). Red lines indicate the cross-sections at species-selective excitation wavelengths ($\lambda_{\text{exc}1} = 579.43$ nm and $\lambda_{\text{exc}2} = 579.17$ nm), of which the corresponding emission spectra are shown in Figure 15.

Furthermore, it is interesting to consider the ratio of the crystal field parameters $B_{20}$ and $B_{22}$, determined from the energy splitting of the $^7\text{F}_1$ multiplet. $B_{20}$ represents the energy splitting between the highest ($^7\text{F}_{1\text{-}3}$) and the lowest energy level ($^7\text{F}_{1\text{-}1}$) in relation to the barycenter, whereas $B_{22}$ displays the energy separation of the $^7\text{F}_{1\text{-}2}$ and the $^7\text{F}_{1\text{-}3}$ level. Obviously, the $^7\text{F}_{1\text{-}1}$ level of species 1 exhibits a significantly lower energy than that of the other species, resulting in a higher absolute value of $B_{20}$ and in turn of the ratio $B_{20}/B_{22}$ (see Table 1). The latter was also predicted by the crystal field calculations and therefore further supports the assignment of species 1 as eightfold coordinated.

This assignment is also in good agreement with the expected relative excitation energies for eight- and nine-fold coordination. Considering the nephelauxetic effect, the excitation energy is dependent on bond covalence, which in turn is mainly determined by the distance and number of the coordinating molecules. Thus, according to MALTA et al. an increase of the overlap polarizability, mainly caused by a contraction of the Eu(III)-to-ligand distance, is accompanied by a red-shift of the excitation wavelength. Hence, the excitation wavelength of the eight-fold coordinated Eu(III) (species 1) is expected to be red-shifted compared to the nine-fold coordinated (species 2), if the contraction of the bond length outweights the loss of one H$_2$O ligand. Preliminary DFT calculations indicated that within the eightfold coordinated species more charge of the Eu(III) is transferred to the ligands than in
[Eu(H₂O)₉]³⁺. Therefore, the bonds are slightly more covalent in species 1, which is in agreement with the species assignment based on the position of the ⁵D₀→⁷F₀ transition.

Table 2: Data collected for the two distinct species in aqueous solution at 5 K.

<table>
<thead>
<tr>
<th></th>
<th>species 1</th>
<th>species 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>number of coordinating</td>
<td>n_H₂O</td>
<td>8</td>
</tr>
<tr>
<td>H₂O molecules</td>
<td></td>
<td></td>
</tr>
<tr>
<td>excitation wavelength</td>
<td>λ_{exc}</td>
<td>579.43</td>
</tr>
<tr>
<td>[nm]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>decay time</td>
<td>τ</td>
<td>123±9</td>
</tr>
<tr>
<td>[µs]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>crystal field energy</td>
<td>ΔE</td>
<td>142±4</td>
</tr>
<tr>
<td>splitting</td>
<td>[cm⁻¹]</td>
<td></td>
</tr>
<tr>
<td>crystal field strength</td>
<td>Nₐ(B₂ₐ)</td>
<td>656±16</td>
</tr>
<tr>
<td>parameter</td>
<td>[cm⁻¹]</td>
<td></td>
</tr>
<tr>
<td>crystal field parameters</td>
<td>B₂₀</td>
<td>-392±11</td>
</tr>
<tr>
<td></td>
<td>[cm⁻¹]</td>
<td></td>
</tr>
<tr>
<td>ratio of crystal field</td>
<td>B₂₀/B₂₂</td>
<td>4.0 (3.1)</td>
</tr>
<tr>
<td>parameters (calc. values)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>point symmetry group</td>
<td></td>
<td>C₁, C₂ or C₅</td>
</tr>
<tr>
<td>asymmetry ratio</td>
<td>r</td>
<td>0.56±0.07</td>
</tr>
</tbody>
</table>

In Figure 15 high-resolution luminescence spectra of the eight- and nine-fold coordinated species are shown. The spectra were obtained from the total luminescence spectrum for site-selective excitation at λ_{exc₁} = 579.43 nm and λ_{exc₂} = 579.17 nm (see Figure 14, red vertical lines).

Figure 15: Normalized luminescence emission spectra (⁵D₀→⁷F₁ and ⁵D₀→⁷F₂ transition) of both species in H₂O, at selective excitation wavelengths indicated in Figure 14 as
vertical red lines. Black curve: species 1, $\lambda_{\text{exc}1} = 579.43$ nm; grey curve: species 2, $\lambda_{\text{exc}2} = 579.17$ nm. The dotted parts of the spectrum of species 2 (approx. at $\lambda_{\text{em}} = 589$ nm and 612 nm) are related to residual emission belonging to species 1 (see Figure 14). For clarity, the inset shows the splitting of the $^5\text{D}_0\rightarrow^7\text{F}_2$ transition in detail; the transition was fitted with five and four Gauss peaks for the eight- and the ninefold coordinated Eu(III) species, respectively.

From the emission spectra one can calculate the asymmetry ratio $r$, it is expected to be larger for the eightfold coordinated species because of larger distortion from inversion symmetry. For species 1, $r_1$ was calculated to be $0.56 \pm 0.07$, whereas for species 2, $r_2 = 0.35 \pm 0.04$ was found (see Table 2). For species 1 literature data are available ($r = 0.56$), which are in excellent agreement with the value at hand and thus further confirm the assignment made for species 1 and 2 (see Table 2).

For eightfold-coordinated Eu(III) a square antiprismatic coordination polyhedron (ideal polyhedron: $D_{4h}$ symmetry) and for ninefold coordinated [Eu(H$_2$O)$_3$]$^{3+}$ a tricapped trigonal prismatic coordination polyhedron (ideal: $D_{3h}$ symmetry) is expected, based on crystal data of model compounds. In the case of species 1, we found that the $^5\text{D}_0\rightarrow^7\text{F}_1$ transition shows three STARK levels, and five were found for the $^5\text{D}_0\rightarrow^7\text{F}_2$ transition (corresponding to the maximum STARK splitting; see Figure 15). Therefore, the lowest point symmetry groups possible ($C_1$, $C_2$ or $C_3$) can be assigned to species 1. For the ninefold coordinated species 2, a $C_{2v}$ symmetry can be determined from the STARK splitting pattern (see Figure 2): the $^5\text{D}_0\rightarrow^7\text{F}_1$ transition shows 3 lines (the peak at 589 nm belongs to species 1 as can be seen in Fig. 1, see the cross section for 579.17 nm) and the $^5\text{D}_0\rightarrow^7\text{F}_2$ transition shows 4 lines (see inset of Figure 15, the peak at 612 nm belongs to species 1). These findings suggest that in the frozen solutions distorted coordination polyhedra are present. Regarding the dynamic interchange between species 1 and 2 in liquid samples, with a water molecule entering/leaving the coordination polyhedron, the latter is not able to stay in an ideal symmetry at all and a lowering of the average symmetry down to $C_{2v}$ and even lower symmetry for the liquid state can be expected. Thus, in the frozen solutions a snapshot is seen. Changing the solvent from H$_2$O to D$_2$O, independent on the counter ion, virtually the same TLS was obtained and no isotopic effect in the luminescence spectra was detectable.

In order to further support the species assignment of the spectral analysis, luminescence decays under site-selective excitation conditions were recorded in H$_2$O as well as in D$_2$O. In H$_2$O for $\lambda_{\text{exc}1} = 579.43$ nm and $\lambda_{\text{exc}2} = 579.17$ nm mono-exponential luminescence decays were obtained, with decay times $r_1 = (123 \pm 9)$ µs (species 1; 8 H$_2$O) and $r_2 = (109 \pm 8)$ µs (species 2; 9 H$_2$O; see Table 2), respectively. In aqueous solutions, the major contribution in the deactivation of Eu(III) is attributed to the presence of hydroxyl groups in the first coordination sphere. Hence, due to the absence of OH-induced quenching, the luminescence decay times measured in D$_2$O solutions are considerably longer: (3.5 ± 0.12) ms for species 1 and (3.7 ± 0.18) ms for species 2.

Utilizing the correlation between decay time and the extent of OH coordination, equations such as Equation (7) have been derived empirically.

$$n_{\text{H}_2\text{O}} = 1.11 \cdot \left( \frac{1}{\tau_{\text{H}_2\text{O}}} - \frac{1}{\tau_{\text{D}_2\text{O}}} - 0.31 \right)$$ (19)

In spite of being frequently used to estimate the number of coordinated water molecules ($n_{\text{H}_2\text{O}}$) from luminescence decay time measurements, such correlations have certain
limitations, especially when comparing complexes with strongly different ligands, in different media or under different physical conditions. However, they work very well in the case of eight- and ninefold coordinated Eu(III)(aq) measured under identical experimental conditions: the decay time data of the present study are in good agreement with literature data, such as of YAMASE et al. \( (r = 130 \pm 10 \mu s \text{ for } [\text{Eu(H}_2\text{O)}]_{33}^{3+} \text{ determined in a solid host crystal at } 4.2 \text{ K}) \). Moreover, the findings enable an extension of the data basis for Equation (19), which so far was based on measurements of Eu(III) complexes with \( n_{\text{H}_2\text{O}} \leq 6 \). Combining literature data with our data set, the coefficients of Equation (19) are only slightly changed, and hence the overall validity of the equation is further supported. Thus, the time resolved approach further supports the assignments that were made based on spectral data: species 1 (\( \lambda_{\text{exc}} = 579.43 \text{ nm; longer decay time} \)) \( \rightarrow \) eightfold coordinated, species 2 (\( \lambda_{\text{exc}} = 579.17 \text{ nm; shorter decay time} \)) \( \rightarrow \) ninefold coordinated. From the spectroscopic data collected it may be further concluded that the majority of Eu(III) is coordinated by nine H\(_2\)O molecules.

**Influence of chloride or sulphate anions on the speciation of europium in D\(_2\)O monitored by site-selection spectroscopy at 5 K**

In the preceeding chapter the “frozen” equilibrium between the eight- and ninefold Eu(III) species in H\(_2\)O at ultra-deep temperature (= 4 K) using FLN spectroscopy was characterized in depth. The equilibrium was chosen as a sensitive intrinsic probe to monitor even small effects of the ionic strength on the solution conditions. In the present paragraph high-resolution site-selective luminescence spectroscopy was applied to monitor the influence of different inorganic ligands – namely perchlorate, chloride, and sulphate – on the equilibrium between eight- and nine-fold coordinated Eu(III) in D\(_2\)O (The deuterated solvent was chosen because the strong OH-group related quenching was eliminated and significantly higher luminescence intensities were obtained improving the signal-to-noise ratio of the measurements).

While sulphate was expected to be a relatively strong ligand, perchlorate as well as chloride are considered a weak ligands not entering the first coordination sphere of the Eu(III) ion. The influence of these anions on the luminescence characteristics was monitored up to an ionic strength of \( l = 6 \). Based on the spectroscopic results conclusions on the second coordination sphere depending on the counter ion are drawn.

Figure 16 shows the excitation spectra of Eu(III) in the presence of the different anions for an ionic strength.
Figure 16: Excitation spectra of a 0.2 M Eu(III) solution in the presence of different counter ions for the wavelength range of 578.6 nm < $\lambda_{ex}$ < 580.0 nm, which corresponds to the $^5D_0 \rightarrow ^7F_2$ transition (in D$_2$O, $I = 0.4$ in case of perchlorate and chloride, $I = 0.7$ in case of sulphate).

It can be seen that perchlorate and chloride yielded almost identical excitation spectra with two distinct peaks at $\lambda_{ex} = 579.17$ nm and $\lambda_{ex} = 579.43$ nm corresponding to [Eu(D$_2$O)$_9$]$^{3+}$ and [Eu(D$_2$O)$_8$]$^{3+}$, respectively. Considering the relative height of the two peaks, the equilibrium seems to be largely independent on the anions. The nearly unaltered excitation spectrum of Eu(III) suggests that perchlorate and chloride are weak ligands forming only outer-sphere complexes.

In contrast, in the presence of sulphate ions a distinctly altered excitations spectrum was found. The observed strong change is attributed to the formation of inner-sphere complexes, in which water molecule are removed from the first coordination sphere by the sulphate. Compared to highly crystalline samples like EuCl$_3$·6H$_2$O (solid), which show very sharp peaks, in case of sulphate an increased inhomogeneous broadening of the excitation spectrum is found. Moreover, a closer inspection of the excitation spectrum showed a slight asymmetry which is an indication that different species may be present in the sample, although according to a species analysis based on literature data only Eu(SO$_4$)$_2$$^-$ complexes are expected.
Figure 17: Asymmetry ratio \( r \) of a 0.2 M Eu(III) solution with several counter ions in D₂O (\( I = 0.4 – 0.7, \lambda_{ex1} = 579.58 \) nm and \( \lambda_{ex2} = 579.17 \) nm)

From the emission spectra obtained under site-selective excitation the asymmetry ratio \( r \) was calculated (Figure 17). The difference in the absolute values of \( r \) between chloride and perchlorate on the one hand side and sulphate on the other side underlines that the complexation mode of these ions is different. In general, the replacement of water (or D₂O in the present study) from the first coordination sphere of europium by an (in)organic ligand leads to changes in complex geometry (symmetry), which in turn are expected to have an impact on the intensity of the hypersensitive \( ^5D_0 \rightarrow ^7F_2 \) transition (and subsequently on \( r \)).

Compared to asymmetry ratio of sulphate the asymmetry ratio \( r \) of perchlorate is five times smaller. The distinct increase of \( r \) in case of sulphate is a strong indication for the formation of inner-sphere complexes. Chloride and perchlorate yielded smaller values of \( r \) pointing to outer-sphere complexes with water (or D₂O) distributed relatively symmetrically in the first coordination sphere of europium. Due to the stronger polarizability of chloride in comparison to the perchlorate, the intensity of the \( ^5D_0 \rightarrow ^7F_2 \) is expected to be higher yielding a slightly higher \( r \) (see Figure 17).

In addition also site-selectively excited luminescence-decays were recorded. In all cases mono-exponential luminescence decays were obtained. The calculated luminescence decay times are summarized in Table 3. Here, for sulphate the shortest luminescence decay times were found indicating that sulphate ions are intrinsically quenching the Eu(III)-luminescence (possibly via a S=O bond vibration). The comparison of the luminescence decay times for the eight- and nine-fold coordinated species in case of chloride or perchlorate and for “red” and “blue” excitation in case of sulphate also revealed slight but distinct differences. While for perchlorate very similar values for the luminescence decay times of the two species were found, in case of chloride and sulphate slightly different numbers were calculated. The
perchlorate data underline the very weak potential of the ion to enter the first coordination sphere of europium independent on the number of surrounding water molecules. On the other hand chloride seems to respond to the number of water molecules in the first coordination sphere of europium. Chloride ions may even quench the Eu(III) luminescence in the special case of inner-sphere complexation. Although from the spectral measurements no indication for an inner-sphere complexation of chloride was found, the slight difference in the decay times may be seen as an effect resulting from chloride located in the second coordination sphere of the eight-fold coordinated species. Here, the chloride may approach the europium ion slightly closer due a decrease in the shielding by the water molecules of the first coordination sphere.

Table 3: Luminescence-decay times of the $^{5}D_{0}$–sublevel of a 0.2 M Eu(III) ($I = 0.4 – 0.7$) solution with different counter ions in D$_2$O ($^{*}\lambda_{\text{ex}} = 579.58$ nm).

<table>
<thead>
<tr>
<th>Counter ion</th>
<th>$\tau$ [ms] $\lambda_{\text{ex}} = 579.48$ nm</th>
<th>$\tau$ [ms] $\lambda_{\text{ex}} = 579.17$ nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu$^{3+}$/Cl$^{-}$</td>
<td>3.54 ± 0.03</td>
<td>3.88 ± 0.09</td>
</tr>
<tr>
<td>Eu$^{3+}$/ClO$_4^{-}$</td>
<td>3.59 ± 0.07</td>
<td>3.50 ± 0.07</td>
</tr>
<tr>
<td>Eu$^{3+}$/SO$_4^{2-}$</td>
<td>2.78 ±0.05$^{a}$</td>
<td>2.98 ± 0.06</td>
</tr>
</tbody>
</table>

Variation of the ionic strength

Since sulphate showed an inner-sphere complexation already at moderate ionic strength, only chloride and perchlorate were further investigated up to an ionic strength of $I = 12$. In the experiments luminescence excitation spectra as well as site-selectively excited emission spectra (calculation of asymmetry ratio $r$) and luminescence decay times were collected.

Perchlorate: In Figure 18 the excitation-spectra of Eu(III) as a function of ionic strength for the range of 0.5 < $I$ < 12 are shown. The normalized spectra indicate that the relative amount of eight- and nine-fold coordinated europium is influence by the ionic strength (see Figure 18). The increase of the relative contribution of the nine-fold coordinated species can be seen from the ratio of the related areas (fitted with a Gaussian function) in the excitation spectrum. The shift of the equilibrium towards the nine-fold coordinated species upon increasing the ionic strength is strongest for the range of $I < 4$. A similar tendency is seen for the asymmetry ratio. The asymmetry ratio $r$ decrease from 0.5 at low ionic strength to about 0.3 at ionic strength $I > 2$. It seems that at medium to high ionic strength the small differences between eight- and nine-fold coordinated europium are “overruled” by the presence of a large excess of perchlorate.

In Table 4 the luminescence decay times for both species determined at different ionic strength obtained for site-selective excitation conditions are compared. Although the ionic strength was varied over a large range, neither for the eight-fold nor the nine-fold coordinated europium aquo species any clear influence on $\tau$ was found, which is in good agreement with the findings of BUENZI ET AL. This further stresses the fact that perchlorate shows – if any - only very weak specific interactions with europium.
Figure 18: Normalized excitation spectra of Eu(III) solutions in D$_2$O in the wavelength range of 578.9 nm < $\lambda_{ex}$ < 579.7 nm, which corresponds to the $^5$D$_{0} \rightarrow ^7$F$_{0}$ transition, as a function of ionic strength (counter ion was perchlorate; T = 5 K).

Table 4: Luminescence-decays of Eu(III) in D$_2$O as a function of ionic strength (counter ion was perchlorate; $^a$$\lambda_{ex}$ = 579.48 nm; $^b$$\lambda_{ex}$ = 579.17 nm; T = 5 K).

<table>
<thead>
<tr>
<th>Ionic strength [mol/L]</th>
<th>[Eu(D$_2$O)$_8$]$^{3+}$ $^a$$\tau$ [ms]</th>
<th>[Eu(D$_2$O)$_9$]$^{3+}$ $^b$$\tau$ [ms]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.75</td>
<td>3.60 ± 0.12</td>
<td>3.54 ± 0.06</td>
</tr>
<tr>
<td>1.50</td>
<td>3.59 ± 0.07</td>
<td>3.50 ± 0.07</td>
</tr>
<tr>
<td>2.50</td>
<td>3.43 ± 0.15</td>
<td>3.45 ± 0.12</td>
</tr>
<tr>
<td>6.53</td>
<td>3.52 ± 0.19</td>
<td>3.45 ± 0.09</td>
</tr>
<tr>
<td>8.52</td>
<td>3.51 ± 0.05</td>
<td>3.56 ± 0.03</td>
</tr>
<tr>
<td>11.62</td>
<td>3.40 ± 0.03</td>
<td>3.50 ± 0.07</td>
</tr>
</tbody>
</table>

Chloride: The overall intensity of the $^5$D$_{0} \rightarrow ^7$F$_{0}$ transition increases with increasing ionic strength. Like for perchlorate the relative amount of eight- and nine-fold coordinated aquo species of europium changed with increasing ionic strength. In Figure 19 the ratio of the surface integrals obtained from a Gaussian fit is plotted in dependence of ionic strength. As seen for chlorated the relative contribution of [Eu(H$_2$O)$_8$]$^{3+}$ drops with increasing chloride concentration (ionic strength). In contrast to perchlorate the asymmetry ratio $r$ is increasing with increasing chloride concentration. In Figure 20 the asymmetry ratios of the eight- and nine-fold coordinated species are shown. For both species a comparable increase of $r$ is found. While the eight- and nine-fold coordinated species show a small difference in their
related luminescence decay times, for each species no effect of the ionic strength adjusted by the chloride concentration was observed (see Table 5). This is in accordance with the findings for chlorate, which did also not induce any alteration of the luminescence decay time.

Table 5: Luminescence-decays of $^5\text{D}_0$–sublevel of Eu(III) solutions in D$_2$O as a function of ionic strength (counter ion chloride; $^a\lambda_{\text{ex}} = 579.48$ nm; $^b\lambda_{\text{ex}} = 579.17$ nm; $T = 5$ K).

<table>
<thead>
<tr>
<th>ionic strength $I$</th>
<th>$[^\text{Eu(D}_2\text{O)}_8]^{3+}$ $\tau^a$ [ms]</th>
<th>$[^\text{Eu(D}_2\text{O)}_9]^{3+}$ $\tau^b$ [ms]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.12</td>
<td>3.39 ± 0.08</td>
<td>3.73 ± 0.07</td>
</tr>
<tr>
<td>0.60</td>
<td>3.48 ± 0.04</td>
<td>3.79 ± 0.02</td>
</tr>
<tr>
<td>1.14</td>
<td>3.54 ± 0.03</td>
<td>3.88 ± 0.09</td>
</tr>
<tr>
<td>3.10</td>
<td>3.45 ± 0.04</td>
<td>3.80 ± 0.04</td>
</tr>
<tr>
<td>4.60</td>
<td>3.43 ± 0.04</td>
<td>3.85 ± 0.04</td>
</tr>
<tr>
<td>6.20</td>
<td>3.45 ± 0.06</td>
<td>3.80 ± 0.04</td>
</tr>
</tbody>
</table>

Figure 19: Normalized excitation spectra of Eu(III) solutions in D$_2$O in the wavelength range of $578.9$ nm $< \lambda_{\text{ex}} < 579.7$ nm, which corresponds to the $^5\text{D}_0 \leftrightarrow ^7\text{F}_0$ transition, as a function of ionic strength (counter ion chloride; $T = 5$ K).

The intensity increase of the $^5\text{D}_0 \leftrightarrow ^7\text{F}_0$ transition has been described by BREENN and HORROCKS was attributed to an inner-sphere complexation of chloride ions, which contradicts findings of STUMPF et al., who describe a luminescence quenching by chloride due to inner-sphere
complexation. From the spectral and time-resolved luminescence data presented in this study, it can be concluded that no inner-sphere complexation by chloride is observed. Especially the spectral data point to an outer-sphere complexation, since no spectral shift is observed (like in case of sulphate), only the asymmetry ratio \( r \) was found to increase (for both species). The increased intensity of the \( ^5D_0 \rightarrow ^7F_0 \) transition and the alteration of \( r \) are related to alterations of the second coordination sphere (outer-sphere binding) of the europium ion by the increased concentration of chloride ions. A distortion in the second coordination sphere will also slightly influence the inner coordination sphere and subsequently may be reflected by small changes in the transition probabilities of the different electronic transitions of the europium ion (e.g., the \( ^5D_0 \rightarrow ^7F_0 \) transition or the \( ^5D_0 \rightarrow ^7F_2 \) transition).

![Figure 20](image)

**Figure 20:** Asymmetry ratios of Eu(III) solutions in D\(_2\)O as a function of ionic strength (counter ion chloride; \( T = 5 \) K).

### 3.4 Molecular ruler

**Distribution of binding sites in model polymers**

The distribution of binding sites in natural occurring polymers, like humic and fulvic acids, as well as on mineral surfaces is a key question for the understanding of sorption processes between metal ions and complexing agents like organic and inorganic ligands. As model
system for natural occurring polymers, poly (acrylic acid) acid (PAA\textsuperscript{8}) was used. For a first insight on the distribution of inorganic binding sites on mineral surfaces Kaolinit KGa 2 was used. In the field of a final disposal of nuclear waste, the metal ions of main interest are actinide and lanthanide ions. As it is known that the energy transfer mechanism proposed by Förster can be applied to lanthanide ions, this study deals with the intra-lanthanide energy transfer (ILET). Here, Eu(III) and Tb(III) can be used as donors. A suitable acceptor is Nd(III). In contrast La(III) cannot act as an acceptor for ILET. Due to this fact, from measurements with La(III) one can observe effects on the donor luminescence resulting only from the presence of additional metal ions, which can compete for binding sites. The main difference in the addition of La(III) or Nd(III) to solutions containing PAA and Tb(III) is shown in Figure 21.

![Figure 21: Influence upon addition of different lanthanide ions (left: La(III), right: Nd(III)) on the time-dependent Tb(III) luminescence in complexes with PAA 450 000. The concentration of Nd(III) and La(III) increases from 0 mmol L\textsuperscript{−1} up to 0.91 mmol L\textsuperscript{−1}. \(\lambda_{\text{ex}} = 377\ \text{nm},\ \lambda_{\text{em}} = 545\ \text{nm},\ \text{pH} 5,\ c_{\text{TB(III)}} = 0.2\ \text{mmol L}^{-1},\ c(\text{PAA}) = 5\ \text{g L}^{-1}\).](image)

While upon addition of Nd(III) to Tb(III)-PAA complexes the Tb(III) luminescence decay becomes faster, the addition of La(III) shows nearly no effect. Only a slight increase in the Tb(III) luminescence decay time could be observed. A comparable behavior was also found for Eu(III) as donor. From the measurements with La(III) it can be deduced, that the quenching of the donor’s luminescence is not only an effect of a replacement of donor ions from binding sites, but must be the result of a different process. The quenching of the luminescence is caused by an intra-lanthanide energy transfer (ILET). As mentioned above, La(III) cannot act as acceptor in an ILET. Therefore, the donors luminescence decay time is not quenched due to the presence of La(III) ions. As shown in Equation (10) the donor’s luminescence decay time in presence of an energy acceptor like Nd(III) depends on the Förster distance \(R_0\) and the distance \(R\) between donor and acceptor. The calculation of distances from the quenching of the donor’s luminescence requires the knowledge of the

\textsuperscript{8} PAA with two different molecular weights – 450 000 g mol\textsuperscript{−1} (PAA 450 000) and 1 800 g mol\textsuperscript{−1} (PAA 1 800) – was included.
value of $R_0$. In this study, it was tried to calculate $R_0$ according to Equation (5). Therefore, the orientation factor was set to $\kappa^2=2/3$ and the refractive index to $n = 1.334$. The overlap integral $J$ can be calculated according Equation (6) from the donor luminescence spectrum and the acceptor absorption spectrum. A crucial parameter is the donor quantum yield $\Phi_D$.

In case of Eu(III) the quantum yield can be calculated from the luminescence emission spectrum

$$\Phi_{D^{3+}} = \frac{\tau(Eu^{3+})}{\rho(Eu^{3+})} \cdot \frac{4 \pi}{3h} n^2 D_{ND,1}$$  \hspace{1cm} (20)

with $D_{MD,1} = 884 \cdot 10^{-8} \text{ D}^2$, $\rho_1$ is the energy difference between the $^5D_0$ and the $^7F_1$ energy level in Eu(III), $\tau(Eu^{3+})$ is the luminescence decay time of the Eu(III) in absence of any energy acceptors, $h$ is Planck’s constant and $\rho(Eu^{3+})$ is the proportion of the luminescence intensity of the $^5D_0 \rightarrow ^7F_1$ transition to the total luminescence intensity. In case of Tb(III) the equation for the luminescence quantum yield is

$$\Phi_{D^{3+}} = \frac{\tau(Tb^{3+})}{\rho(Tb^{3+})} \cdot \frac{A_{D_{4}}}{A_{D_{6} - ^7F_0}} \cdot \Phi_{D^{3+}}$$  \hspace{1cm} (21)

The Einstein coefficient for the spontaneous transition $^5D_4 \rightarrow ^7F_6$ can be calculated according Strickler-Berg from the absorption spectrum of the Tb(III) ion. The luminescence decay time of the Tb(III) is given by $\tau(Tb^{3+})$. Here, $A(Tb^{3+})$ is the proportion of the luminescence intensity of the $^5D_4 \rightarrow ^7F_6$ transition to the total Tb(III) luminescence intensity. At this stage, the luminescence quantum yields for both donor lanthanide ions can be calculated from spectroscopic parameters like luminescence emission and/or absorption spectrum as well as luminescence decay time. Figure 22 shows the resulting Förster distances $R_0$ for Eu(III) or Tb(III) as donors and Nd(III) as acceptor in complexes with PAA as function of pH.

**Figure 22:** Förster distances $R_0$ as a function of pH for the donor-acceptor pair Eu(III)/Nd(III) (squares) and Tb(III)/Nd(III) (circles) in complexes with PAA 1 800 (closed symbols) or PAA 450 00 (open symbols).
For both donor-acceptor pairs – Eu(III)/Nd(III) and Tb(III)/Nd(III) – independent of the molecular weight of the PAA similar Förster distances were found. In case of Eu(III)/Nd(III) the Förster distance increases from values around $R_0 = 5.2$ Å at pH 3 to $R_0 = 6.3$ Å at pH 8. For the same pH range the donor-acceptor pair Tb(III)/Nd(III) gives Förster distances between 6.5 Å and 7.3 Å. The increase in the Förster distance results mainly from the increase of the quantum yield of the donor luminescence. Taking into account, that the transfer efficiency can only measured with an accuracy between $1% < \eta < 99\%$, the distance range, which can be observed with time-resolved measurements is $0.5 R_0 < R < 2R_0$.

According to Equation (9) it should be possible to deduce distances between a suitable acceptor like Nd(III) and a donor lanthanide ion like Tb(III) or Eu(III) from luminescence decay measurements in absence and presence of Nd(III). As can be seen from Figure 21, the donor luminescence decay becomes non-monoexponential upon addition of Nd(III). In the system under investigation, the lanthanide ions are complexed to binding sites (in this case carboxylic groups) on a polymer chain. As the concentration of the lanthanide ions are chosen, that no saturation of binding sites can happen, the lanthanide ions are randomly distributed on the polymer chains. Furthermore, the polymer chains itself will have their certain conformation, which results from the number of charges arising from deprotonation of carboxylic groups as a function of pH and complexation of lanthanide ions. Therefore, the found non-monoexponential behavior of the luminescence decays of the donor lanthanides is addressed to a distribution of distances between the lanthanide ions acting as donor and acceptor. As shown in Equation (11) and (12), a Gaussian distribution can be applied to fit the measured luminescence decays. From the fitting, the mean distance between the lanthanide ions and the width of the distribution can be obtained.

![Graph showing the distribution of distances obtained by time-resolved luminescence measurements.](image)

**Figure 23:** Distribution of distances obtained by time-resolved luminescence measurements. The black (PAA 1 800) and gray (PAA 450 000) filled domains results from averaging of the fitting of the donor’s luminescence decay according Equation (8) in measurements with both donor-acceptor pairs – Eu(III)/Nd(III) and Tb(III)/Nd(III).
In Figure 23 the pH dependence of the distances between the donor lanthanide ion and acceptor lanthanide ion is shown. For both PAA the distance decreases slightly from pH 3 to a range between pH = 3.5 and pH = 4.0. At pH values above pH 4 the distance increases. Above pH = 5.5 the behavior for both PAA changes. For PAA 450 000 a virtually linear increase in the distance between donor and acceptor lanthanide ion was found, whereas for PAA 1 800 distances could only be deduced up to a pH = 5.5. At higher pH values the distance of both, donor and acceptor, lanthanide ions are too far for an efficient energy transfer.

The main difference between both PAA samples is the molecular weight and consequently the average length of the polymer chains. It is attempting to assume, that in case of PAA 450 000 donor and acceptor lanthanide ion are complexed to the same polymer chain and with increasing pH the unraveling of the polymer chain can be observed, reflected by a steady increase in the donor-acceptor distance. With increasing pH the degree of deprotonation of the carboxylic groups increases. Therefore, it is more likely for PAA 1 800 that donor and acceptor lanthanide ion are located at different polymer chains even at slightly acidic pH values. As a consequence, the mean distance between both ions is too far for an energy transfer as every polymer chain can diffuse freely through the solution.

As for both PAA the lanthanide ions are complexed by functional groups (binding sites) of the polymer chain, the distances of the lanthanide ions reflect the distribution of binding site along this polymer chain.

**Distances between binding sites on mineral surfaces**

The distribution of binding sites is also of interest in sorption processes. Here, mineral phases can act as inorganic complexation agents. The objective of this study is to apply the ILET – which was studied very detailed in the interaction of lanthanide ions with PAA – also to these sorption phenomena. The underlying idea is that sorption on mineral surfaces occurs at specific sites with certain distances to each other.

For this study Tb(III)/Nd(III) was chosen as donor-acceptor pair and KGa-2 as mineral phase. As a starting point, isotherms for the adsorption of Tb(III) onto KGa-2 were measured at pH 3 and pH 5. The amount of Tb(III) adsorbed to KGa-2 were calculated from the difference between the Tb(III) concentration in the solution before and after addition of 1 g of KGa-2. Before the luminescence measurements supernatant and solution was separated by centrifugation.
Figure 24: Adsorption isotherm of Tb(III) onto KGa-2 at room temperature and pH 3. In these measurements 1 g KGa-2 was added to 10 mL Tb(III) solution. The amount of sorbed Tb(III) was calculated from the difference of the Tb(III) concentration before and after addition of KGa-2 to this solution. The line results from the fitting of the experimental points according Equation (22).

The results of the sorption experiments are shown in Figure 24. A Langmuir isotherm was fitted to the experimental points

\[ q = \frac{q_{\text{max}} K c}{1 + K c} \]  

(22)

with \( q_{\text{max}} \) the maximum number of sorption sites, \( K \) the equilibrium constant of the sorption process and \( c \) the concentration of the unsorbed Tb(III). The fitting showed a slight increase in the maximum number of binding sites from \( q_{\text{max}} = (4.9 \pm 0.5) \times 10^{-6} \) mol·g\(^{-1}\) at pH 3 to \( q_{\text{max}} = (6.4 \pm 0.6) \times 10^{-6} \) mol·g\(^{-1}\) at pH 5, which was expected as deprotonation increases with pH. The sorption constant \( K \) increases in the same pH range from \( \lg(K/L\cdot\text{mol}^{-1}) = 4.5 \pm 0.2 \) to \( \lg(K/L\cdot\text{mol}^{-1}) = 5.1 \pm 0.3 \). In the experiments with Tb(III) and Nd(III) the lanthanide ion concentration was fixed to \( c(\text{Ln(III)}) = 4 \times 10^{-4} \) mol·L\(^{-1}\) to avoid saturation of the sorption sites.
Figure 25: Left: Decrease in averaged luminescence decay time of Tb(III) (spheres) upon increasing Nd(III) concentration due to a transfer of energy. The energy transfer efficiency $\eta$ (stars) was calculated according Equation (8).

Right: From the efficiency of the energy transfer, the distances between Tb(III) and Nd(III) was calculated using Equation (7) and $R_0 = 9.12 \text{ Å}$. This value was taken from the literature referenced in the text.

Figure 25 show some results of the sorption experiments, when Tb(III) and Nd(III) are present. After addition of KGa-2 and equilibrating of the suspension the solid and liquid phase were separated by centrifugation. With increasing Nd(III) concentration a decrease of the averaged luminescence decay time of Tb(III) was found. A similar decrease did not showed up neither in the solution before nor in the supernatant after addition of KGa-2 (data not shown). Only adsorbed to a surface, both lanthanide ions are located close enough for an energy transfer.

As above derived, the decrease in luminescence decay time of Tb(III) can be connected to the distance between Tb(III) and Nd(III) (cf. Equation (7) and (8)). In this case the value of the Förster distance $R_0 = 9.12 \text{ Å}$ was taken from the literature\(^9\). The calculations show a decrease of the donor-acceptor distance from $R = 1.2 \text{ nm}$ down to $R = 0.85 \text{ nm}$ following an increase of the Nd(III) concentration from 1 µmol·L\(^{-1}\) up to 200 µmol·L\(^{-1}\). As the distances derived stay virtually constant at concentration above 100 µmol·L\(^{-1}\) it appeared, that 0.85 nm should be the shortest possible distance between the lanthanide ions and hence, the distance between suitable sorption sites for lanthanide ions.

4. Summary

Eu(III) luminescence spectroscopy, both in the steady-state and the time-resolved mode, is an appropriate technique to study the properties of complexes between heavy metal ions and humic substances (or model compounds of such), which play a key role in the distribution of metal species in the environment. Unfortunately, room temperature luminescence spectra of Eu(III) complexes with aromatic and aliphatic carboxylic acids – model compounds of binding sites in humic substances – are too broad to fully exploit their potential analytical information content. It is shown that under cryogenic conditions fluorescence-line-narrowing (FLN) is achieved, and the highly resolved spectra provide detailed information on the complexes with different model ligands. Total luminescence spectra (TLS) were recorded, using the $^5D_0$→$^7F_0$ transition for excitation and the $^5D_0$→$^7F_1$ and $^5D_0$→$^7F_2$ transitions for emission. The energy of the excitation transition depends on the ligand involved and the structure and composition of the complex. For most ligands, discontinuities in the high-resolution TLS indicated that more species, i.e. distinct complex structures coexisted in the sample. Selective excitation was performed to measure the species-associated luminescence decay times $\tau$. The latter strongly depends on nearby OH oscillators from coordinating water molecules or ligand hydroxyl groups. Furthermore, the asymmetry ratios $r$ were calculated and the variation of the excitation energy $E_{\text{exc}}$ with the splitting of the $^7F_1$ triplet ($\Delta E$) was determined, which yielded the crystal field strength parameter $N_v(B_{20})$, as well as the crystal field parameters $B_{20}$ and $B_{22}$.

The results extracted can uniquely complement data obtained from X-ray techniques. Moreover, limitations of other techniques due to averaging (e.g. EXAFS) can be overcome using site-selective excitation. All ligands investigated bind to the Eu(III) ion via oxygen (either neutral or charged) and there are just slight differences between the ligands with respect to the interacting groups (COO$^-$ and/or OH). Consequently, the observed distinct differences in the high-resolution excitation and emission spectra (e.g., position of the $^7F_0$→$^5D_0$ transition, STARK splitting) have to be attributed to heterogeneity of the sample, the number of different species as well as the stoichiometry of the complex, the corresponding geometry, and the capability of the ligand to form chelates. The latter is directly correlated with the strength and kinetic lability of the complexes formed. From the STARK splitting of the $^7F_1$ and $^7F_2$ multiplets a symmetry point group analysis was performed.

The interpretation of the data in terms of covalence of the bonds formed (nephelauxetic effect) is far from straightforward and should only be done with great care. The excitation energy is determined by several factors, each with ligand-specific contributions (covalent bonding, symmetry of the coordination polyhedron, STARK splitting), otherwise all lines in the jackstraws plots would coincide. Especially the different geometries of complexes have a significant impact on the STARK splitting. This in turn can affect the energy of the $^7F_0$→$^5D_0$ transition, opposite to the shift caused by the nephelauxetic effect.

The overall comparison of $N_v(B_{20})$ for aromatic carboxylates, aliphatic acids, and methoxybenzoates suggests to classify these ligands into different groups: “loose” complexes with low crystal field strength parameters (e.g. 4HB, BA, 4MB, GL, 3HP and GA), and more rigid complexes with high $N_v(B_{20})$ values (e.g. 2HB, PHA, 3MB).

A straightforward interpretation of the cryogenic luminescence decay times with respect to the number of water molecules left in the first coordination sphere of Eu(III) is crucial. The reliability of this approach depends on whether a thorough calibration can be performed. In addition to the better spectral resolution and higher specificity of the excitation wavelength,
an important advantage of the cryogenic approach is the suppression of activated decay processes, thus providing a clearer picture of the influence of OH oscillators. Two major effects on the luminescence decay times have to be considered: i) water molecules in the second coordination sphere and ii) especially the presence of a hydroxyl group in α-position. Depending on the topology of the ligand, quenching contributions from coordinating OH groups and steric restrictions play a role and need to be considered.

The photophysical characterization of different europium aquo species is difficult at room temperature since the exchange of water molecules in the first coordination sphere is fast compared to the luminescence decay: \(k \approx 1.6 \times 10^9 \text{ s}^{-1}\) (water exchange) vs. \(9 \times 10^3 \text{ s}^{-1}\) (luminescence decay rate). Under the experimental ultra low temperature conditions applied an equilibrium representative for temperatures close to the freezing point of the solution was investigated, which is reasonable because after the solutions are frozen any reaction involving a major molecular movement – such as ligand exchange - should become extremely slow. Possible changes in the structure of the polycrystalline ice matrix surrounding Eu(III) i) are very weak and are not reflected in the spectral properties and ii) may be similar for the two aquo species investigated.

A clear spectroscopic evidence for the presence of two Eu(III) species in H\(_2\)O as well as in D\(_2\)O was found. These two species are assigned to eightfold coordinated (minor fraction) and ninefold coordinated (major fraction) aquo ions, based on an in-depth analysis of the high-resolution TLS and of the luminescence decays. The eightfold coordinated species 1 shows a longer decay time, has shorter Eu(III)-water distances and a less symmetrical arrangement in comparison with the ninefold coordinated species 2.

As a continuation of our spectroscopic investigations of Eu(III) under kryogenic conditions (T \(\approx 5\) K) the influence of counter ion as well as the of the ionic strength on the luminescence characteristics was evaluated. High-resolution total luminescence spectra of Eu(III) were collected in the presence of different inorganic counter ions (perchloride, chloride, and sulphate) covering a ionic strength of the medium up to \(l = 6\). For the different inorganic counter ions the effect on the equilibrium of eight- and nine-fold coordinated water was investigated determining fundamental spectroscopic parameters such luminescence decay time or crystal field parameters. Switching the solvent from H\(_2\)O to D\(_2\)O greatly eliminated the strong luminescence quenching effect of OH-oscillators and allowed to monitor less effective interactions of europium with different anions. Monitoring the equilibrium between eight- and nine-fold coordinated deuterio species at increasing concentrations of chlorate and chloride showed distinct differences in the excitation spectra, in the site-selective emission spectra as well as in the site-selectively excited luminescence decay times. The high resolution power of ultra-low temperature luminescence measurements resolved effects of the second coordination sphere on the luminescence of europium. Perchlorate and chloride form exclusively outer-sphere complexes with Eu(III). In contrast, sulphate ions form inner-sphere complexes and significantly alter the equilibrium of eight- and nine-fold coordinated species. From the luminescence decay times obtained for “red-edge” and “blue-edge” excitation it may be concluded that more than one species is present in the sulphate ions containing system, probably due to variation in the coordination of the sulfate ligand between mono- or bidentate binding or due to a different number of coordinated D\(_2\)O molecules – but from the spectral measurements no clear distinction can be made. Perchlorate and chloride form only outer-sphere complexes with Eu(III) and influence only subsequently the first coordination sphere – at a much smaller extent. Both ions shift the
equilibrium towards \([\text{Eu(D}_2\text{O)}_9]^{3+}\) when increasing the concentration of the corresponding anion. The asymmetry ratio showed different trends for the two anions with increasing ionic strength of the medium. While perchlorate showed no distinguishable effect on the eight- and nine-fold coordinated species, chloride affected the two species clearly in different ways. This can be also concluded from the differences in the luminescence decay times.

Depending on the electronic properties of the organic ligand the observed luminescence properties – especially the luminescence decay time – of the lanthanide complex are defined. For Eu(III) it could be shown that ligands with the capability to form charge transfer states in the complex are prone to a strong ligand-specific quenching. For salicylic acid (and related compounds) the temperature dependence of the ligand-specific quenching was evaluated. It was found that the determined activation energies for different ligands all lay within the same range indicating that the corresponding luminescence quenching in those complexes may be related to the same fundamental process. From transient absorption spectroscopy experiments it was concluded that the formation of an LMCT state with the Eu(III) complex is responsible for the efficient radiationless deactivation. Lanthanide ions such as Tb(III) (or La(III)) do not show comparable transient signals because the formation of a LMCT state in the complex with this class of ligands is not possible.

Energy transfer is a powerful tool to derive distances between energy donors and energy acceptors from luminescence measurements. In case of lanthanide ions, this energy transfer is referred to as ILET – intra-lanthanide energy transfer. From the experiments with PAA it can be concluded, that it is possible to derive any parameter needed for the calculation from luminescence measurements (emission and absorption). ILET can be applied to dissolved as well as sorbed species. Here, ILET was used to deduce information about the distribution of binding sites in a natural polymer analogue and on a mineral surface. In these type of calculations more sophisticated models, like distance distributions, can be included, which gives additional information – beyond mean distances – about the distribution. Furthermore, to be able to measure distances between 5 Å to 12 Å extends the observation range of distances accessible by other methods like EXAFS measurements.
Berichtsblatt

1. ISBN oder ISSN
   Noch nicht bekannt

2. Berichtsart (Schlussbericht oder Veröffentlichung)
   Schlussbericht

3. Titel
   Spektroskopische Untersuchungen zum erweiterten Prozessverständnis in binären und ternären Huminstoff - Tongestein – Lanthanoid Systemen: Thermodynamische und kinetische Kenngrößen

4. Autor(en) [Name(n), Vorname(n)]

5. Abschlussdatum des Vorhabens
   30.6.2011

6. Veröffentlichungsdatum
   Eingereicht zur Veröffentlichung

7. Form der Publikation
   Forschungsbericht

8. Durchführende Institution(en) (Name, Adresse)
   Universität Potsdam, Institut für Chemie (Physikalische Chemie)
   Karl-Liebknecht-Str. 24-25
   14476 Potsdam-Golm

   nicht bekannt

10. Förderkennzeichen *)
    02E10216

11. Seitenzahl
    48

12. Literaturangaben
    9

13. Fördernde Institution (Name, Adresse)
   Bundesministerium für Wirtschaft und Technologie (BMWi)
   11019 Berlin

14. Tabellen
    5

15. Abbildungen
    25

16. Zusätzliche Angaben
   -

17. Vorgelegt bei (Titel, Ort, Datum)
   -

18. Kurzfassung

Schlagwörter
   zeitaufgelöste Laserspektroskopie, Lumineszenz, Lanthanoide, Huminstoffe, Modellliganden

20. Verlag
   Wissenschaftliche Berichte des KIT

21. Preis
   nicht bekannt

*) Auf das Förderkennzeichen des BMBF soll auch in der Veröffentlichung hingewiesen werden.

In order to improve the understanding of fundamental processes related to nuclear waste disposals on a molecular level, stationary and time-resolved luminescence experiments were carried out. In the experiments i) temperature in the interval between 5 K < T < 333 K, ii) ionic strength between 0.2 < I < 6 as well as iii) the ligands itself were varied. Different (in)organic ligands were investigated in complexes with lanthanide ions. Here, the full spectrum of complexity with respect to the ligands was investigated – from low molecular weight compounds (e.g., salicylic acid) to model polymers to natural organic matter (e.g., humic substances) and mineral surfaces. The intra- and intermolecular deactivation processes occurring in the different complexes characterized in great detail using different luminescence parameters such as luminescence decay time, asymmetry ratio, ligand-field strength or the process-related activation energy.

**Keywords:**
time resolved laser spectroscopy, luminescence, lanthanides, humic substances, model ligands