Journal of Luminescence 146 (2014) 440–444

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Luminescence properties, centroid shift and energy transfer of Ce^{3+} in aqueous chloride solutions

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ARTICLE INFO

Article history:
Received 4 August 2013
Received in revised form
9 October 2013
Accepted 12 October 2013
Available online 19 October 2013

Keywords:
Energy transfer
Hydrated lanthanide ions
Centroid shift
Photodissociation
5d–4f transition

ABSTRACT

This paper focuses upon three themes: all related to aqueous cerium chloride solutions.

First, the features in the absorption spectra of $CeCl_3$ solutions do not shift noticeably with concentration and are at similar energies to bands in the solid-state absorption spectrum of $Ce(H_2O)_9^{3+}$, with the exception of the weak band at 297 nm which is due to $Ce(H_2O)_8^{3+}$. The broad emission band in solution is only due to $\left[Ce(H_2O)_8^{3+}\right]^*$ and the emission quenches at concentrations >0.06 M. Bands in the excitation spectra of aqueous $CeCl_3$ solutions apparently change position with increasing concentration, due to absorption by $Ce(H_2O)_9^{3+}$ which does not contribute to emission. At concentrations above 1 M, there is total extinction of incident radiation for wavelengths shorter than 310 nm.

Second, this system is chosen to illustrate the revised calculation of centroid shift, by taking into account the vibronic nature of spectral features, in contrast with the pure electronic transition of the free ion. Similar calculations are applicable to other Ce^{3+} systems.

Thirdly, excitation spectra are employed to demonstrate the energy transfer occurring from Ce^{3+} to Tb^{3+} and Eu^{3+} in aqueous chloride solutions, which is an unusual energy transfer, occurring from 5d to 4f states and between hydrated lanthanide ions in solution.

1. Introduction

The emission intensities of lanthanide ions (Ln^{3+}) in aqueous solutions are usually very weak due to strong nonradiative quenching by O–H vibrations. However Gd^{3+}, Tb^{3+}, Eu^{3+} and Ce^{3+} ions do emit characteristic luminescence. In these cases the multiphonon nonradiative processes are slower due to the large energy gaps below the luminescent terms. The emission of Ce^{3+} ions is much stronger than that of other Ln^{3+} because it corresponds to a first-order allowed $5d^1$–$4f^1$ transition, so that it is visible even in solutions of very low concentration. The role that Ce^{3+} plays in solution has been especially studied in this work via room temperature and liquid nitrogen temperature excitation and emission spectra of $CeCl_3$ solutions.

The energy transfer studies of Ln^{3+} in solution have been largely confined to ligand – Ln^{3+} energy transfer by the antenna effect [1–4]. There are several papers about energy transfer between Ln^{3+} in the environments of micelles [5,6], where lanthanide complex anions are associated with a cation micellar surface. Energy transfer from Tb^{3+} to other Ln^{3+} was measured in solution from luminescence quenching, with comparisons of the nature of anion and solvent [7], and we have previously reported the energy transfer of Gd^{3+} to other Ln^{3+} ions in solution [8,9]. In this work, we demonstrate the energy transfer from Ce^{3+} to Tb^{3+} and Eu^{3+} in aqueous chloride solutions. This transfer is unique because it corresponds to that from the 5d state to 4f states, and also because it is between hydrated lanthanide ions in solution.

2. Experimental

Rare earth oxide powders: $CeCl_3$ 99.9% (Strem Chemicals), Tb_4O_7, Eu_2O_3 99.99% (International Laboratory, USA), were dissolved in aqueous hydrochloric acid (Scharlau Chemie, Germany) in order to obtain solutions of high concentration. The solutions were poured into quartz cells with 1 cm path length for optical measurements. Absorption spectra were measured by a Perkin-Elmer Lambda 19 UV/VIS/NIR spectrometer using a resolution of 2 nm. Emission and excitation spectra were acquired by a Jobin-Yvon Horiba Fluorolog spectrometer with resolution of up to 1 nm. The experiments were also performed by housing the quartz cell in a liquid nitrogen dewar flask.

3. Results and discussion

The absorption spectrum of Ce^{3+} doped into solid $La(C_2H_5SO_4)_3 \cdot 9H_2O$, which has a tricapped trigonal pyramidal

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http://dx.doi.org/10.1016/j.jlumin.2013.10.030

arrangement of aqua ligands, exhibits bands at 256, 238, 224, 211 and 200 nm [10]. This is consistent with D_{3h} site symmetry of Ce^{3+}, with transitions from a Γ_7 ground state to $D^{+}_{3/2}$ ($\Gamma_7+\Gamma_9$) and $D^{+}_{5/2}$ ($\Gamma_7+\Gamma_8+\Gamma_9$) crystal field states. Fig. 1 shows the absorption spectra of Ce^{3+} at various concentrations in aqueous chloride solutions. The bands at 252, 238, 221 and 211 nm are at similar energy to those above and are assigned to the lowest four of the five $4f^1 \rightarrow 5d^1$ electronic transitions of the ion $Ce(H_2O)_9^{3+}$, since also the spectrum is independent of the anion present in the solution [11]. From Raman and X-ray diffraction results [12] it has been concluded that the first coordination shell of the cations comprises aqua ligands and that the cations are arranged highly symmetrically. The structure of the absorption bands does not change or shift noticeably with increasing Ce^{3+} concentration or changing pH. The fifth absorption band has been assigned at 200 ± 1 nm [13,14].

The peak maxima of the above absorption bands have been taken by Dorenbos in order to calculate the centroid shift of $5d^1$, i.e. the shift in the $5d^1$ barycentre from the free ion value of 51,213 cm^{-1} (6.35 eV) [15]. The values obtained were 0.800 eV for Ce^{3+} in $La(C_2H_5SO_4)_3 \cdot 9H_2O$, and 0.796 eV for $Ce(H_2O)_9^{3+}$. These nephelauxetic shifts appear to be too small, and since they are derived from the comparison of vibronic energies in the condensed phases with the zero phonon line energy in the gaseous state, an alternative logic is now provided in the derivation of these quantities. The $4f^N \rightarrow 4f^{N-1}5d^1$ absorption spectra of Ce^{3+} comprise vibrational progressions based upon zero phonon lines, with the strongest ones being in totally-symmetric vibrational modes, so that peak maxima represent the transition to a particular vibrational level of the excited $5d^1$ state. We have observed that this corresponds to $v'=1$ in a case where the vibrational progressions are well-resolved for Ce^{3+} [16]. The OH_2 vibration in the Raman spectrum of an aqueous solution of Ce^{3+} has a maximum intensity at 3405 cm^{-1} [17]. Hence the lowest $4f^1$–$5d^1$ zero phonon line is estimated to be lower by roughly this energy from the vibronic peak, at ~35,660 cm^{-1} for $Ce(H_2O)_9^{3+}$(aq). An alternative estimation can be made by using the energies of the $5d^1 \rightarrow 4f^1$ emission bands of $Ce(H_2O)_9^{3+}$ in $La(C_2H_5SO_4)_3 \cdot 9H_2O$, at 30,000 and 32,000 cm^{-1}. These bands represent seven unresolved transitions to the spin-orbit split $4f^1$ $^2F_{5/2}$, $^2F_{7/2}$ multiplets of Ce^{3+}. From the comparison of the emission and absorption spectra of $La(C_2H_5SO_4)_3 \cdot 9H_2O$:$Ce^{3+}$ in Fig. 2 of [14], the zero phonon line is estimated from extrapolation at ~35,680 cm^{-1}. The first absorption maximum is then at ~3383 cm^{-1} to higher energy. Although these are estimated values, note that the local coordinated-OH_2 excited state frequency for the first coordination sphere of Ce^{3+} is expected to be slightly lower than the bulk OH_2 ground state frequency probed by Raman spectroscopy, where the O–H bond is slightly stronger. A similar conversion of the other absorption peak maxima into zero phonon line energies leads to the revised centroid shift of ~1.2 eV. A similar argument can be applied to other Ce^{3+} systems when determining the centroid shift, taking into account their vibrational behaviour.

An additional weak band at 297 nm is present in Fig. 1. This additional band has been associated with a ligand dissociated species, and not with a proton-dissociated species since it is independent of $HClO_4$ acid concentration [18]. In the case of aqueous solutions of cerium(III) perchlorate, the presence of an isosbestic point in the absorption spectra of solutions with different concentrations indicated the presence of only two species [18]. The additional absorption band has therefore been associated with the equilibrium between nine and eight aqua-coordinated Ce^{3+} species, with the former dominant [10,11,14]. The weak band at 297 nm becomes more evident at high Ce^{3+} concentrations and is assigned to the lowest $4f^1 \rightarrow 5d^1$ absorption band of $[Ce(H_2O)_8^{3+}]$ [14]. In the presence of other anions, the formation of other 8-coordinated species has however been argued in the literature, also in the form of second sphere complexes $[Ce(H_2O)_8^{3+}]X^-$ [11,17,19–21].

The emission bands of $Ce(H_2O)_9^{3+}$ in $La(C_2H_5SO_4)_3 \cdot 9H_2O$:$Ce^{3+}$ at 312 nm and 333 nm [14] are not apparent in aqueous solution. It is generally accepted that the excited state ion $[Ce(H_2O)_9^{3+}]^*$ rapidly dissociates to give $[Ce(H_2O)_8^{3+}]^*$ [10,14]. The change in coordination number may be anticipated due to the excitation into the $5d^1(e_g)$ orbital [10,22]. Excitation into the Ce^{3+} absorption bands in Fig. 1 gives a $5d^1 \rightarrow 4f^1$ emission spectrum, which consists of a broad feature between 310 and 440 nm with maximum intensity at 360 nm as shown in Fig. 2. This broad band is assigned to unresolved vibronic emission from $[Ce(H_2O)_8^{3+}]^*$ to the $4f^1$ $^2F_{5/2,7/2}$ J-multiplet terms. The emission is strong at very low concentration of Ce^{3+}, and this contrasts with the weak intraconfigurational emission transitions of other Ln^{3+} in solution. The longer wavelength emission of $[Ce(H_2O)_8^{3+}]$, compared with $[Ce(H_2O)_9^{3+}]$, results from the increased 5d orbital splitting associated with a smaller Ce–ligand distance, so that the lowest 5d state is depressed. The emission band is unstructured, unlike those for most Ce^{3+} systems, where two partially-resolved features are observed corresponding to transitions to the distinct ground state J-multiplets. One or two contributing reasons could account for the large breadth and the unstructured character of the emission band. First, the presence of species with different Ce^{3+}–Cl^- distances in $[Ce(H_2O)_8^{3+}]3Cl^-$(aq) would lead to different transition energies. Second, the OH_2 progression interval is

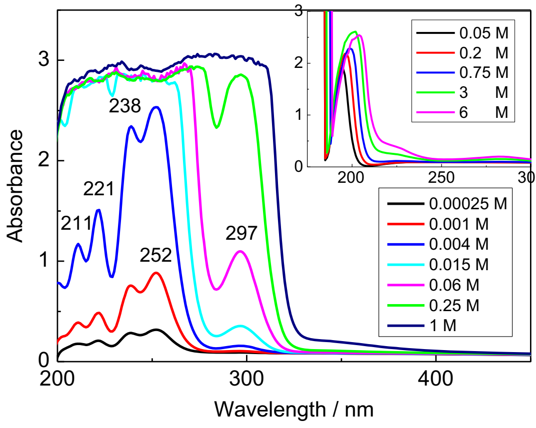

Fig. 1. 300 K absorption spectra of different concentrations of aqueous $CeCl_3$ solutions, from 0.00025 M (bottom) to 1 M (top). The inner figure represents the absorption spectra of different concentrations of HCl solution, with red-shift from 0.05 M to 6 M.

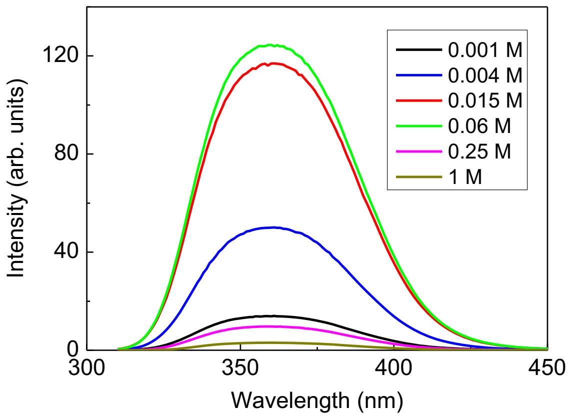

Fig. 2. Emission spectra of different concentrations of $CeCl_3$ solution excited at 300 nm. The concentrations (M) from the bottom of the figure upwards are 1, 0.25, 0.001, 0.004, 0.015, 0.06, respectively.