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Effect of H_2O and D_2O Thermal Anomalies on the Luminescence of Eu^{3+} Aqueous Complexes

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Abstract

Aqueous solutions of luminescent metal-ion complexes, in particular those of lanthanide ions, can play an essential role in biomedical applications. For all these applications, the knowledge about the influence of temperature variations within the physiological range (20-60 ºC) on their optical properties becomes essential. At variance with other liquids, water is unique as it does present an anomalous temperature dependent behavior. In particular, most of water properties present remarkable physico-chemical changes above a certain temperature, which ranges between 30 and 50 ºC. In this work we systematically investigate the effect of temperature on the luminescence properties of Eu^{3+} ions when dissolved either in H_2O or D_2O. An anomalous thermal behavior, manifested as a bilinear trend, with crossover at around 35 ºC for H_2O and 38 ºC for D_2O, is found in a variety of Eu^{3+} optical spectroscopic properties (branching ratio, luminescence lifetime, and emission band shape). The observed changes are here tentatively explained in terms of a different aggregation state of H_2O and D_2O molecules below and above crossover temperature. Such changes in the molecular clustering lead to a temperature induced change in the relative concentrations of the 8-fold and 9-fold coordinated Eu^{3+} complexes. Finally, we have observed that the pH of the aqueous solution plays an essential role in defining the temperature at which the anomaly takes place, so that the differences in the values reported in the literature for the crossover temperature are accounted for.

Introduction

Liquid water is the essential dispersion medium for luminescent compounds and materials with potential bio-applications, such as biomolecules, nanoparticles, and coordination compounds.[1-3] In general, water has been considered as a simple solvent showing the regular properties of any fluid in the physiological temperature range (20-60ºC). However, this assessment is far from being a correct description. Indeed, water is a quite complex fluid that displays unusual properties, such as a density maximum at about 4 ºC, which is still a matter of debate.[4-5] In addition, an anomaly in the dielectric constant of liquid water at about 50 ºC (within the physiological temperature range) has been recently discovered.[6] This anomaly was evidenced as a bilinear behavior in the temperature dependence of the dielectric constant (typically fluids show a linear temperature dependence), with the two linear trends crossing at about 50 ºC, this being denoted as the "crossover temperature" (hereafter T_{cross}).[6-7] Subsequent studies have established that this crossover behavior has its own signature on a variety of physico-chemical properties of liquid water such as thermal conductivity, proton spin-lattice relaxation time, refractive index, surface tension, piezo-optical coefficient, acidity, heat capacity, and isothermal compressibility.[8-11] The dielectric response of water for temperatures below T_{cross} has been tentatively explained by considering the presence of small water molecular clusters with an electric dipole moment (μ) close to that of the ice phase (μ_{ice} = 2.18 D). However, for temperatures above T_{cross}, the dielectric response is better explained as due to individual water molecules with an electric dipole moment close to that of the vapor phase (μ_{vapor}=1.87 D).[7-8, 12] This anomalous de-clustering affects not only intrinsic water properties, but also properties of the solutes and nanoparticles dispersed in it. Indeed, the impact of this crossover on the aqueous dispersion of optically active nanoparticles has been already reported. It does affect the interactions between colloidal lanthanide-doped dielectric nanoparticles, the plasmon resonance of metal nanoparticles, and the spectroscopic properties of small quantum dots.[7-9, 13] Based on all these evidences, it is reasonable to expect that this water structural crossover would also influence the temperature dependence of the luminescent properties of complexes in aqueous environments.[14-16] Nevertheless, despite its great interest from both fundamental and applied points of view, such influence has not been reported so far, to the best of our knowledge.

When investigating the possible influence of water structural crossover on the spectroscopic properties of luminescent complexes, it is critical to select a highly sensitive luminescent entity. In this sense, Eu^{3+} ion-based complexes seem to be especially suitable. Indeed, the Eu^{3+} luminescence has proved its suitability for evidencing small changes in the local environment of this ion.[17-18] Eu^{3+} shows several emission bands in the visible range as a result of radiative de-excitation from the $^5D_0$ excited state to various ^7F_J lower energy states (from J = 0 to 4).[19-20] In particular, the $^5D_0 \rightarrow {}^7F_2$ transition has a forced electric dipole (ED) nature and so its intensity is hypersensitive to local environmental changes.[21-22] In addition, according to the first order perturbation treatment of the Judd-Ofelt theory, the ED $^5D_0 \rightarrow {}^7F_0$ transition is strictly forbidden. However, in some cases, it is weakly observed as a result of

J-mixing, i.e. due to wave functions admixing of the involved states ($^5D_0$ and $^7F_0$) with other $J \neq 0$ states ($^5D_2$ and $^7F_2$) caused by the presence of even parity terms in the crystal field.[21-22] In these cases, this singlet-to-singlet transition ($J=0$ in both involved energy levels) is very convenient as any asymmetry in the band shape clearly indicates the presence of different local environments, i.e. non-equivalent Eu^{3+} species. Finally, the $^5D_0 \rightarrow {}^7F_1$ emission is of singular importance as can also be used to calibrate the full Eu^{3+} emission spectrum originating from the $^5D_0$ excited state. This transition is of magnetic dipole (MD) character and so its intensity is largely independent of the local environment of Eu^{3+} ions.[23] All these features make Eu^{3+} complexes excellent candidates to investigate the water structural crossover in the physiological temperature range.

Under this scenario, we have systematically investigated the temperature dependence of the emission of Eu^{3+} aqueous complexes in both H_2O and D_2O as a new strategy to get further understanding on the physical-chemical phenomena behind the water structural crossover. The reason for considering also deuterated water solutions is double: (i) O-H vibrations strongly quench the Eu^{3+} emission spectrum, while O-D vibrations do not; and (ii) experimental evidence also exists of a structural crossover in D_2O.[13, 24] We here show how certain luminescent features of Eu^{3+} ions (branching ratios and radiative and non-radiative transition rates) are affected by the water structural crossover. In addition, the $^5D_0 \rightarrow {}^7F_0$ emission band, which is sensitive to the presence of different environments (i.e. aqueous complexes with different number of water molecules in the first coordination sphere)[25], and so it is influenced by the relative concentration of the two main coordination complexes $[Eu(H_2O)_8]^{3+}$ and $[Eu(H_2O)_9]^{3+}$.

Methods

$EuCl_3 \cdot 6H_2O$ (99.99%) was purchased from Sigma-Aldrich, whilst D_2O (99.9%) was purchased from Euriso-Top solvents. Both these reagents were used as received without further purification. The starting solutions (0.1 M) were prepared by dissolving 73 mg of $EuCl_3 \cdot 6H_2O$ (0.2 mmol) in 2 ml of deionized water (milliQ) or of deuterium oxide. The concentration used in the experiments is the smallest for which the luminescence signal is detectable by our experimental set-up. It is reasonable to assume that the Cl^- ion, which is weakly coordinating in water to lanthanide ions, does not bind to Eu^{3+}, i.e. that only aqueous complexes of Eu^{3+} ions are present.[26] The pH value at 20 ºC for the Eu^{3+} solution in H_2O was 5.5.

Luminescence experiments were carried out by using a 405 nm laser diode as excitation source. The excitation beam was focused into the sample by an objective lens, which also collects the luminescence. The emission was discriminated from excitation by means of a wavelength selective mirror. Then it was spectrally analyzed by a monochromator (iHR320, Horiba) and recorded by a cooled CCD array detector (Synapse, Horiba). For temperature dependent experiments, the solutions were placed in 200 μm height chamber (Ibidi Inc., μ-

Slide I Leuer 80161). The chamber was placed on a controlled temperature stage. Then the temperature was varied from 10 up to 70 ºC with a resolution of 0.1 ºC. The solutions were maintained for 10 minutes at each particular temperature, so that they were considered to be at thermal equilibrium. The same results were obtained from heating and cooling processes.

Intensity decay measurements were carried out upon pulsed laser excitation by an optical parametric oscillator at 521 nm, i.e. under excitation of the $^5D_1$ energy level. The emitted luminescence was analyzed by a monochromator after passing through appropriate filters. The intensity decay of the transition $^5D_0 \rightarrow {}^7F_1$ of Eu^{3+}, i.e. the decay curve from the $^5D_0$ state, was acquired by using a photomultiplier tube (Hamamatsu, R928) and a digital oscilloscope.

Results & discussion

Figure 1 shows representative emission spectra corresponding to the Eu^{3+} aqueous complexes in D_2O and H_2O solutions at different temperatures, obtained upon laser excitation at 405 nm ($^7F_0 \rightarrow {}^5L_6$ transition of Eu^{3+} (see inset in Figure 1)). The different emission bands can be easily assigned to specific transitions from the excited state $^5D_0$ to different ^7F_J terminal states of the Eu^{3+} ion.[25, 27] As mentioned above, the $^5D_0 \rightarrow {}^7F_1$ transition is of MD character and, therefore, insensitive to the Eu^{3+} environment. Thus, all the emission spectra were normalized to this transition. The analysis of the normalized emission spectra reveals significant temperature-induced changes in the relative intensities (branching ratios) of the different $^5D_0 \rightarrow {}^7F_J$ bands (especially for J=2 and 4), which unequivocally indicates that temperature variation induces small changes in the local environments of Eu^{3+} ions.[19, 23] To account for this temperature-induced environmental effect, it results particularly suitable to study the intensity ratio I_{tot}/I_{MD}, where I_{tot} is the total integrated emission intensity generated from the $^5D_0$ state and I_{MD} is the integrated intensity of the $^5D_0 \rightarrow {}^7F_1$ emission band, which is of MD nature. **Figure 2** displays the I_{tot}/I_{MD} ratio of Eu^{3+} emission as a function of temperature for both H_2O and D_2O solutions. In both cases, a bilinear increasing behavior is observed, with a T_{cross} of about 35ºC for H_2O and 38ºC for D_2O.

In order to elucidate the origin of these spectroscopic changes, we have investigated the temperature dependence of the Eu^{3+} emission decay time of the $^5D_0$ energy level. **Figure 3(a)** shows the decay curves obtained from both H_2O and D_2O solutions at room temperature. In both cases, exponential decays are observed with decay constants of 0.114 ± 0.002 ms for H_2O and 2.81 ± 0.02 ms for D_2O. As previously reported, the strong decrease in the lifetime observed for the H_2O solution is due to efficient vibrational relaxation from the $^5D_0$ excited state of Eu^{3+}, due to the O-H high energy vibrations of the coordinated water molecules.[28-29] The replacement of H_2O by D_2O strongly suppresses this quenching, as the O-D groups have a much lower stretching wavenumber (2500 cm^{-1} compared to 3400 cm^{-1}, implying about 5 and 3.5 vibrational quanta, respectively, to bridge the energy gap to the lower electronic state).[30] Figure 3(b) and 3(c) show the temperature dependence of the $^5D_0$ lifetime for both

Eu^{3+} solutions. In both cases, the lifetime decreases with temperature. In addition, bilinear trends are observed with T_{cross} similar to those found for the temperature dependence of I_{tot}/I_{MD} (Figure 2).

From the experimental data given in Figure 2 and 3 it is possible to estimate the radiative, A_{rad}, and non-radiative, A_{nrad}, transition rates from the $^5D_0$ state as a function of temperature. Werts *et al*.[23] have demonstrated that the radiative lifetime of the $^5D_0$ state, τ_{rad}, can be properly calculated from the $^5D_0 \rightarrow {}^7F_J$ corrected emission spectrum by:

$$\frac{1}{\tau_{rad}} = A_{MD} n^3 \frac{I_{tot}}{I_{MD}} \quad (1)$$

where n is the refractive index of the solvent and A_{MD} is the spontaneous emission probability for the $^5D_0 \rightarrow {}^7F_1$ transition *in vacuo*. This value has been theoretically calculated to give A_{MD}=14.65 s^{-1}.[31] Consequently, using Equation (1) and the obtained temperature trends for I_{tot}/I_{MD} (see Figure 2), we can estimate the temperature dependence of τ_{rad}, included in Figure 2. A decrease of τ_{rad} with temperature is observed from a value of 9.89 ms for D_2O (9.64 ms for H_2O) at 10ºC to a value of 9.44 ms (9.30 ms for H_2O) at 70ºC. The crossover is also evidenced in τ_{rad} for both solutions as a bilinear behavior that reveals a critical temperature close to 35 º C for H_2O and 38 º C for D_2O.

In order to get physical insight into the temperature dependence of τ_{rad}, in the following we focus our attention to the data obtained from the D_2O solution, where the signature of the structural crossover is more evident. **Figure 4(a)** shows the evolution of A_{rad} with temperature (estimated by means of equation (1), $A_{rad}=1/\tau_{rad}$, and from the data in Figure 2). The increase in A_{rad} strongly suggests that a more asymmetric environment occurs as temperature is raised. Such asymmetry leads to a larger admixing of the $4f^6$ wavefunctions with higher energy electronic configurations of different parity and so increasing the radiative rate via electric dipole forced transitions.[20] The bilinear behavior is again a clear indication of two different local environments predominating below and above T_{cross}. The non-radiative rate A_{nrad} can be also obtained at each temperature just by considering that:

$$A_T = A_{rad} + A_{nrad} \quad (2)$$

where A_T is the total depopulation rate ($A_T = 1/\tau_{tot}$, τ_{tot} being the experimental $^5D_0$ lifetime included in Figure 3(c)). Both estimated temperature dependences of A_{nrad} and A_T are included in Figures 4(b) and 4(c). A careful comparison between data included in Figure 4(b) and 4(c) indicates that the major contribution to the variation of lifetime with temperature is due to A_{nrad}, i.e. to non-radiative relaxation. At this point, it is important to mention that while the thermal quenching of Eu^{3+} in H_2O is clearly dominated by multi-phonon relaxation due to the O-H vibrations, for Eu^{3+} in D_2O the non-radiative relaxation via O-D vibrations is not high enough to quench the Eu^{3+} emission, due to the high vibrational O-D frequency (~ 2000

cm^{-1}). As a result, it is reasonable to assume the possibility of some amount of quenching via charge transfer state, as reported to occur in different organic matrices.[32] Indeed, spectral evidence of charge transfer in Eu^{3+} aqueous solutions was given by Jorgensen *et al*. in 1963.[33] Although this aspect must be corroborated, it could qualitatively explain the different slopes in the temperature dependences observed for the luminescence lifetime for H_2O (Figure 3b) and D_2O (Figure 3c).

Up to now, experimental data included in Figure 2, 3, and 4 reveal that the water structural crossover has a clear signature on the thermal quenching of Eu^{3+} aqueous complexes, but they do not provide any information about the physical-chemical effects behind this phenomenon. In order to correlate the water structural changes and the variations in Eu^{3+} emission properties, we now analyze the temperature dependence of the $^5D_0 \rightarrow {}^7F_0$ emission band. As expounded above, this singlet emission is influenced by the existence of non-equivalent local environments. **Figure 5** shows the temperature dependence of the $^5D_0 \rightarrow {}^7F_0$ emission peak. It is observed that this emission experiences a blue shift as the temperature is raised. In addition, a remarkable change in the magnitude of this linear shift is observed at T_{cross}, so that the slope is larger above T_{cross}. Temperature induced $^5D_0 \rightarrow {}^7F_0$ blue shift has been reported to occur for different Eu^{3+} ion doped host crystals as a result of electron-phonon coupling.[34-35] Thus, in a similar way, we can state that the blue shift here observed is due to electron-vibration coupling in the Eu^{3+} complex of solution in D_2O. Indeed, in the short temperature range here investigated, the observed linear trends seem to be reasonable.[34] However, to account for the bilinear behavior, additional features should be considered. The inset in **Figure 5** shows the $^5D_0 \rightarrow {}^7F_0$ emission at two different temperatures: one well below T_{cross} (10ºC) and one well above T_{cross} (60ºC). The spectrum at 10 ºC peaks at 17273.5 cm^{-1} and it has a full with at half maximum of 12 cm^{-1}. It displays a Lorentzian shape that resembles that simulated by means of molecular dynamics and related to $[Eu(H_2O)_8]^{3+}$ complexes.[25] Nevertheless, it is generally accepted that Eu^{3+} ions form two different aqueous complexes, one with 8-fold coordination, $[Eu(H_2O)_8]^{3+}$, and other one with 9-fold coordination, $[Eu(H_2O)_9]^{3+}$. In fact, by means of refined analysis of the molecular dynamics trajectories, Clavaguéra *et al.*[36] predicted that Eu^{3+} ions are prevailingly 8-fold coordinated (about 63%) at room temperature, but a certain fraction (37%) is in 9-fold coordination. Therefore, it is reasonable to assume that, at each temperature, there are two possible Eu^{3+} environments, according to an equilibrium given by:

$$[Eu(H(D)_2O)_8]^{3+} + H(D)_2O \rightleftarrows [Eu(H(D)_2O)_9]^{3+} \quad (3)$$

As a result, the observed $^5D_0 \rightarrow {}^7F_0$ emission should be a convolution of two emission bands due to non-equivalent Eu^{3+} sites. We now state that the dominant coordination below T_{cross} is 8 and so its emission shape must be mostly due to this coordination.[25, 27, 36-38] As the temperature is raised, the corresponding peak position shifts towards blue with a constant slope up to T_{cross}. However, above T_{cross} the peak position blue shifts with a larger slope. In

addition, the spectrum becomes comparatively broader and more asymmetric (see the spectrum at 60 ºC in the inset in Figure 5) than those obtained below $T_{cross.}$ It seems that a new component of higher energy grows, accounting for the observed broadening and the increasing asymmetry of the $^5D_0 \rightarrow {}^7F_0$ emission profile at temperatures above T_{cross}. Thus, the increase in shape asymmetry as well as part of the blue shift observed for the emission above T_{cross}, could be explained as a result of an increase of the concentration of 9-fold coordinated Eu^{3+} ions with respect to the 8-fold ones. Consequently, the main effect of the crossover would be to produce a relative increase in the concentration of the Eu^{3+} complexes with coordination 9, with emission at higher energy, with respect to the Eu^{3+} complexes with coordination 8. For the 8-fold coordinated complex, molecular dynamics simulations have suggested that the 8 coordinating water molecules are arranged to form a square antiprism around Eu^{3+} ions, these ions facing O atoms of the surrounding water molecules (see Figure 6).[37] For the 9-fold coordinated complex, the structure has not been assigned to any well-known local structure, and so it is speculative (see Figure 6).[39] Nevertheless, the smaller coordination number (8) is responsible for smaller Eu-O distances, presumably leading to increased overlap of the electronic clouds of the two ions and to partial localization of the europium electrons on the oxygen ligands. Due to this nephelauxetic effect, a shift towards lower energy in the $^5D_0 \rightarrow {}^7F_0$ emission peak is expected in comparison to the aqueous complex with higher coordination number, this being in accordance with the asymmetric broadening at the high energy side of the $^5D_0 \rightarrow {}^7F_0$ emission band observed over T_{cross} (see inset in Figure 5).[22, 40-41]

Furthermore, the pronounced change in the relative concentration of the Eu-aqueous complexes that we propose to occur above $T_{cross,}$ can be tentatively explained by considering how water molecules interact below and above T_{cross}. It has been proposed that water molecules are arranged as small clusters for temperatures below T_{cross}, whilst above T_{cross} water properties can be better described by considering weakly interacting water molecules.[7-8, 12-13] The increase in concentration of these "free" water molecules above T_{cross} would shift the hydration equilibrium of the Eu^{3+} species (Equation (3)) to the right hand side and increases the concentration of $[Eu(H_2O)_9]^{3+}$ complexes, as we have schematically displayed in Figure 6. This would explain the changes that we have observed in both temperature induced blue shift and in band shape above T_{cross} (see again Figure 5).

Moreover, the temperature effect on the relative concentrations of the two hydrated coordination compounds can account for the crossover effect on the de-excitation rates, and so it could explain the experimental results given in Figures 2 and 3. Both A_{rad} and A_{nrad} increase with temperature (Figure 4). The increase of A_{nrad} can be simply explained by the increasing probability of multiphonon relaxation with temperature. Indeed, above T_{cross}, the number of O-H(D) oscillators coordinated to Eu^{3+} increases, accounting for the higher slope of A_{nrad} as a function of temperature above T_{cross} (see Figure 4(b)). Note that the highly symmetrical structure of $[Eu(H_2O)_8]^{3+}$ (see Figure 6) seems to predominate below T_{cross}.[27] Consequently, the emission from the $^5D_0$ energy level at temperatures below T_{cross} (mostly

due to 8-fold coordinated sites) is mainly ascribed to the MD radiative transition to the $^7F_1$ terminal level.[42] This clearly results in low values for I_{tot}/I_{MD} and A_{rad} below T_{cross}, as found in the experimental results included in Figure 2 and 4(a) respectively. On the other hand, the progressive intrusion of a ninth water ligand above T_{cross} is likely to distort this geometry, and therefore generate a less symmetric Eu^{+3} complex (see Figure 6). According to the Judd-Ofelt theory, this would be reflected in higher values of forced ED transition rates for the 9-fold coordinated complexes, leading to an increase of I_{tot}/I_{MD} and the subsequent decrease of τ_{rad} for the $^5D_0$ excited state (see Figure 2). In fact, when the Eu^{3+} environment is more asymmetric, A_{rad} is expected to increase for ED forced transitions due to a larger admixing of the *4f* orbitals with the excited *5d* orbitals.[20] Moreover, the temperature induced increase of A_{rad} below and above T_{cross} can be somehow explained as a result of an increasing asymmetry. In fact, a significant increase of the asymmetry of water molecules structure with temperature has been previously shown by means of X-ray and Raman techniques.[43] We therefore propose that these asymmetric distortions in the Eu^{3+} local environment (affecting to both 8- and 9-fold coordinated complexes) account for the increase in A_{rad} with temperature (see Figure 4a).

At this point, it is important to note that the T_{cross} values here reported are within the T_{cross} range reported in the literature (from 20 to 50 ºC). It is an interesting question why there is such a broad range of reported values for T_{cross} in the literature. We here state that this spreading in T_{cross} is very likely due to the different pH values of the aqueous solutions. To support this statement we have taken different data previously reported and investigated how the pH affects T_{cross}.[7, 13, 44-50] **Figure 7** shows how T_{cross} changes with different pH values at 20ºC for different aqueous solutions. In some cases, the pH was simply measured as a function of temperature for samples with different initial pH (the pH value at 20ºC). pH values as a function of temperature present a bilinear behavior, the T_{cross} value being dependent on the pH value at 20 ºC.[44-50] In other cases, we used data corresponding to aqueous solutions (with a given initial pH at 20ºC) that displayed the bilinear behavior on different physical properties, or aqueous dispersions of optically active nanoparticles that displayed temperature induced changes as a result of the water structural crossover.[7, 13] Within data dispersion, a clear trend is found revealing that T_{cross} increases with pH and seems to saturate for pH values higher than 9. Nevertheless, the results given in Figure 7 reveal that pH plays an important role in the water structural crossover. Indeed, the T_{cross} value obtained for the Eu^{3+} ions in the aqueous solution investigated in this work falls nicely within the general trend.

Conclusions

In summary, in this work we provide experimental evidence of the fundamental role that the water structural crossover plays in the temperature dependence of the optical spectroscopy of diluted solutions of Eu^{3+} aqueous complexes. It is here confirmed that two coordination

compounds coexist in equilibrium, $[Eu(H(D)_2O)_8]^{3+}$ and $[Eu(H(D)_2O)_9]^{3+}$, giving rise to two non-equivalent species whose relative population depends on the structure of water molecules clusters. Thus, the water structural crossover leads to the appearance of a bilinear behavior in the temperature dependence of a variety of Eu^{3+} spectroscopic properties. This bilinear behavior is explained in terms of a temperature induced redistribution between the $[Eu\ (H(D)_2O)_8]^{3+}$ and $[Eu(H(D)_2O)_9]^{3+}$ coexisting complexes. At temperatures below crossover temperature, the 8-fold coordinated complex is predominant, while at temperatures above crossover temperature the 9-fold coordinated complex considerably increases its concentration. This behavior is interpreted as due to the increased concentration of "free" water molecules above the crossover temperature. The effect of this anomaly in the temperature dependence of spectroscopic properties has been traditionally ignored and points out the need of revisiting the previous interpretation of the physics behind the thermal quenching of luminescent aqueous dispersions. Finally, from an applied point of view, the results reported herein will have important implications on the temperature dependence of numerous properties of aqueous solutions, which are of great importance in biochemistry.

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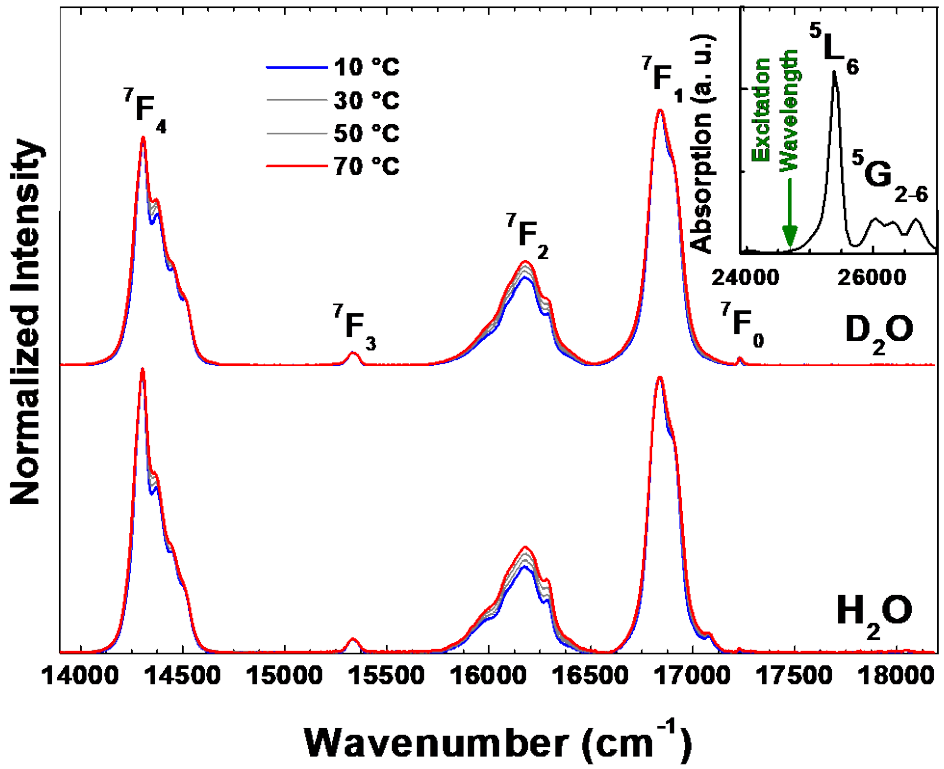


Figure 1. Emission spectra of the Eu^{3+} in D_2O (0.1 M) (top) and Eu^{3+} in H_2O (0.1 M; pH 5.5) (bottom) solutions at diverse temperatures under excitation at 405 nm (laser power 50 mW). These spectra have been normalized to the $^5D_0 \rightarrow {}^7F_1$ emitted intensity. Inset: absorption

spectrum of Eu^{3+} in D_2O; the arrow indicates the excitation wavelength. Spectra have been corrected by the spectral response of the detector.

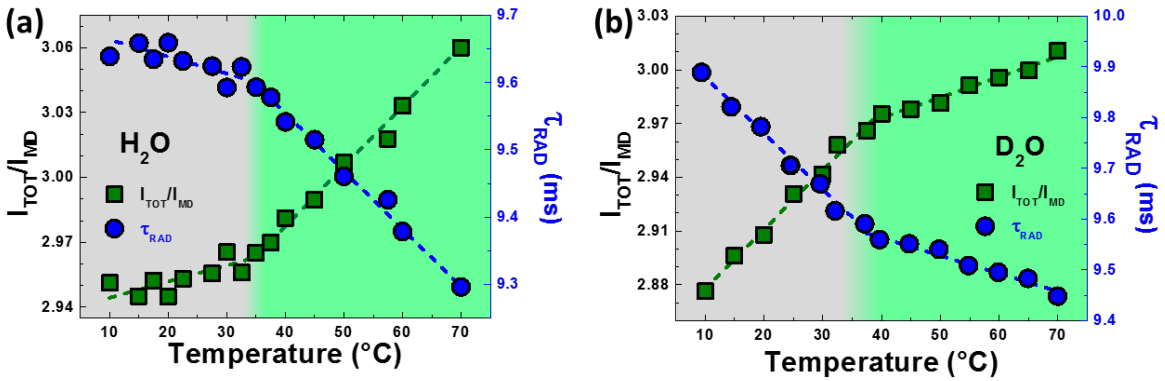


Figure 2. Temperature dependence of the total emitted intensity from the $^5D_0$ level relative to the MD $^5D_0 \rightarrow {}^7F_1$ transition (squares) and of radiative lifetime of this energy level (calculated from I_{TOT}/I_{MD} data using Equation (1)) (circles) for (a) the Eu^{3+} ions in H_2O and (b) the Eu^{3+} ions in D_2O solutions. Colored backgrounds delimit the temperatures below and above T_{cross}. Dashed lines are guides to the eye.

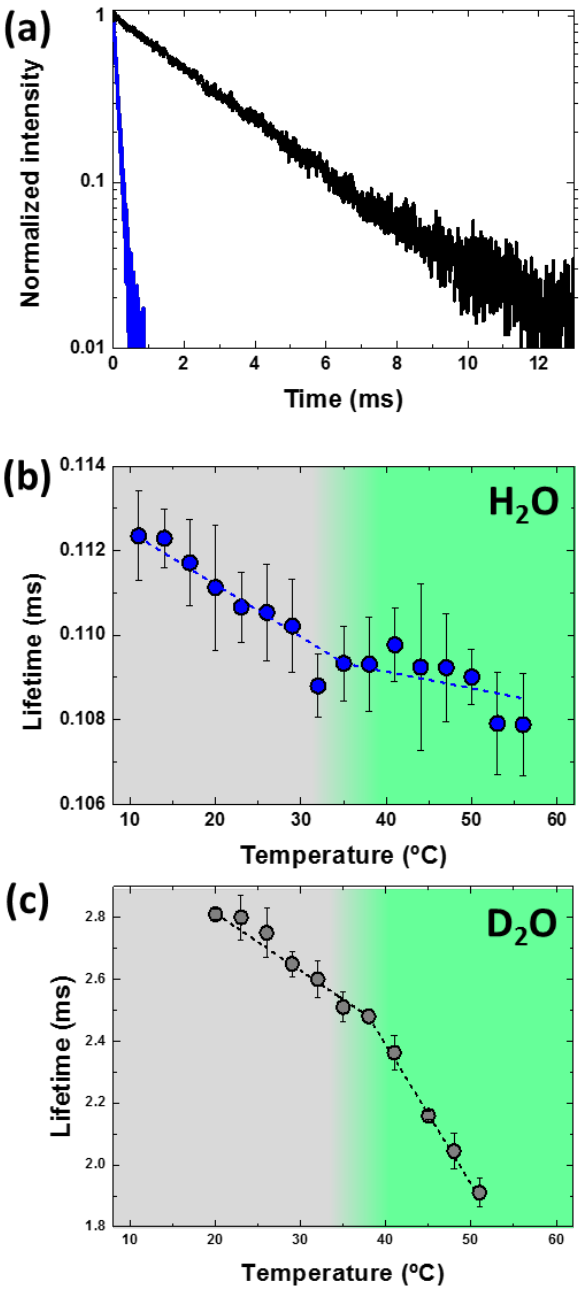


Figure 3. (a) Intensity decay curves obtained for the Eu^{3+} in H_2O and Eu^{3+} in D_2O solutions from the $^5D_0$ energy level, at 20 ºC. Lifetime of the $^5D_0$ energy level of Eu^{3+} (b) in H_2O solution and in (c) D_2O solution as a function of temperature (excitation wavelength: 521 nm). Colored backgrounds delimit the temperatures below and above T_{cross}. Dashed lines are guides to the eye.

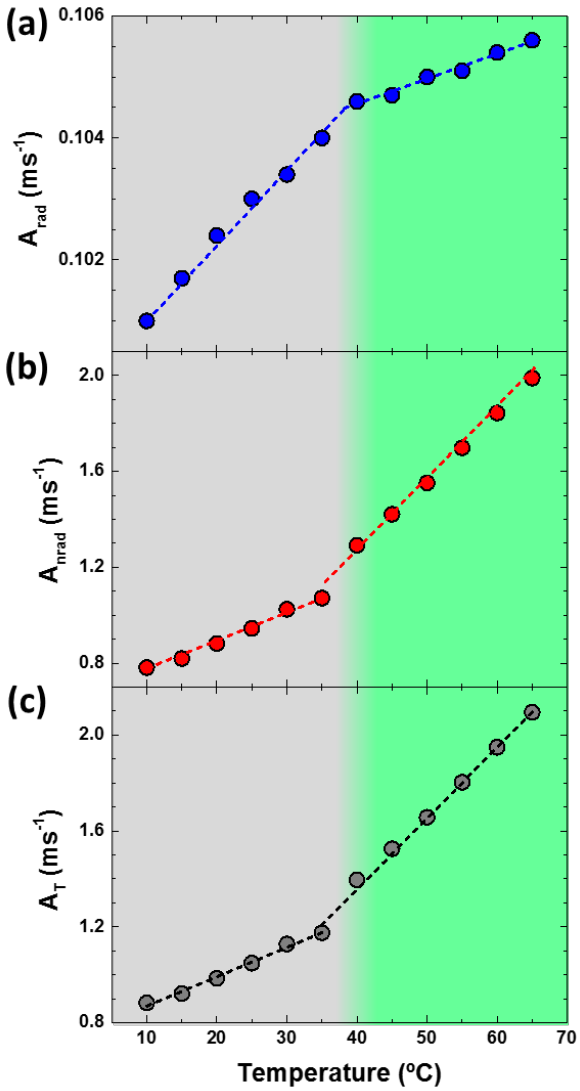


Figure 4. Temperature dependence of (a) the radiative, (b) non-radiative, and (c) total de-excitation rates estimated for Eu^{3+} in D_2O solution. Colored backgrounds delimit the temperatures below and above T_{cross}. Dashed lines are a guide to the eye.

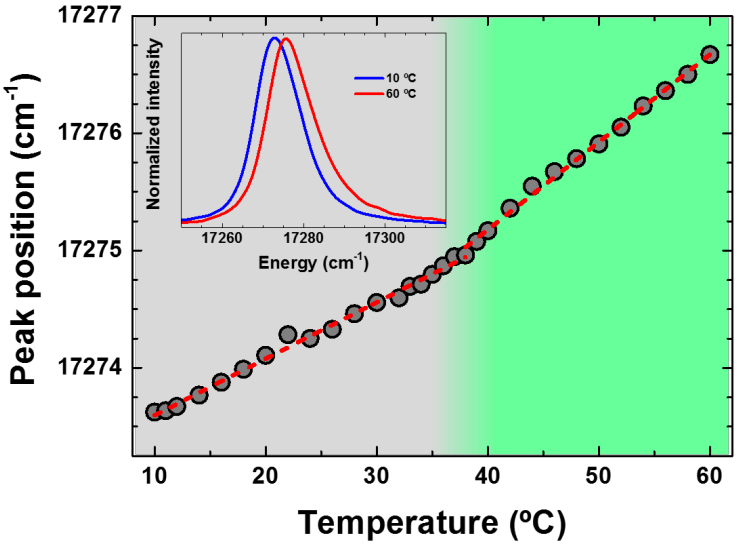


Figure 5. Peak position of $^5D_0 \rightarrow {}^7F_0$ emission band of Eu^{3+} in D_2O solution as a function of temperature (excitation wavelength: 405 nm). Colored backgrounds delimit the temperatures below and above T_{cross}. Dashed lines are guides to the eye. Inset: Emission spectra of this emission band at diverse temperatures.

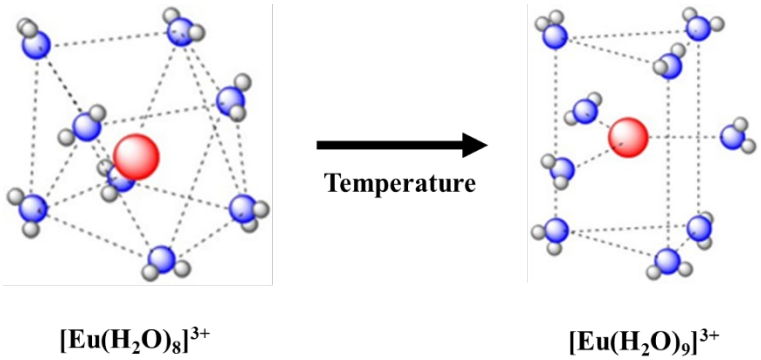


Figure 6. Schematic representations of the two Eu local environments ($[Eu(H_2O)_8]^{3+}$ and $[Eu(H_2O)_9]^{3+}$), where Eu^{3+} ion is schematized as a red sphere and the coordinated water molecules as blue (O^{2-}) and grey (H^+) spheres.

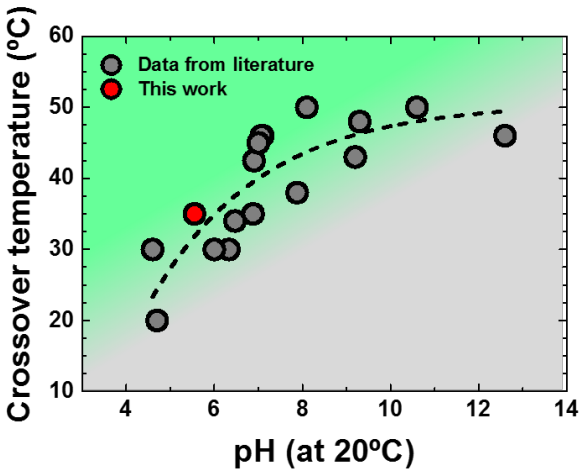
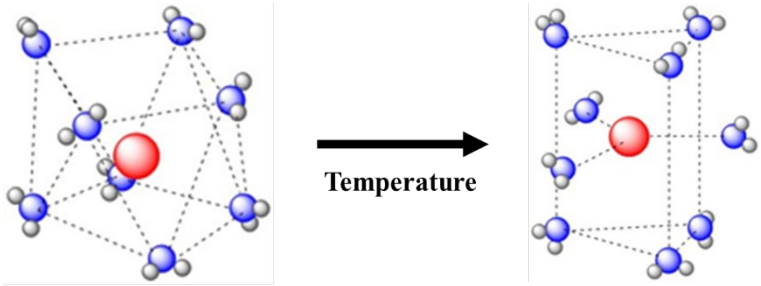


Figure 7. T_{cross} obtained from different aqueous solutions of different pH at 20 ºC and from other experimental works on the water structural crossover as a function of the pH at 20 ºC (gray dots). Data taken from References.[4, 7, 27] T_{cross} spectroscopically measured in this work for the Eu^{3+} in H_2O solution (red dot). The dashed line is a guide for the eye.



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