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A STUDY ON PHOTOACOUSTIC PHASE SPECTRA OF RARE EARTH COMPLEXES WITH OXINE

Keywords: Photoacoustic spectroscopy; Phase spectra; Rare earth complexes; Relaxation processes

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ABSTRACT

Photoacoustic phase is the time delay that occurs from light to acoustic signal. The phase includes two components: one is the time delay that occurs during the process in which light absorbed by a sample converts into heat; the other is the time delay caused from heat to acoustic signal. A modified formula of PA phase is presented based on the R-G theory considering the phase caused by non-radiative relaxation processes. The phase is associated with absorption coefficient (β), thermal diffusion length of sample (μ_s), the longest lifetime of all excited states (τ), and the ratio of rapid to slow heat component (R). When the photoacoustic signal is saturated the phase is associated with only τ and R . The effect of different rare earth ions on the PA phase spectra of the ligand (oxine) in the rare earth complexes are reported and are well explained by using the phase formula of PA saturation.

INTRODUCTION

Photoacoustic Spectroscopy (PAS) is suitable for any type of solid, whether it be crystalline, powder, or gel. It has been widely used to investigate the chemical and physical properties of many kinds of samples [1,2]. Unlike conventional transmission spectroscopy, PAS can provide both amplitude and phase information on the response of a photoacoustic system to an optical excitation process [3]. The phase data contain contributions from a number of sources: the geometry of the photoacoustic cell, the response of the detecting system, the interaction between the sample and its backing, the optical absorption coefficient,

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the nonradiative decay paths, etc. In an actual photoacoustic 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 solid sample under study, as well as the relaxation times associated with the nonradiative de-excitation processes that give rise to the PAS signal [4].

Recently, we have studied the absorption properties and relaxation processes of rare earth complexes [5-7]. PAS has been found to be very suitable for investigating the solid rare earth complexes by providing their PA amplitude spectra. In addition, the PA phase spectrum comes to great interest. The phase spectra of several kinds of rare earth complexes have been reported and some theoretical interpretations of the phase spectra have been given [8-10]. In this paper, a modified formula of PA phase is presented based on the R-G theory. The effect of different rare earth ions on the PA phase spectra of the ligand in the rare earth complexes are reported and are well explained by using this formula.

THEORY

Rosencwaig and Gersho [3] firstly presented a one-dimensional theoretical model of the PA response of solid state samples (R-G model). They discussed the effect of the optical absorption coefficient of the solid on the phase for the limiting case of optically transparent and opaque specimens in which the nonradiative de-excitation processes are supposed to occur instantaneously. Mandelis et al [10] extended the R-G theory. Considering the finite relaxation time of the nonradiative deexcitation processes, they presented a new phase formula for an optically opaque and thermally thick solid sample:

$$\Psi = \operatorname{tg}^{-1}(-\omega \tau_\beta) + \operatorname{tg}^{-1}(\omega \tau) - \operatorname{tg}^{-1}(-1/(1-(2\omega \tau_\beta)^{1/2}))$$

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 μ_β ($=1/\beta$) within the solid. From the formula the value of phase (Ψ) increases with the relaxation time (τ) increasing. This is suitable for the two-level system, but not for a multi-level system.

Photoacoustic phase is the time delay that occurs during the process from light absorbed by a sample to acoustic signal being detected by microphone. The phase includes two components: one is the time delay that occurs during the process in which light absorbed by a sample converts into heat; the other is the phase caused from the transition of heat to acoustic signal.

1. The Phase that Comes from Light Converting into Heat

According to the literature [11], a multilevel system energy level T has the longest lifetime of all the states, its lifetime is τ . $I = 1/2I_0(1+\cos(\omega t))$, for intensity modulated incident light; I_0 is the intensity of incident light; $\omega = 2\pi f$; f is the chopping frequency to irradiate the solid sample. The rate of heat production is given as

$$U = U_0 + U(\omega) \exp(i\omega t) \quad (1)$$

where U_0 and $U(\omega)$ are the non-oscillatory and oscillatory parts, respectively. Only $U(\omega)$ can contribute to the phase, so we only consider $U(\omega)$ as

$$U(\omega) = A \cdot I_0 (H + m_T L \exp(-i\varphi_T)) \quad (2)$$

where L represents that part of the energy involved in the level T relaxation (i.e. slow heat); H represents that part of the energy involved in the other level (except level T) relaxation (i.e. fast heat); and $m_T = (1 + \omega^2 \tau^2)^{-1}$; $\varphi_T = \operatorname{tg}^{-1}(\omega \tau)$

The phase of the formula (2) is given as

$$\varphi_T = \operatorname{tg}^{-1}(\omega \tau / (1 + R(1 + \omega^2 \tau^2))) \quad (3)$$

where $R = H/L$, the ratio of rapid to slow heat component.

2. The Phase that is Caused from Heat to Acoustic Signal

The R-G theory has discussed the PA signal of the solid sample systematically, but the nonradiative deexcitation processes were supposed to be instantaneous. It says that there wasn't the phase from the light absorbed by the sample to heat. So the phase data of the R-G theory is that from heat to acoustic signal.

According to the R-G theory, the PA signal (the variation of the gas pressure) is as

$$\Delta P(t) = \frac{\beta I_0 \gamma P_0 \exp(i(\omega t - \pi/4))}{2\sqrt{2}k_s l_g \alpha_g T_0 (\beta^2 - \sigma_s^2)} \left(\frac{(r-1)(b+1)\exp(\sigma_s l) - (r+1)(b-1)\exp(-\sigma_s l) + (b-r)\exp(-\beta l)}{(g+1)(b+1)\exp(\sigma_s l) - (g-1)(b-1)\exp(-\sigma_s l)} \right) \quad (4)$$

the meaning of parameters in the formula are the same with the literature [3], where β is the optical absorption coefficient of the sample, l is the pathlength of the sample, $g = k_g \alpha_g / k \alpha$, $r = (1-i)\beta/2\alpha$, $\sigma_s = (1+i)\alpha$, and α is the heat diffusion coefficient.

We can ignore g since $g \ll 1$, when the gas is air at room temperature and pressure. For an optically opaque and thermally thick sample both the optical absorption depth ($\mu_\beta = 1/\beta$) and the thermal diffusion length ($\mu_s = 1/\alpha$) are much less than the sample thickness (l). Under these conditions $\exp(-\beta l) \approx 0$ and $\exp(-\sigma_s l) \approx 0$. Eq. (4) can be rewritten as

$$\Delta P(t) = \frac{\beta I_0 \gamma P_0}{2\sqrt{2}k_s l_g \alpha_g T_0} \cdot \frac{r-1}{(\beta^2 - \sigma_s^2)} \cdot \exp(i(\omega t - \pi/4)) \quad (5)$$

Following Rosencwaig and Gersho [3], the amplitude and the phase of the PA signal may be separated conveniently using

$$\Delta P(t) = Q \exp(i(\omega t - \pi/4)) = q \exp(i(\omega t - \pi/4) - i\varphi)$$

where q and $-\varphi$ is the amplitude and the phase of Q , respectively. when Q_1 and Q_2 are the real and imaginary parts of Q , respectively, then $Q = Q_1 + iQ_2 = q \exp(-i\varphi)$, $\varphi = \operatorname{tg}^{-1}(-Q_2/Q_1)$.

By writing the components of Q in the polar notation for the complex quantities

$$r-1=[(\omega\tau_\beta)^{-1}+1-(2/\omega\tau_\beta)^{1/2}]^{1/2}\exp(i\varphi_1)$$

$$\beta^2 - \sigma_s^2 = \beta^2[1+(\omega\tau_\beta)^2]^{1/2} \exp(i\varphi_2)$$

The expression for the phase can take on a simple form

$$\Psi_2=\pi/4-\varphi_1+\varphi_2=\pi/4+\operatorname{tg}^{-1}(-\omega\tau_\beta)-\operatorname{tg}^{-1}(-1/(1-(2\omega\tau_\beta)^{1/2})) \quad (6)$$

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 μ_β within the solid sample.

3. The Phase of photoacoustic saturation

The total phase is the sum of the above two parts.

$$\Psi=\Psi_1+\Psi_2=\operatorname{tg}^{-1}(\omega\tau/(1+R(1+\omega^2\tau^2)))+\pi/4+\operatorname{tg}^{-1}(-\omega\tau_\beta)-\operatorname{tg}^{-1}(-1/(1-(2\omega\tau_\beta)^{1/2})) \quad (7)$$

When photoacoustic signal is saturated (generally $\beta>10^4$),

$$\operatorname{tg}^{-1}(-\omega\tau_\beta)-\operatorname{tg}^{-1}(-1/(1-(2\omega\tau_\beta)^{1/2}))=\pi/4$$

So

$$\Psi=\pi/2+\operatorname{tg}^{-1}(\omega\tau/(1+R(1+\omega^2\tau^2))) \quad (8)$$

EXPERIMENTAL

1. Synthesis of the Rare Earth Complexes with Oxine

The Ln_2O_3 was converted to LnCl_3 by treatment with concentrated HCl. A procedure [12] was introduced to synthesize the complex. A solution of chloride was added to a solution of oxine with ammonia acetate buffered solution. The precipitation was accomplished by the addition of aqueous ammonia slowly. The precipitation was filtrated, washed three times with water and dried under 130°C for five hours. The elemental analyses and infrared spectra were performed and were consistent with their molecular structure.

2. Photoacoustic Measurements

The photoacoustic amplitude and phase spectra were recorded in the region of 300 to 600nm. The excitation source was a 500 w xenon lamp. The light source was modulated by a variable speed mechanical chopper at a different frequency. The acoustic signal was detected with the sample placed in a locally built photoacoustic cell fitted with an ERM 10 electret microphone and then was fed to a lock-in-amplifier (LI-574A) to which a reference signal was input from the chopper. The amplitude signals were normalized for changes in lamp intensity using the reference signal of carbon black.

RESULTS AND DISCUSSION

1. Amplitude Spectra of $\text{Ln}(\text{ox})_3$

The PA signal is obtained by detecting the heat generated through the nonradiative released by the sample after absorbing the modulated incident light, it doesn't necessarily coincide

with the absorption spectrum. It reveals the absorption and relaxation information of a sample.

The PA amplitude spectra of $\text{Ln}(\text{ox})_3$ ($\text{Ln}=\text{Nd, Eu, Gd}$) in the range 300-600 nm at a frequency of 12 Hz are shown in the Fig. 1. The PA bands of oxine in the complexes are assigned to the $\pi-\pi^*$ transition. They are saturated within 340-400 nm. It is due to the fact that the π electron conjugated system of the complexes is much larger than that of the free-base oxine and has a higher molar absorptivity so that $\mu_B < \mu_s < l$. The absorption coefficient of the $\pi-\pi^*$ transitions of oxine is higher than that of f-f transitions of rare earth ions, so the absorption peaks of Eu^{3+} were covered by the $\pi-\pi^*$ transition of oxine; the absorption peaks of Nd^{3+} (except 574 nm) were covered also; Gd^{3+} has no absorption within this region.

The PA relative intensity of oxine in $\text{Gd}(\text{ox})_3$ is the smallest, because the excited state of Gd^{3+} is higher than the triplet state of oxine, energy can't transfer from oxine to Gd^{3+} , which makes more energy radiant by the luminescence of oxine. The nonradiative part is relatively small. In addition, the PA relative intensities of oxine in $\text{Nd}(\text{ox})_3$ is stronger than that in $\text{Eu}(\text{ox})_3$, because Eu^{3+} is a fluorescent ion, the energy that transfers from oxine to Eu^{3+} partly radiate, so that the amount of heat given out from $\text{Nd}(\text{ox})_3$ is more than that from $\text{Eu}(\text{ox})_3$. The models of relaxation and intramolecular energy transfer processes of $\text{Ln}(\text{ox})_3$ ($\text{Ln}=\text{Nd, Eu, Gd}$) are shown in Figure 2.

2. The Phase Spectra of $\text{Ln}(\text{ox})_3$

The phase spectra of $\text{Ln}(\text{ox})_3$ are shown in Fig. 3. The phase of $\text{Ln}(\text{ox})_3$ at 340-400 nm maintain constant. The phase data of $\text{Nd}(\text{ox})_3$ is the biggest, it is 3° larger than that of $\text{Eu}(\text{ox})_3$ and is 9° bigger than that of $\text{Gd}(\text{ox})_3$ within the region of 340-400 nm.

The energy level of triplet state of oxine is $18,500 \text{ cm}^{-1}$. It is higher than some energy levels of Eu^{3+} and Nd^{3+} , so that in the complexes of $\text{Eu}(\text{ox})_3$ and $\text{Nd}(\text{ox})_3$ the energy may transfer from the triplet state of oxine to the excited state of Nd^{3+} and Eu^{3+} . The lifetime of the triplet state becomes shorter, which makes the relaxation time shorten. From the formula of madelis when the relaxation time becomes short the phase data should reduce. But the result is reversal.

According to the formula (8), when photoacoustic signal is saturated, the phase is

$$\Psi = \pi/2 + \tan^{-1}(\omega r / (1 + R(1 + \omega^2 T^2)))$$

When ωr is very small, the formula may be simplified to

$$\Psi = \pi/2 + \tan^{-1}(\omega r / (1 + R)) \quad (9)$$

When ωr is very big so that $(\omega r)^2$ is far bigger than 1, the formula may be rewritten to

$$\Psi = \pi/2 + \tan^{-1}(1/R\omega r). \quad (10)$$

From the formula (10) the phase doesn't always increase with the relaxation time increasing. When the relaxation time is long enough or the frequency is big enough, the phase reduces with the relaxation time increasing.

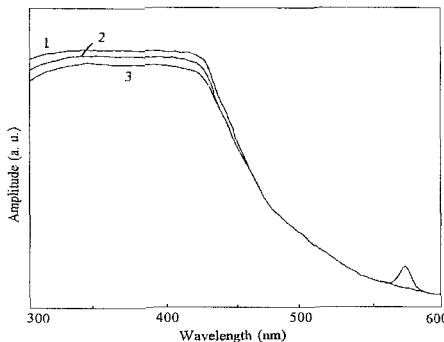


Fig. 1 Amplitude spectra of $\text{Ln}(\text{ox})_3$ ($\text{Ln}=\text{Nd, Eu, Gd}$) at a chopping frequency of 12 Hz
 1 $\text{Nd}(\text{ox})_3$; 2 $\text{Eu}(\text{ox})_3$; 3 $\text{Gd}(\text{ox})_3$

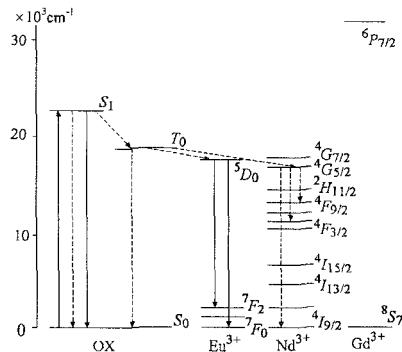


Fig. 2 Models of relaxation and intramolecular energy transfer processes of $\text{Ln}(\text{ox})_3$ ($\text{Ln}=\text{Nd, Eu, Gd}$) (\rightarrow radiative process; \cdots nonradiative process)

Because the lifetime of the triplet state of quinoline is about 13 s in EPA [13], the lifetime reduces when the temperature increases, but when rare earth ions and oxine form the complexes, the rigidity of molecular structure increases, which makes the lifetime longer. At room temperature the lifetime of the triplet state of oxine in the solid complexes should be long. Eu^{3+} and Nd^{3+} shorten the lifetime of the triplet state of oxine in the solid complexes($\text{Ln}(\text{ox})_3$), so according to the formula (10) the phase of $\text{Eu}(\text{ox})_3$ and $\text{Nd}(\text{ox})_3$ are bigger than that of $\text{Gd}(\text{ox})_3$ within 340-400 nm.

At the same time because the energy that transfers from oxine to Eu^{3+} radiates partly, R in the $\text{Eu}(\text{ox})_3$ is bigger than that in the $\text{Nd}(\text{ox})_3$. Thus, the phase in the $\text{Eu}(\text{ox})_3$ is smaller than that in the $\text{Nd}(\text{ox})_3$.

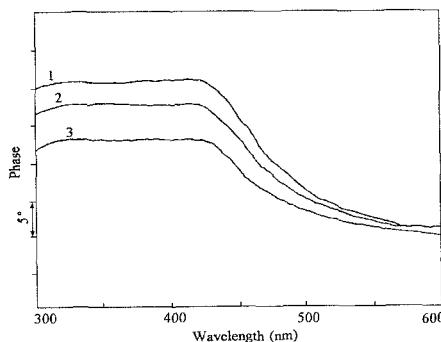


Fig.3 Phase spectra of $\text{Ln}(\text{ox})_3$ ($\text{Ln}=\text{Nd, Eu, Gd}$) at a chopping frequency of 12 Hz
 1 $\text{Nd}(\text{ox})_3$; 2 $\text{Eu}(\text{ox})_3$; 3 $\text{Gd}(\text{ox})_3$

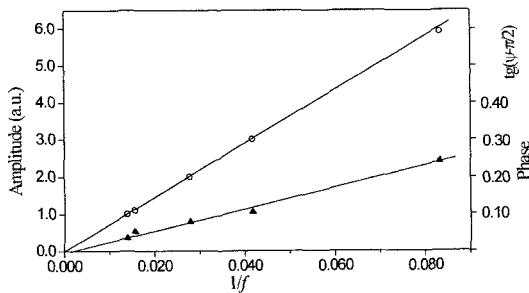


Fig.4 Dependence of the PA amplitude (○) and phase (▲) of $\text{Eu}(\text{ox})_3$ at 380 nm on the chopping frequency

3. The Effect of Frequency on the Amplitude and Phase

The dependence of the PA amplitude and phase upon the chopping frequency was studied. The amplitude and phase data of $\text{Eu}(\text{ox})_3$ at 380 nm at different frequencies were recorded. As plotted in Fig. 4, the amplitude has a relationship with the frequencies as $q=k\omega^1$, which is consistent with the case of photoacoustic saturation of the R-G theory. The phase data at the different frequency was obtained by taking the phase of carbon black at the same frequency as the reference ($\pi/2$). The phase decreases when the chopping frequency increases, $\text{tg}(\Psi-\pi/2)$ is proportional to $1/f$, which is consistent with the formula (10).

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