

Device for measurements of selective luminescence excitation spectra of europium (III) based on a nitrogen and dye laser system

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Eu(III) selective excitation spectroscopy involving the ${}^7F_0 \rightarrow {}^5D_0$ transition has been briefly characterized as an important luminescence technique for metal binding sites. An experimental system consisting of a nitrogen laser and a tunable dye laser has been modified for measurements of the Eu(III) excitation spectra. The experimental setup gives a possibility of concurrent registration of excitation spectra and luminescence decay curves for every wavelength of excitation. The system is controlled by a PC using a specially written program for collecting and processing the ${}^7F_0 \rightarrow {}^5D_0$ spectra of Eu(III).

1. Introduction

Several trivalent lanthanides, Ln(III), show characteristic luminescence spectra in the visible and near-IR region. Unlike in the case of *d*-transition metal ion complexes for which the electronic excited states are strongly coupled to the environment via the ligand field (which provides an efficient deexcitation mechanism), in lanthanide complexes the coupling between *f*-excited electronic states and the environment is much weaker. Thus, the radiationless deexcitation processes in lanthanide complexes are relatively inefficient and the luminescence is observed for the middle of the lanthanide series. Among the luminescent lanthanide(III) ions, Eu(III) and Tb(III) are the two most extensively studied in solution. The other members exhibit luminesce which is much less strong unless in the solid state [1].

Both Eu(III) and Tb(III) have forbidden *f*–*f* absorption bands in the UV with molar absorption coefficients less than 3 and well resolved emission bands in the visible range. The maximum absorption of Eu(III) is at 394 nm ($\epsilon \sim 2.75$) and that of Tb(III) is at 368 nm ($\epsilon \sim 0.36$). The emission bands of Eu(III) originate from electronic transitions from the lowest excited state, 5D_0 , to the ground state manifold, 7F_J ($J = 0-6$). For the Eu(III) ion, the intensity, the splitting and the energy of luminescence bands as well as relative intensities of the different bands are

very sensitive to the symmetry and detailed nature of the ligand environment [1]–[3]. For the ${}^7F_0 \rightarrow {}^5D_0$ excitation spectra of Eu(III), both the ground state and the excited state are nondegenerate and cannot be further split by the ligand field. Thus, each Eu(III) environment shows a single absorption peak.

Certain excited states of some lanthanides are able to relax by emission of photons. While such electronic transitions within a $4f^n$ configuration are still Laporte forbidden, an intense laser beam can be used as an excitation source to access the excited state and monitor its luminescence decay quantitatively even in dilute solutions. This process is called laser-induced lanthanide ion luminescence and it has been developed and exploited as a probe for biological systems [4].

The excited state lifetime is efficiently quenched by OH oscillators of inner sphere H_2O molecules bound to the Eu(III) ion. The difference in the decay of the excited state in H_2O and D_2O is proportional to the number of water molecules n coordinated to the first coordination sphere as described by the equation proposed by HORROCKS and SUDNICK [5]

$$n = 1.05 [k(H_2O) - k(D_2O)] \quad (1)$$

where $k(H_2O)$ and $k(D_2O)$ are the exponential decay constants for the luminescence intensity of the excited states in H_2O and D_2O , respectively. The uncertainty has been estimated as ± 0.5 H_2O molecules.

${}^7F_0 \rightarrow {}^5D_0$ selective excitation spectroscopy of Eu(III)

The $4f^6$ electronic configuration of Eu(III) has a nondegenerate ground state 7F_0 and a nondegenerate long-lived emitting state 5D_0 . In other words, the ligand field splits neither the ground nor the emissive states. The Eu(III) ion may be selectively excited by tuning a dye laser to the wavelength of ${}^7F_0 \rightarrow {}^5D_0$ transition in the 578 to 581 nm region and the emission can be monitored at 615 nm (${}^5D_0 \rightarrow {}^7F_2$). The multiplet excitation to higher 5D_j states is followed by rapid decay to the long-lived 5D_0 state. The consequence of this unique 0–0 transition is that in the excitation spectrum of metal complex solution, the number of peaks observed directly corresponds to the number of Eu(III) environments present. If each Eu(III) complex has a constant number of water molecules, the luminescence lifetime is constant. When the luminescence intensity of the ${}^7F_0 \rightarrow {}^5D_0$ transition is recorded for a total photon number emitted by a sample, after the laser pulse excitation, a characteristic constant equivalent to the molar absorptivity for each species is obtained [6].

The relationship is given as follows:

– for absorbance

$$A = \varepsilon cl \quad (2)$$

where: A – absorbance, ε – molar absorptivity (very small), c – concentration of a species and l – the path length of the sample cell,

– for luminescence

$$I = \Phi I_0 kcl = K'c \quad (3)$$

where: I is the luminescence intensity, Φ – the luminescence quantum yield, I_0 – the intensity of the excitation light, k and K are constants.

The selective excitation spectroscopy of the Eu(III) ${}^7F_0 \rightarrow {}^5D_0$ band has been used as an important technique for the study of the lanthanides [6]–[8]. The red shift of spectral maxima has been used for examination of the coordination around the metal ion, *e.g.*, covalency of the metal-ligand bond or number of bound donor groups to the metal ion, in various systems containing the Eu(III) ion by several authors (*cf.* [9]). Correlations between the frequency of the ${}^7F_0 \rightarrow {}^5D_0$ band of Eu(III) and the total formal ligand charge or the maximum ligand coordination number have been observed [10], [11]. Excitation spectroscopy of the Eu(III) ${}^7F_0 \rightarrow {}^5D_0$ band is a powerful technique providing details about the number of chemical environments of the Eu(III) ion and quantitative relations between them.

2. Experimental

2.1. Reagents

Aqueous solutions of the europium perchlorate were prepared by dissolution of Eu_2O_3 (99.99%, Aldrich) in perchloric acid. The pH of the samples was adjusted to ~ 2 with solutions of NaOH or HClO_4 .

Samples containing Eu(III) with picolinic acid N-oxide (NO-pic) plus 1,10-phenanthroline (phen) were prepared by mixing the components to obtain the solution composition of Eu:NO-pic:phen = 1:3:1, and pH adjusted to ~ 4.5 .

2.2. Instrumentation

The existing system consisted of a nitrogen laser and a tunable dye laser enlarged so that it could be used for measurements of the ${}^7F_0 \rightarrow {}^5D_0$ selective excitation spectra of Eu(III) [12]. A key feature of an experiment should be a possibility of concurrent

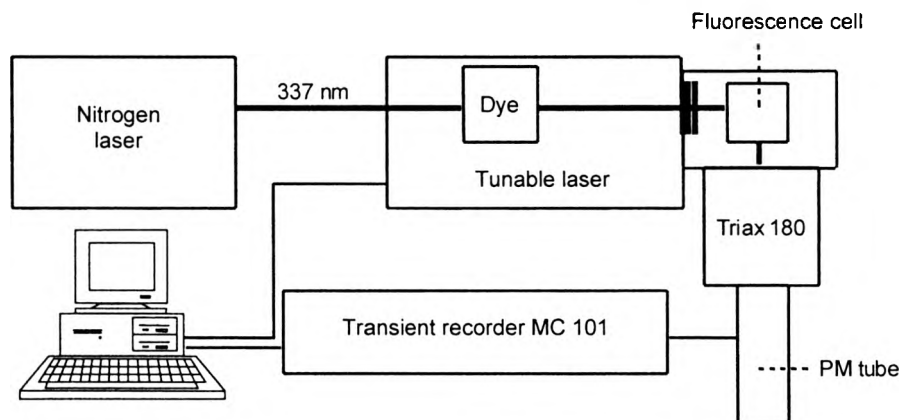


Fig. 1. Experimental setup for luminescence lifetime and excitation spectra of Eu(III) measurements.

registration of excitation spectra and luminescence decay curves for every wavelength of excitation. The presented (Fig. 1) setup is a modification of an experimental system for measurements of luminescence lifetime of excited states of Ln(III) ions [12]. A schematic diagram of the instrumentation is shown in Fig. 1.

A nitrogen laser (KB 6211, Cobrabid, Poznań, Poland) pumped a tunable dye laser in a biprism configuration similar to dye laser generator described in [13] equipped with the computer controlled step motor. This allows scanning of the dye laser emission wavelength through the whole dye emission range with a precision of 0.1 Å. The laser beam from the dye laser passes through the sample cell. The light emitted by a sample is observed at 90° to direction of exciting beam, collected at the entrance slit of monochromator (Triax180) and detected by a M12 FCV 51 photomultiplier. An electric signal from PM tube is fed into a transient recorder MC 101 (Mescomp) interfaced to an PC computer.

For experiments involving Eu(III), the laser dye was P3CDOMAT (synthesized at Szczecin Technical University, Poland [14]) and the dye was pumped by the output line of the nitrogen laser at 337 nm with 10 Hz repetition rate. Pulse energy of dye laser was ~0.1 mJ at 580 nm. Due to the low energy of exciting pulse heating of the sample can be neglected.

The data acquisition program MCIS, written specially for this purpose, acquires the ${}^7F_0 \rightarrow {}^5D_0$ selective excitation spectra of Eu(III) in two modes. In the first one a maximal amplitude of the signal at a given wavelength is collected while in the second an integrated luminescence signal is registered. At the same time the individual luminescence decay curves for every excitation wavelength can be stored.

3. Results and discussion

Selective spectra measurements

The spectra of Eu(III) ${}^7F_0 \rightarrow {}^5D_0$ band recorded using the experimental system (Fig. 1) show peaks originating from different forms. Thus, a deconvolution procedure of the ${}^7F_0 \rightarrow {}^5D_0$ selective excitation spectra of Eu(III) should be

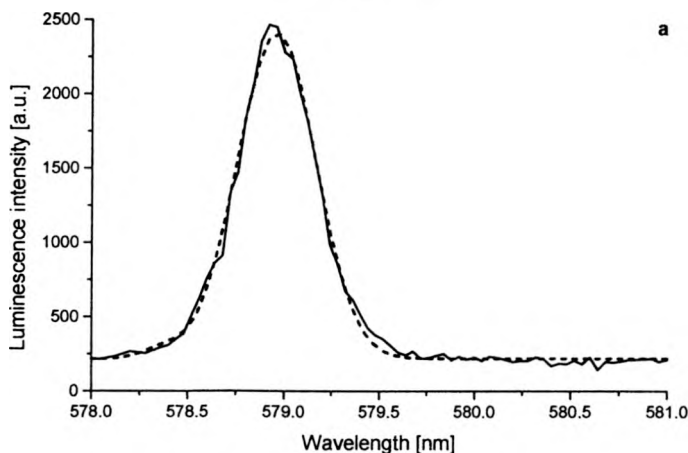


Fig. 2a

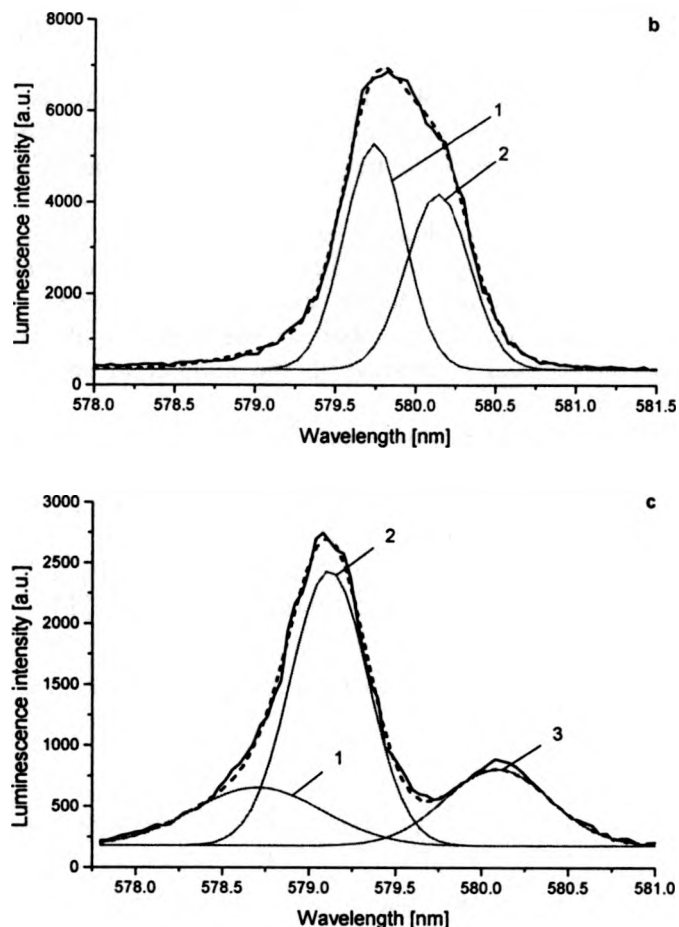


Fig. 2. Selective excitation of the Eu(III) $^5D_0 \rightarrow ^7F_0$ band for solutions of $\text{Eu}(\text{ClO}_4)_3$ (a), $\text{Eu}:\text{NOpic} = 1:3$, $\text{pH} = 7.00$ (b), $\text{Eu}:\text{NOpic}:\text{phen} = 1:3:1$, $\text{pH} = 5.40$ (c), obtained by analysing at 615 nm ($^5D_0 \rightarrow ^7F_2$ transition) and its deconvolution using a Gaussian-type function: — experimental data, --- calculated data.

performed. The wavelength shift of maximal absorption of different complex forms can usually be barely resolved after deconvolution of the collected curve, because peaks originating from different forms are strongly overlapped. For this purpose the procedure based on the Levenberg-Marquardt [15] non-linear algorithm was used, based on Lorentzian or Gaussian model functions. Similarly, the luminescence decay curves have been fitted using single, double and/or triple exponent model. As a result, a number of species (for every complex form) in the solution studied can be determined. Examples of spectra of the Eu(III) $^7F_0 \rightarrow ^5D_0$ band, as experimental curves are shown in Fig. 2a-c. After the fitting procedure they are resolved to distinct peaks of species, showing a single, double and triple complex form systems.

Based on luminescence properties of Eu(III) and recording the ${}^7F_0 \rightarrow {}^5D_0$ excitation spectra the following advantages can be expected:

1. When observing the hypersensitive band of Eu(III) at 615 nm, the luminescence signal of the complexes can be detected at concentrations by several orders of magnitude lower than the concentration required by other (e.g., potentiometric) methods.

2. Individual species in complexation equilibrium show distinct Lorentzian, Gaussian or Lorentzian–Gaussian type of spectral peaks. The peak maxima of different complexes usually appear at different energies and can be resolved.

3. In the application of this method, the number of the bands and the luminescence decay constants can be used to distinguish the number of species present in the equilibrium system.

Using the modified experimental system we observed that in the case of uncomplexed Eu(III) ($\text{Eu}(\text{H}_2\text{O})_9^{3+}$), in the concentration range from 0.5 M to 10^{-2} M and at constant ionic strength (0.1 M NaClO_4), no changes on the ${}^7F_0 \rightarrow {}^5D_0$ excitation spectra of Eu(III) appeared.

The peak maximum of $17\,275\text{ cm}^{-1}$ obtained for uncomplexed Eu(III) is in excellent agreement with the value obtained by other authors [8], [16], [17].

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