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Luminescence lifetime of lanthanide(III) ions in aqueous solution containing azide ion

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Abstract

Luminescent lanthanide ions have been studied using Time-Resolved Laser-induced Luminescence Spectroscopy. The luminescence lifetimes, τ, of excited states of several trivalent lanthanide (Ln^{3+}) ions (Ln=Nd, Sm, Eu, Gd, Tb and Dy) in aqueous solution, containing azide ion (N_3^-), have been measured to evaluate the quenching effect of N_3^-. The luminescence decay constants k_{obs} of Ln^{3+} (Ln=Nd, Sm, Eu, Gd, Tb and Dy) were measured in H_2O solution, and in the case of Eu^{3+} also in D_2O solution. The calculated values of the decay constants indicate that, under the conditions of this work, N_3^- strongly quenches the excited states of Gd^{3+}, Eu^{3+} and Tb^{3+}. The order of the energy gap, ΔE, between the emitting and the ground state of the Ln^{3+} ion is Gd>Tb>Eu, while that of the quenching rate constants by azide, k_{N3}, show the following order: Gd>Eu>Tb. In the case of Nd^{3+}, Sm^{3+} and Dy^{3+} no quenching effect was observed.

Keywords: Azide; Lanthanide(III) ions; Luminescence lifetime; Quenching rate constants

1. Introduction

Several trivalent lanthanides show luminescence spectra in solution. In aqueous solution luminescence is observed only from the middle part of the lanthanide series. Among the luminescent Ln^{3+} ions, Eu^{3+} and Tb^{3+} are the two most extensively studied in practical applications [1,2]. In aqueous solutions the dominant mode of luminescence quenching of the excited ions occurs via coupling of the Ln^{3+} excited state to O–H oscillators of water molecules coordinated to the ion. The luminescence lifetime of an excited state of the Ln^{3+} ion is linearly proportional to the number of H_2O molecules in the inner coordination sphere of this ion [3–5]. The correlation between the luminescence lifetime of the excited state and the hydration number of Ln^{3+} ions studied in aqueous (H_2O and D_2O) solutions have been used to identify details of solution phase: composition and structure of the first coordination sphere of these ions in solution [2]. This correlation is a result of an efficient energy transfer from the Ln^{3+} excited state to the O–H oscillators of bound water molecules. An increase in the number of water molecules in the first coordination sphere leads to a decrease in the luminescence lifetime. Replacement of the O–H oscillators by O–D ones, in deuterated media, causes that the vibronic coupling of the Ln^{3+} excited state with the O–D oscillators is less efficient. The N–H oscillators, having vibronic frequencies closely similar the O–H ones, are also effective as non-radiative deactivators of the excited Ln^{3+}. It has been demonstrated that the deactivating frequency of a bound N–H oscillator is more effective for Eu^{3+} (1.5 times) [6,7] and less effective (~two-thirds) for Tb(III) [8] that of a bound water OH oscillator. The quenching process becomes less effective with increasing energy gaps, ΔE, between the emissive state and the highest sublevel of the ground state of Ln^{3+}.

Our previous studies [9,10] have shown that N_3^- is highly effective in quenching of the luminescent excited state of the Eu(III) ion and its deactivating power is even stronger than O–H (of coordinated water molecules) and N–H oscillators. Thus, it is of great interest to know the N_3^- quenching effects of the Ln^{3+} ion excited states. In this paper the relation between the luminescence decay constants k_{obs} (i.e. the reciprocal of the excited states

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lifetime) of Ln^{3+} ions and an azide concentration is studied.

2. Experimental details

Lanthanide(III) stock solutions were prepared by dissolving an appropriate amount of the oxide (99.9%) (Wako Pure Chem. Ind. Ltd.) in perchloric acid. Working solutions of 10^{-2} M were prepared from the stock solutions and the pH adjusted to 2.00 by addition of aliquots of standard solutions of NaOH and $HClO_4$. For the studies in D_2O aliquots of $Eu(ClO_4)_3$ solution were evaporated to dryness, followed by dissolution in D_2O. This procedure was repeated four times. Solution of NaOD and $DClO_4$ were used to adjust the pH values (2.00) in these systems. Sodium azide (NaN_3, Wako) analytical grade was used as received to prepare solutions in H_2O and D_2O.

The Ln^{3+} ions in the samples were excited to the excited states by a pulsed laser beam, using excitation wavelength 593 nm for Nd^{3+}, 402 nm for Sm^{3+}, 394 nm for Eu^{3+}, 266 nm for Gd^{3+} and 355 nm for Tb^{3+} and Dy^{3+}, respectively. Subsequently, the emission from the lowest luminescent level to the ground state manifold (i.e. ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$ (890 nm) for Nd^{3+}, ${}^4G_{5/2} \rightarrow {}^6H_{7/2}$ (594 nm) for Sm^{3+}, ${}^5D_0 \rightarrow {}^7F_1$ (591 nm) for Eu^{3+}, ${}^6P_{7/2} \rightarrow {}^8S_{7/2}$ (312 nm) for Gd^{3+}, ${}^5D_4 \rightarrow {}^7F_5$ (544 nm) for Tb^{3+} and ${}^4F_{9/2} \rightarrow {}^6H_{15/2}$ (477 nm) for Dy^{3+}) was measured to obtain the luminescence lifetime. The 593, 394 and 401 nm laser beam were obtained with a pulsed (10 Hz) 308 nm output of a Lambda Physik COMPex201 XeCl excimer laser pumping Rhodamine 6G (Lambda Physik) in methanol solution and PBBO (Lambda Physik) in dioxan solution, respectively, in Lambda Physik SCANmate2 dye laser head. The 266 nm (fourth harmonic) and 355 nm (third harmonic) laser beams were obtained directly with a pulsed (10 Hz) nm output of a Spectron SL-803 Nd:YAG laser. The pulsed power was typically 4–8 mJ and the pulse width was in a the nanosecond range. The emission light was focused on a polychrometer (HR320, ISA Jobin-Yvon) and detected by a diode array multichannel analyser (DIDA-512, Princeton Instruments Inc.). A gated pulse generator (PG-200, Princeton Instruments Inc.) was used for time resolution. The spectrometer was controlled by a spectrometric multichannel analyser system (SMA, Tokyo Instruments Inc.) installed on a personal computer. The emission light was collected at 90° into an Oriel 77257 monochromator using an optical fiber and detected by a Hamamatsu R928 photomultiplier tube. The signal was fed into Hewlett-Packard 54510A digitizing oscilloscope which was connected to a NEC PC-9801RX computer through a GP-IB interface. The luminescence decay curves observed in this work were fitted to single-exponential curves with correlation coefficients of 0.99–0.999.

3. Results and discussion

The luminescence lifetimes, τ, of excited states of Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+} and Dy^{3+} we have measured in aqueous solutions. Results obtained in H_2O solutions in the absence of N_3^- are shown in Table 1. The majority of luminescence lifetime measurements reported in the literature has been devoted to europium and terbium ions and it is a good agreement between the data [1,2,11]. Some discrepancies among the data are observed for Nd^{3+}, Sm^{3+}, Gd^{3+} and Dy^{3+} [1,11,12]. The discrepancies can be explained by various experimental conditions of the studied solutions (purity of compounds, concentration, composition, temperature) as well as by a trace contamination of simple inorganic ions (like SCN^-, NO_3^- or N_3^-) that strongly quench excited states of Ln^{3+}, particularly of Gd^{3+} [13].

The luminescence lifetimes of Eu^{3+}, Gd^{3+} and Tb^{3+} observed in solutions containing azide ion decreased, indicating that the quenching behaviour of N_3^- is due to energy transfer from the excited states to N–N vibrations. The most effective quenching of the luminescence lifetime was observed in the case of Gd^{3+} ion. In this case the gap energy, defined as the difference between the emitting state and the next lower lying state, is the largest (32 200 cm^{-1}). The values of luminescence lifetimes for Eu^{3+}, Gd^{3+} and Tb^{3+} ions as a function of azide concentration, measured in H_2O solution and in the case of Eu^{3+} also in D_2O solution, are presented in Table 2.

Dependence of the luminescence decay constants (reciprocal of the of the excited state lifetimes) on N_3^- concentration is presented in Fig. 1. The k_{obs} values were used to calculate the N_3^- quenching rate constants, k_{N3}, of Ln(III) in aqueous solution using the following Eq.:

$$k_{obs} = k_f + k_{aq} + k_{N3} \times [N_3^-] = k_0 + k_{N3} \times [N_3^-] \qquad (1)$$

where k_f is the radiative rate constant, k_{aq} the quenching rate constant by water, and k_{N3} the quenching rate constant by azide.

The calculated values of the decay constants indicate that, under the conditions of this work, N_3^- strongly quenches the excited states of Gd(III), Eu(III) and Tb(III).

Table 1
Luminescence lifetimes (μs) of Ln^{3+} ions measured in H_2O solution, no azide added

Nd^{3+}	Sm^{3+}	Eu^{3+}	Gd^{3+}	Tb^{3+}	Dy^{3+}
0.031±0.002	2.69±0.01	112.4±0.7	1480±20	442±2	2.49±0.02

Table 2
Luminescence lifetimes (μs) of the Eu^{3+}, Gd^{3+} and Tb^{3+} ions in aqueous solution as a function of the azide ion concentration

$[N_3^-]$ ($mol\ l^{-1}$)	Eu^{3+} (H_2O)	Eu^{3+} (D_2O)	Gd^{3+} (H_2O)	Tb^{3+} (H_2O)
0	112.4±0.7	4020.0±6.0	1480.0±20.0	442.0±2.0
0.00001			1380.0±14.2	
0.00005			1025.0±11.6	
0.0001		3880.0±5.0	850.0±11.2	
0.0002			548.0±9.3	
0.0004			215.0±3.2	
0.0006			170.0±2.6	
0.0008			152.0±2.1	
0.0010		911.0±3.6	136.0±1.4	
0.05		191.3±0.9		
0.01	111.4±0.6	95.4±0.7		441.0±1.8
0.02	94.1±0.4	50.3±0.6		435.4±1.8
0.04	44.8±0.4	31.5±0.3		416.7±1.4
0.06	31.6±0.2	22.0±0.2		367.7±1.5
0.08	24.1±0.2			313.8±1.1
0.10	20.5±0.1	16.0±0.1		244.2±1.2
0.15				139.7±1.4
0.20	11.6±0.1			92.0±0.0
0.30				65.2±0.6
0.40				50.0±0.6
0.50	6.34±0.06			34.7±0.5

The calculated values of the rate constants, k_{N3} [M^{-1} s^{-1}], of N_3^- are as follows: (7.04±0.26)×10^6 for Gd(III), (2.63±0.06)×10^5 for Eu(III), (5.74±0.23)×10^4 for Tb(III) in H_2O and (5.3±0.42)×10^5 for Eu(III) in D_2O, respectively.

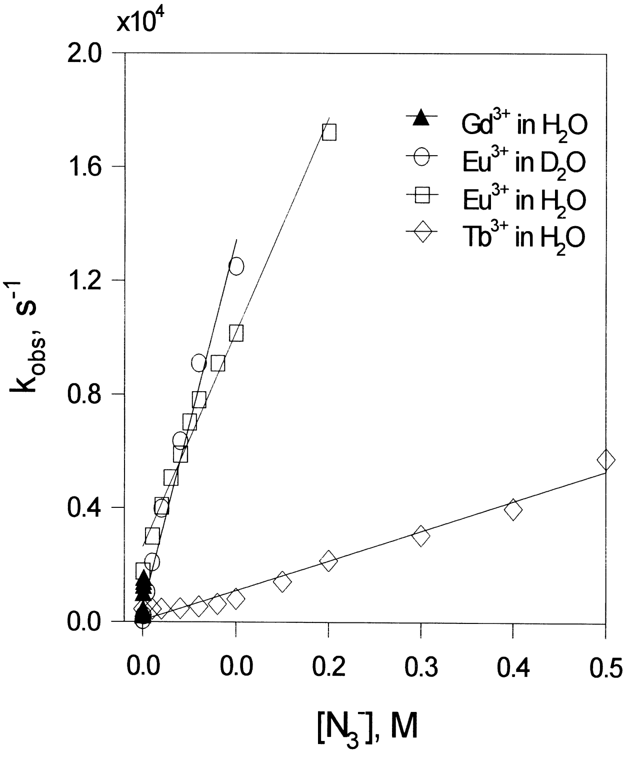

Fig. 1. Dependence of the luminescence decay constants of Ln^{3+} on azide concentration.

In the case of Nd^{3+}, Sm^{3+} and Dy^{3+} the energy difference between the lowest luminescent and highest non-luminescent levels are smaller (than those of Gd^{3+}, Eu^{3+} and Tb^{3+}) and no quenching effect was observed. The order of the energy gap, Δ*E*, between the emitting and the ground state of the Ln^{3+} ion is Gd (~32.200 cm^{-1})> Tb (14 804 cm^{-1})>Eu (12 255 cm^{-1}) [14], while that of the k_{N3} constants show the following order Gd>Eu>Tb. The obtained values of k_{N3} show that the quenching effects of the azide ion on the Ln^{3+} excited states do not obey the energy gap law (e.g. the k_{aq} of Ln^{3+} increase with decreasing of Δ*E*). This suggests that the interaction of Eu^{3+} is much stronger than that of Tb^{3+} perhaps reflecting that its oxidation state is more stable. Since the azide ion shows strong reducing properties, it could be contributed a partial formation of Eu^{2+} in the quenching process, additionally to the energy transfer process.

The azide ion is a very efficient quencher of the excited states of Gd^{3+}, Eu^{3+} and Tb^{3+} ions, and it does not quench excited states of Nd^{3+}, Sm^{3+} and Dy^{3+} ions, which reflects the energy gap, Δ*E*, between the lowest luminescent and highest non-luminescent levels of the Ln^{3+} ions. In the case of Eu^{3+} anomaly in the quenching pattern, as a result of its possible reduction to the Eu^{2+} ion, was observed [15]. This problem requires further studies and the mechanism of quenching is being studied using the chemiluminescence method in Eu^{3+}/Eu^{2+} systems.

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