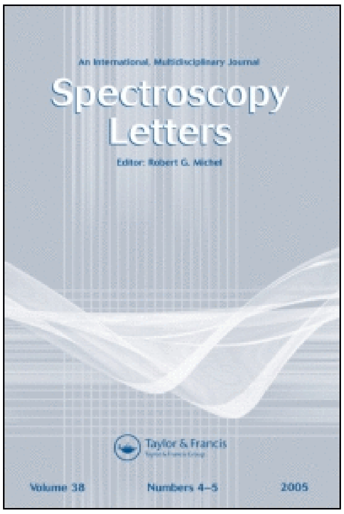

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Photoacoustic Phase Study on the Relaxation Processes of $Nd(DBM)_3$

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PHOTOACOUSTIC PHASE STUDY ON THE RELAXATION PROCESSES OF $Nd(DBM)_3$

Key words: PA amplitude and phase spectra, rare earth, dibenzoylmethide

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ABSTRACT

Measurement are reported on the phase of the photoacoustic signal of Nd-Dibenzoylmethide ($Nd(DBM)_3$) sample for a range of chopping frequencies between 56HZ-722HZ. By applying to theoretical models, the utility of phase data to evaluate the optical absorption coefficient and nonradiative relaxation time of solid state complexes are discussed. And modified theoretical models have been established.

INTRODUCTION

The investigation of luminescence properties of rare earth complexes is always an interesting project in the field of chemistry,physics and materials science[1-5]. The photoacoustic (PA) spectroscopy is currently being explored as a tool in this investigation because of its ability to measure solid state samples which is difficult for conventional techniques. It is capable of providing information about the nonradiative relaxation processes that occur after a sample has been excited[6,7].

An important characteristic of PAS is that it provides information about both the amplitude and phase of the response of a sample. The phase data contains contributions from a number of sources associated with the system under study. These include the relaxation time associated with the nonradiative decay paths, the optical absorption coefficient of the sample, the interaction between the sample and its backing and the dimension of the PA cell. In a PA measurement of microcrystalline metal complexes, the sample and cell dimensions are long enough compared with the thermal diffusion length in the sample. So the phase of the PA response will be directly related to the relaxation time and optical absorption coefficient.

In the recent papers, we have studied the absorption properties and relaxation processes of rare earth β-diketonate complexes[8-10]. We found out that the PA amplitude spectra could reveal the typical absorption of both the ligands and the rare earth ions in the different regions. Because the relaxation processes of the ligands and the rare earth ions are significantly different, how to use the PA phase spectra to reveal these processes comes to great interest . We detect the dependence of phase signal of rare earth β-diketonate, $Nd(DBM)_3$, on the light chopping frequencies in the range of 56-722 HZ. From the $\phi \sim \omega$ curve, we discuss the relationship between the phase signal and the optical absorption coefficient(β) and the relaxation time(τ) of rare earth complexes. And established a modified phase model of the relaxation processes of rare earth complexes.

THEORY

The Photoacoustic data contains contributions from many factors. In an actual PA measurement, many of the nonsample related parameters may be maintained constant and the phase data may therefore be used to provide information about the optical and thermal properties of the sample.

In Rosencwaig and Gersho's(R-G) one dimensional theoretical model of the PA response of solid state samples[6], the nonradiative relaxation processes are supposed to occur instantaneously. So the PA signal can be given as:

$$\begin{aligned}\Delta P(t) &= \frac{A\beta\mu_s}{\omega[(\beta\mu_s+1)^2+1]^{1/2}}\exp\{j[\omega t-\frac{\pi}{4}-\tan^{-1}(\frac{\beta\mu_s+2}{\beta\mu_s})]\}\\ &= q\exp[j(\omega t+\varphi)] \qquad (1)\end{aligned}$$

with ω, the chopping frequency; β, the optical absorption coefficient of the sample; μ_s , the thermal diffusion length; and q,φ are the amplitude and the phase of the PA signal.

So $$\varphi = -\frac{\pi}{4} - \tan^{-1}(\frac{\beta\mu_s + 2}{\beta\mu_s}) = -\frac{\pi}{4} - \tan^{-1}(1 + \frac{2}{\beta\mu_s}) \tag{2}$$

The first use of PA phase signal to measure the nonradiative relaxation time was employed by Merkle and Powell[11]. Then Mandelis made extensions of the R-G PA model to include the relaxation time of nonradiative processes[12]. The PA signal thus has the form:

$$\Delta P(t,\omega) = (\frac{p_0 I_0 \eta\beta}{2K_s T_0 L})\mathrm{Re}[(\frac{\exp[i(\omega t - \frac{\pi}{4})]}{\sqrt{2}a_g(1+i\omega\tau)(\beta^2 - \sigma_s{}^2)})$$
$$\times(\frac{(r-1)(b+1)\exp(\sigma_s l) - (r+1)(b-1)\exp(-\sigma_s l) + 2(b-r)\exp(-\beta l)}{(b+1)\exp(\sigma_s l) + (b-1)\exp(-\sigma_s l)})]$$
$$= q\exp[i(\omega t - \frac{\pi}{4} - \varphi)] \tag{3}$$

For an optically opaque and thermally thick sample, the most useful case in experiment, both the optical absorption depth,μ_β, and the thermal diffusion length, μ_s, are much less than the sample thickness. Under these conditions $\exp(-\beta l)\cong 0$ and $\exp(-\sigma_s l)\cong 0$. So that the variable component of the PA phase is given by:

$$\varphi = \tan^{-1}(-\omega\tau_\beta) + \tan^{-1}(\omega\tau) - \tan^{-1}(\frac{-1}{1-(2\omega\tau_\beta)^{1/2}}) \tag{4}$$

where $\tau_\beta = 1/\beta^2\alpha_s$ is a characteristic relaxation time for the system corresponding to the thermal transit time from a depth $\mu_\beta(=1/\beta)$within the solid.

The simplified theoretical model is still complicated, and because of the lack of experimental results, this model can not directly reveal the optical and thermal properties of rare earth complexes. In this paper, we choose Nd(DBM)₃, which has its typical absorption and relaxation properties, to be the sample. Based on the theoretical model and experimental data, to reveal the relaxation processes of rare earth complexes.

EXPERIMENTAL

In recent work of our laboratory, we had already carefully studied the nonradiative relaxation processes of rare earth complexes in different absorption regions. Now we use the microcrystalline Nd(DBM)$_3$ as solid state sample, to measure the variation of PA phase signal under different chopping frequency, in the region of ligand and rare earth ion absorption, respectively.

1. Preparation of Nd (DBM)$_3$

The Nd$_2$O$_3$ was converted to NdCl$_3$ by treatment with concertrated 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 complex was recrystallized and air dried. The elemental analyses and infrared spectra were performed and were consistent with the expected formulae.

2. Detection of PA Phase Signal

The PA spectra were measured on a single-beam spectrometer constructed in our lab[13]. A 500w xenon lamp was employed. The light beam passed a CT-30F monochromator with computer scanned wavelength and was modulated by mechanical chopper. The PA cell was fitted with an ERM 10 electret microphone. The output signal of microphone was fed to a lock-in-amplifier(LI-547A) with a reference signal inputted from the chopper.

The PA amplitude spectrum of Nd(DBM)$_3$ was recorded against the wavelength of light in the range of 350-700nm. The measurement of PA phase signal is taken within chopping frequency range of 56-722 HZ. In order to avoid the interference of electric power, the chopping frequency is moderated not to be the multiple of 50 HZ. The powder sample was compacted in the cell to obtain thermally thick sample with reduced porosity.

RESULTS AND DISCUSSION

1. Dependence of the PA phase ϕ upon chopping frequency ω

FIG.1 is the PA amplitude spectrum of Nd(DBM)$_3$ in the range of 350-700nm. The strong and broad band in the region of 414nm represents the absorption of DBM. In the region of 536 and 586nm are the characteristic absorption bands of Nd^{3+} ion. We also choose the

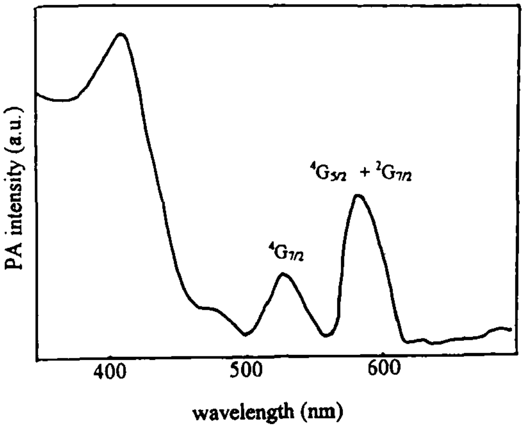

FIG. 1. PA amplitude spectrum of $Nd(DBM)_3$

signal in 500 and 566nm,which have no PA response at all, to be the reference signals. In the chopping frequency range of 56-722HZ, the PA phase signal of 414, 536,586,500 and 566nm were measured, respectively(TABLE I). The phase signal change versus chopping frequency curves are shown in FIG.2.

In FIG.2, we find out that the phase signals in the 500 and 566nm region change irregularly as the chopping frequency increases. In the region of ligand and ion absorption(414, 536 and 586nm), the phase shift increases as the frequency increases, and it begins to saturate at the high frequency region.

FIG.2 also shows the contributions of the optical absorption coefficient and relaxation time to the PA phase shift. In order to get further information of the dependence of PA phase (ϕ) on optical absorption coefficient(β) and relaxation time(τ). The $\mathrm{tg}\varphi$ versus chopping frequency ω and $\omega^{1/2}$ curves are shown in FIG3,4, respectively.

2. Explanation of relationships between φ and β,τ by using theoretical models

The PA signal in the region of 414nm represents the relaxation processes of DBM ligand after excitation. Because of the paramagnetic effect of rare earth ions to the ligand, part of the energy absorbed by DBM can be transferred to Nd^{3+} through triplet energy level of the

TABLE I : PA phase data of $Nd(DBM)_3$

φ\ω(HZ)	56	64	68	72	78	84	108	144	168	204
414nm	0	-15	-20	-25	-32	-40	-50	-62	-67	-75
500nm	0	-5	-7	-12	/	-7	-12	-15	-17	-15
536nm	0	/	-13	-20	-28	-40	-48	-53	-55	-55
566nm	0	-5	-10	-10	-12	-2	-14	-14	-17	-19
586nm	0	-15	-20	-25	-32	-40	-48	-58	-63	-68

φ\ω(HZ)	233	272	332	384	428	484	532	636	722
414nm	-80	-82	-85	-85	-87	-85	-85	-80	-75
500nm	-17	-17	-12	-10	-12	-10	-7	-10	-10
536nm	-60	-58	-58	-55	-53	-53	-53	-53	-48
566nm	-22	-24	-22	-22	-22	-22	-22	-22	-17
586nm	-68	-70	-70	-68	-68	-63	-60	-50	-40

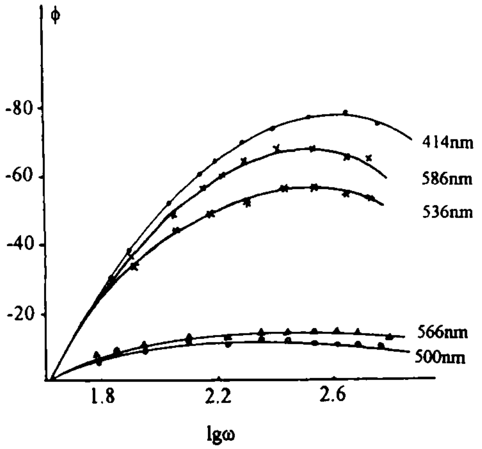

FIG. 2. PA phase shift versus chopping frequency

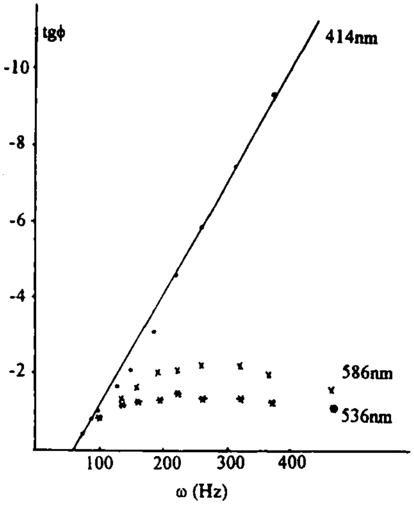

FIG.3. tgϕ versus chopping frequency ω

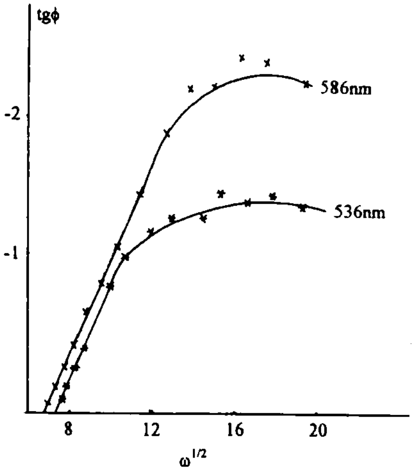

FIG.4. tgϕ versus ω$^{1/2}$

ligand. Since the lifetime of triplet state is about 10^{-3} s, the relaxation time τ is a factor that can not be neglected for the PA phase signal of 414nm. We can learn from FIG.3 that $tg\varphi=k\omega$ (k is a constant). This is a special condition of Mandelis model when $\omega\tau_\beta \to 0$. So we use the Mandelis model to explain the relaxation processes in the 414nm region.

Because of its conjugated π - $\pi^\bullet$ structure , the absorption coefficient β of Nd(DBM)$_3$ in the region of ligand absorption is very high (β ~ $10^5 cm^{-1}$). So $\tau_\beta = 1/\beta^2\alpha_s \to 0$. Under this condition and when the chopping frequency ω is not high enough, the $\omega\tau_\beta \to 0$. So that the Mandelis model can be given by:

$$\varphi = \tan^{-1}(\omega\tau) + \frac{\pi}{4} \tag{5}$$

In the experimental PAS measurement, there is an instrumental contribution ϕ_0 which is independent of β,τ, and ω. Then

$$\phi' = \tan^{-1}(\omega\tau) + \frac{\pi}{4} + \phi_0 = \tan^{-1}(\omega\tau) + \phi_0{}' \tag{6}$$

In order to eliminate the instrumental effect, we choose the relative signal ϕ ($\phi = \phi' - \phi_0'$) to be the phase signal (see TABLE I). So that

$$\phi = \phi' - \phi_0{}' = \tan^{-1}(\omega\tau)$$
$$tg\phi = \omega\tau \tag{7}$$

In a given absorption region, the relaxation time τ is constant. Then $tg\phi$ has a lineary relationship with ω(0-400HZ). As the chopping frequency increases, the contribution of $\omega\tau_\beta$ can not be neglected. So that the lineary relationship can no longer exist. All these conditions are shown in FIG.3.

In the region of Nd^{3+} absorption (536 and 586nm), the absorption coefficient are lower than that of the 414nm. As we know, the energy level of Nd^{3+} are often intermixed and the relaxation processes undergoes a nonradiative channel most readily. So the relaxation time of Nd^{3+} is essentially instantaneous. In this case, we can use the R-G model

$$\phi = \tan^{-1}(1 + \frac{2}{\beta\mu_s}) = \tan^{-1}(1 + \frac{2}{\beta(\frac{2\alpha_s}{\omega})^{1/2}}) \tag{8}$$

so that $$tg\phi = 1 + \frac{2}{\beta(2\alpha_s)^{1/2}}\omega^{1/2} \tag{9}$$

FIG.4. shows that in a small range of chopping frequency(for 586nm, 0-200HZ; for 536nm, 0-120HZ), this lineary relationship can be demonstrated. But for a wide range of chopping frequency, the following model is more reasonable[14].

$$\phi = \tan^{-1}(\omega\tau) + \tan^{-1}(1 + \frac{2}{\beta\mu_s})$$

$$= \tan^{-1}(\omega\tau) + \tan^{-1}(1 + \frac{2}{\beta(\frac{2\alpha_s}{\omega})^{1/2}}) \qquad (10)$$

when $\beta \sim 10^5\ cm^{-1}$ and τ is long enough, the second item can be neglected, then $\phi = \tan^{-1}(\omega\tau)$, the PA phase signal is directly related to the relaxation time.

When $\omega\tau \to 0$, the first item can be neglected.This is consistent with the R-G model.

But when β is not high enough and the second item is comparable to the first item, none of the two items can be neglected. The PA signal is related to both the relaxation time and optical absorption coefficient.

We use the modified theoretical model, through controlling the chopping frequency, to reveal the relaxation processes of rare earth complexes. And the result is satisfying.

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