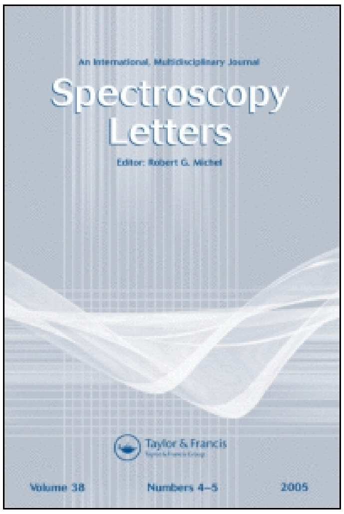

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

A Study of the Intramolecular Energy Transfer of SM(DBM)$_3$ Complex by Photoacoustic and Fluorescence Spectroscopy

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To cite this Article Su, Qingde , Wang, Qin , Lu, Jingei and Ni, Qidao(1997) 'A Study of the Intramolecular Energy Transfer of SM(DBM)$_3$ Complex by Photoacoustic and Fluorescence Spectroscopy', Spectroscopy Letters, 30: 2, 345 — 354
To link to this Article: DOI: 10.1080/00387019708006993
URL: http://dx.doi.org/10.1080/00387019708006993

SPECTROSCOPY LETTERS, 30(2), 345-354 (1997)

A STUDY OF THE INTRAMOLECULAR ENERGY TRANSFER OF $SM(DBM)_3$ COMPLEX BY PHOTOACOUSTIC AND FLUORESCENCE SPECTROSCOPY

keywords: Photoacoustic, Rare earth complexes, energy transfer

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ABSTRACT

The photoacoustic(PA) studies of the nonradiative processes in dibenzoylmethide(DBM) Sm^{3+} complex:$Sm(DBM)_3$ are reported. Compared with the PA spectra of $La(DBM)_3$ and $Gd(DBM)_3$, the paramagnetic effect of the 4f-electrons of Sm^{3+} to DBM and the intramolecular energy transfer from DBM to Sm^{3+} is discussed. The excitation spectra of $Sm(DBM)_3$ are also reported to study the relaxation properties of Sm^{3+} and the energy transfer between DBM and Sm^{3+}. A model of relaxation and energy transfer processes of $Sm(DBM)_3$ is established.

1. INTRODUCTION

The absorption and fluorescence spectroscopy of rare earth complexes have been used in studies on the investigation of optical properties of rare earth ions(Ln^{3+}) and the organic ligand[1]. It was first observed by Crosby[2] that an intramolecular energy transfer process from the ligand to the Ln^{3+} will occur if the lowest triplet level of the ligand lies above the emission level of the Ln^{3+}. Later Kleinerman[3] pointed out that a reversal process may also occur if the emission level of the Ln^{3+} lies above the triplet level of the ligand. Since then, several researchers have studied the mechanism of the intramolecular energy transfer of rare earth complex in solution or in the solid state[4-6]. Since the relaxation process of a complex may be affected by the high-frequency vibrations such as those of OH group in the solution,recently, more and more attentions have been paid on the solid state[7,8]. However, the absorption spectroscopy has limits for use in the solid state because of the nontransparent and scattering property of the solid. Thus an alternative technique must be found in the absorption determination of solid state complexes.

The photoacoustic(PA) spectroscopy is a recently developed technique for studying the properties of opaque or scattering substances[9,10]. The PA signal is obtained by detecting the heat generated through the nonradiative processes after absorption.. A particularly advantage of PAS is its ability to reveal the detail process of intramolecular energy transfer since the energy transfer is a nonradiative process. With the conjunction of fluorescence spectroscopy, PA spectroscopy is a promising technique in the field of solid state complex studies[11-13].

The PA and fluorescence spectra of $Sm(DBM)_3$ microcrystalline complex are reported and the intramolecular energy transfer process of $Sm(DBM)_3$ is discussed. We will show in this paper that both sides of the energy transfer processes, from the ligand to the Ln^{3+} and from the Ln^{3+} to the ligand,can occur. This is consistent with the fluorescence behavior of $Sm(DBM)_3$.

2. EXPERIMENTAL

The $Ln(DBM)_3$ complexes (Ln=Sm,La ,Gd) were prepared in a standard technique[14]: The RE oxide was converted to the chloride by treatment with concentrated HCL. A solution of the chloride in absolute ethanol was added to a solution of DBM ligand in the same solvent. The precipitation was accomplished by the addition of piperidine.The complexes were recrystallized and air dried. The elemental analyses and infrared spectra of the $Ln(DBM)_3$ were performed and were consistent with the expected formulae.

The PA spectra were measured on a single-beam spectrometer constructed in our lab[15]. A 500w xenon lamp, a CT-30F monochromator and a PA cell fitted with an ERM 10 electret microphone were used. The chopper frequency was 12 HZ. The output signal of the microphone was amplified by a preamplifier and fed to a lock-in-amplifier(LI-547A) with a reference signal inputted from the chopper. The final signal was normalized for the changes in lamp intensity using a reference by carbon-black and the normalization coefficient was moderated to be a constant.. The PA spectra of the microcrystalline samples of $Ln(DBM)_3$ were recorded at room temperature in the range of 300-800nm.

The absorption spectra in the range of 300-800nm were recorded for solution in the methanol-ethanol(1:3) mixture in the Shimadzu UV 240 UV-Vis spectrophotometer.The fluorescence spectra of microcrystalline $Ln(DBM)_3$ were taken with a PE LS-50 spectrophotometer.

3. RESULTS AND DISCUSSION

3.1 Photoacoustic Spectra

Photoacoustic(PA) spectroscopy provides a method for monitoring nonradiative decay processes that can occour in samples following their absorption. So the PA band appears in the location of absorption and it reveals the absorption and relaxation information of a sample.

The PA spectrum of $Sm(DBM)_3$ microcrystalline complex is shown in FIG.1. Compared with the PA spectrum of the free-base DBM, the broad band located around 410nm is assigned to the $\pi-\pi^*$ transition of DBM. The PA band of $Sm(DBM)_3$ in the region of 410nm is significantly stronger than that of the free-base DBM. This is due to the fact that the π electron conjugated system of $Sm(DBM)_3$ is much larger than that of the free-base DBM and has a higher molar absorptivity.

The PA spectra of $Gd(DBM)_3$ and $La(DBM)_3$ are also detected. For different Ln^{3+}, the relative intensity of PA band in the region of ligand absorption changes significantly. Since the absorptivity of $Ln(DBM)_3$ does not depend on the central Ln^{3+}[16], the PA intensity of $Ln(DBM)_3$ is capable of revealing the change of non-radiative energy transfer processes caused by Ln^{3+} on the ligand.

3.2 Effect of Ln^{3+} on the Ligand

It is known that after excitation, there are two relaxation processes:radiative process and nonradiative process. The PA signal (A) is only respond to the nonradiative process and it can be given by[17]:

$$A = kP_{abs}\,\gamma \qquad (1)$$

where P_{abs} is the absorbency of the sample, γ is the probability for nonradiative transitions after excitation and k is a coefficient which is determined by the thermal properties of the sample and by the spectrometer. For a given sample and detecting condition, k is a constant. Since the absorption of $Ln(DBM)_3$ is not affected by different Ln^{3+}, the PA signal of $Ln(DBM)_3$ is in proportion to the probability for nonradiative transitions, γ.

TABLE I shows the relative intensity of PA signal of $Ln(DBM)_3$ (Ln=Sm,La,Gd) in the region of DBM absorption. We use the relative intensity (peak/base) to diminish the background effect. The PA signal of $Sm(DBM)_3$ is significantly stronger than that of $La(DBM)_3$. This is due

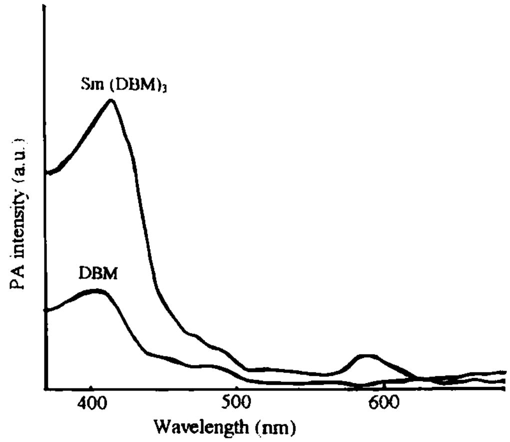

FIG. 1. PA spectra of $Sm(DBM)_3$ complex and free-base DBM.

TABLE I. Relative PA intensity of $Ln(DBM)_3$ complexes

Ln	PA intensity ratio(peak/base)	Relative PA intensity
La	3.8	27.9
Sm	13.6	100.0
Gd	17.6	129.4

to the paramagnetic effect: The paramagnetic 4f-electron of Ln^{3+} can bring about a mixing of the singlet(S) and triplet(T) states of ligand and permits the otherwise forbidden nonradiative intersystem crossing from the excited singlet state to the lower lying triplet state. Then the intensity of PA signal increases as the nonradiative transition probability(γ) increases. The relatively weak PA signal of $La(DBM)_3$ is due to the absence of any 4f-electrons of La^{3+}.

After the triplet state of the ligand is excited by intersystem crossing from the excited singlet, it can relax directly to the ground state or to some lower lying states through nonradiative processes. A study of the 4f level of Ln^{3+} shows that the radiative 4f level of Sm^{3+} are lower than the triplet state of DBM. An intramolecular energy transfer from the ligand excited triplet state to the 4f level of Sm^{3+} may occur, followed by characteristic emissions of Sm^{3+}. As to $Gd(DBM)_3$, the 4f levels of Gd^{3+} are higher than the triplet state of DBM and the triplet state relaxes directly to the ground state through nonradiative processes(there is no phosphorescence in room temperature). The nonradiative transition probability(γ) of $Sm(DBM)_3$ is smaller than that of $Gd(DBM)_3$ because of the radiative emissions of Sm^{3+}. As a result the PA signal of $Sm(DBM)_3$ is weaker than that of $Gd(DBM)_3$.

In conclusion, with the comparation of the spectra of $La(DBM)_3$ and $Gd(DBM)_3$, the PA signal of $Sm(DBM)_3$ represents the paramagnetic effect of Sm^{3+} to DBM and the intramolecular energy transfer from DBM to Sm^{3+}.

3.3 The Fluorescence Spectra and Model of Energy Transfer Processes

In order for a further study of the intramolecular energy transfer between DBM and Sm^{3+},and because of the radiative characteristics of Sm^{3+}, the emission and excitation spectra of $Sm(DBM)_3$ are detected.(FIG. 2a,b)

In the emission spectrum(λex=410nm), the 420-460nm band is attribute to the emission of DBM ,and the three acute and narrow band(563,605and638nm) are attributed to the characteristic emissions of the first excited state of $Sm^{3+}(^4G_{5/2})$. Since the excitation wavelength is fixed at the optimal absorption of DBM(λex =410nm), the presence of Sm^{3+} emission demonstrates the energy transfer from DBM to Sm^{3+}.

The excitation spectra are obtained by fixing on the Sm^{3+} emission (λem=563,605 and638nm). In each of the three spectra, there exists a fairly strong excitation band (510,555

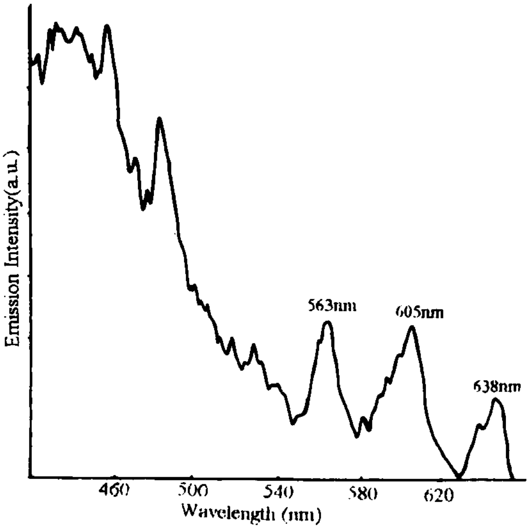

FIG.2a. Emission spectrum of Sm(DBM)$_3$ complex. (λ_{ex}=410nm).

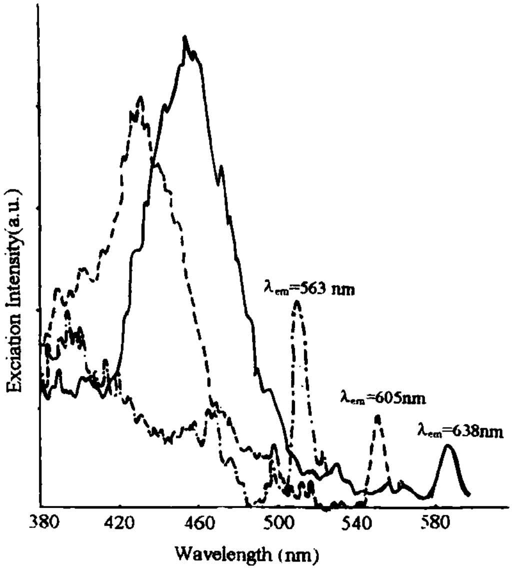

FIG.2b. Excitation spectra of Sm(DBM)$_3$ complex.

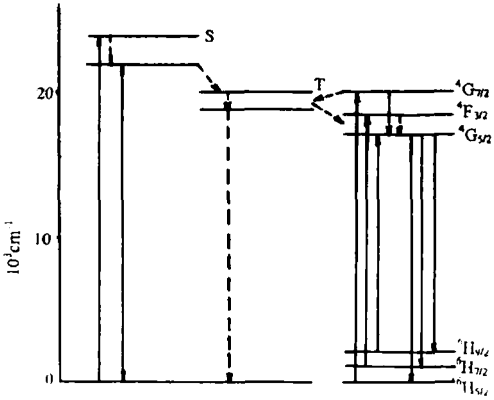

FIG.3. Model of relaxation and intramolecular energy transfer processes of $Sm(DBM)_3$ complex.

——— radiative ------- nonradiative

and 586, respectively), which can be attributed to the transition of Sm^{3+} from the ground state $^6H_{5/2}$, $^6H_{7/2}$ or $^6H_{9/2}$ to the excited state $^4G_{7/2}$, $^4F_{3/2}$ or $^4F_{3/2}$, respectively. Then the excited energy will be transfered from the $^4G_{7/2}$ or $^4F_{3/2}$ to the first excited state of Sm^{3+} , $^4G_{5/2}$. Thus, Contribute to the three emissions of the $^4G_{5/2}$ state.

$^6H_{5/2}$-------→$^4G_{7/2}$-------→$^4G_{5/2}$-------→$^6H_{5/2}$

$^6H_{7/2}$-------→$^4F_{3/2}$-------→$^4G_{5/2}$-------→$^6H_{7/2}$

$^6H_{9/2}$-------→$^4F_{3/2}$-------→$^4G_{5/2}$-------→$^6H_{9/2}$

The 438nm and 465nm excitation band in the λem=605nm and λem =638nm spectrum demonstrate the intramolecular energy transfer from DBM to Sm^{3+} and is coincident with the PA and emission spectra. When it comes to the λem=563nm spectrum, the expected band does not appear. This seemed anomalous phenomenon indicates the fact that the emissions of Sm^{3+} not only depends on the first excited state, $^4G_{5/2}$, but also depends on the other two excited state, $^4G_{7/2}$ and $^4F_{3/2}$. Since the $^4G_{7/2}$ state is higher than the lower triplet state of DBM, when the energy was transfered from the DBM to $^4G_{7/2}$, it has the oppotunity to be re-transfered to the triplet state of DBM. Thus an energy transfer from Sm^{3+} to DBM occurs, which decrease the energy contribution of DBM to the emission of 563nm. The model of relaxtion and intramolecular energy transfer processes of $Sm(DBM)_3$ is established (FIG. 3). It shows the π - π * transition of DBM, f-f transitions of Sm^{3+}, the relaxation processes of DBM and Sm^{3+}, and the intramolecular energy transfers between DBM and Sm^{3+}.

ACKNOWLEDGEMENT

We thank the National Natural Science Foundation of P.R. China for supporting this program.

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Received: August 5, 1996
Accepted: Oct. 11. 1996