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SPECTROCHIMICA ACTA PART A

Spectrochimica Acta Part A 63 (2006) 55-59

www.elsevier.com/locate/saa

# Photoacoustic phase study on the frequency dependence of phase angle and triplet state lifetime of Nd(III)-acetylacetonate

Bin Hu, Da Chen, Qingde Su\*

Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China

Received 27 January 2005; accepted 21 April 2005

#### Abstract

The amplitude and phase of the photoacoustic (PA) signal generated in the rare earth complex powder of Nd(III)-acetylacetonate (Nd(AA)<sub>3</sub>) were examined. By using the reasonably simplified formula about phase angle at the wavelengths assigned to  $\pi$ - $\pi$ <sup>\*</sup> transition of ligand and f-f transitions of Nd<sup>3+</sup>, the instrumental contribution to phase angle at different chopping frequency was calculated. The frequency dependence of sample phase angle, the relative phase angle shift caused by instrumental factors and the calculation of triplet state lifetime of sample under study were also discussed. Being independent of sample, the instrumental contribution to phase angle was regarded as a parameter representing the situations of instruments and measurement and it became an approach to calculate the relaxation time of ligand in rare earth complex.

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Keywords: Photoacoustic angle; Frequency dependence; Instrumental contribution; Rare earth complex

### 1. Introduction

Photoacoustic spectroscopy (PAS) is a technique used in the study of optical absorption. The PA response is generated when optical absorption causes a rapid local heating in the sample under investigation. The subsequent thermal expansion generates a pressure wave that is detected acoustically [1]. From the analysis of the PA signal, the information about the absorption of the sample is obtained. PAS is being used extensively in the optical and thermal characterization of wide spectrum of materials [2]. For instance, some researches about rare earth complexes were reported [3–5]. The great interest in the study of rare earth complexes is mainly due to their close relationship to rare earth structure chemistry, rare earth functional materials, environmental chemistry and biochemistry [6–8].

One of the important characteristics of PAS is that it provides information about both amplitude and phase of response of a sample. Phase information contains contributions from a number of sources associated with the sample under study, the geometry of the photoacoustic cell, the response of the detecting system, etc. In actual measurements, many of the non-sample related parameters are always regarded constant. In this paper the influence from the chopping frequency to the instrumental contribution of phase angle and the relaxation time of ligand are discussed. Then a method to calculate the triplet state lifetime of Nd(AA)<sub>3</sub> by instrumental contribution at different chopping frequencies is presented.

#### 2. Theory

In the Rosencwaig–Gersho's model of PA, the nonradiative relaxation process was supposed to occur instantaneously [9]. The first use of PA phase signal to measure the nonradiative relaxation time was employed by Merkle and Powell [10]. Then Mandelies presented a phase formula for optically opaque and thermally thick samples [11]:

$$\phi = \tan^{-1}(-\omega\tau_{\beta}) + \tan^{-1}(\omega\tau) - \tan^{-1}\left(\frac{-1}{1 - (2\omega\tau_{\beta})^{1/2}}\right)_{(1)}$$

<sup>\*</sup> Corresponding author. Tel.: +86 551 3606642; fax: +86 551 3606642. *E-mail address:* qdsu@ustc.edu.cn (Q. Su).

<sup>1386-1425/\$ –</sup> see front matter 2005 Elsevier B.V. All rights reserved. doi:10.1016/j.saa.2005.04.028

where  $\tau$  is the lifetime of the excited states,  $\omega = 2\pi f$  and f is the chopping frequency of the light,  $\tau_{\beta} = 1/\beta^2 \alpha_s$  is a characteristic relaxation time for the system corresponding to the thermal transit time from a depth  $\mu_{\beta}$  (=1/ $\beta$ ) within the solid.

In the PAS investigation of rare earth complexes, both R–G model and Mandelies model are used. Since the triplet state lifetime of ligand is not low enough to neglected while the absorption coefficient  $\beta$  of ligand is very high, Eq. (1) is simplified to Eq. (2). While the relaxation process of rare earth ion is essentially fast, the R–G model, Eq. (3) is used [12].

$$\phi = \tan^{-1}(\omega\tau) + \frac{\pi}{4} \tag{2}$$

$$\phi = \tan^{-1} \left( 1 + \frac{2}{\beta \mu_{\rm s}} \right) \tag{3}$$

 $\mu_{\rm s}$  is the thermal diffusion length. In fact, the experimental value of phase angle includes a relative phase angle shift due to the instrumental parameters. Eq. (2) and (3) are rewritten as

$$\phi_{\text{E(ligand)}} = \phi_0 + \tan^{-1}(\omega\tau) + \frac{\pi}{4}$$
(4)

$$\phi_{\rm E(central\,ion)} = \phi_0 + \tan^{-1} \left( 1 + \frac{2}{\beta \mu_{\rm s}} \right) \tag{5}$$

where  $\varphi_E$  is the experimental phase angle and  $\varphi_0$  is the instrumental contribution, which includes phase shifts due to cell resonance, the positioning of the sample with respect to the light beam, and the positioning of the monochromator slits with respect to the chopper slots [13].

# 3. Experimental

#### 3.1. Synthesis of rare earth complex

The complex was synthesized according to the procedure given in Ref. [14].  $Nd_2O_3$  was converted to  $NdCl_3$  by treatment with concentrated HCl. A solution of the chloride in absolute ethanol was added to a solution of acetylacetone (AA) in the same solvent. The precipitation was accomplished by addition of ammonia. The element analyses and infrared spectra were indicative of the structure formulae.

#### 3.2. PA measurement

The PA spectra were obtained on a single-beam spectrometer. A 500 W Xenon lamp, a CT-30F monochromator and a PA cell fitted with an ERM10 electret microphone were used. The output signal of the microphone was fed to a lock-in amplifier (LI-574A) and was collected on an A/D converter and dealt with by computer. The PA amplitude and phase spectra were recorded in the region of 300–800 nm, and the amplitude spectra were normalized against the carbon black to account for the variation due to the light source and spectrometer.

#### 4. Results and discussion

#### 4.1. Photoacoustic spectra and phase information

The amplitude spectrum of Nd(AA)<sub>3</sub> (Fig. 1) shows that there exists a very strong absorption in the wavelength around 330 nm, which is assigned as the  $\pi$ - $\pi$ <sup>\*</sup> electronic transition of AA. The peaks at 530 nm and 584 nm are assigned correspondingly to the f–f transitions (<sup>4</sup>I<sub>9/2</sub>  $\rightarrow$  <sup>4</sup>G<sub>7/2</sub>, <sup>4</sup>I<sub>9/2</sub>  $\rightarrow$  <sup>4</sup>G<sub>5/2</sub> +<sup>2</sup>G<sub>7/2</sub>) [10,15].

To learn about the frequency dependence of phase angle and instrumental contribution, the PA amplitude and phase information were obtained at different chopping frequency, from 9 to 470 Hz. The phase angles at 330 nm, 530 nm and 584 nm versus different chopping frequencies are shown in Fig. 2.



Fig. 1. PA amplitude spectra of Nd(AA)3.



Fig. 2. PA phase shift vs. chopping frequency.

The phase angles change irregularly with the increase of chopping frequency. At the low frequency region, the relationship between  $\Phi_{\rm E}$  and *f* is nearly linear. When *f* increases to high value, the phase shift becomes saturated.

# 4.2. Calculations of instrumental contribution and relaxation time

First, considering that the optical absorption coefficient  $\beta$  of AA around 330 nm is high enough,  $\tau_{\beta}$  in Eq. (1) was neglected reasonably and  $\tan^{-1}(-1/(1-(2\omega\tau_{\beta})^{1/2}))$  was regarded as a constant. Based on Eq. (4),  $\varphi_{E(330 \text{ nm})}$  was given as:

$$\phi_{\rm E(330\,nm)} = \phi_0 + \frac{\pi}{4} + \tan^{-1}(\omega\tau_{\rm (AA)}) \tag{6}$$

Second, because the energy levels of Nd<sup>3+</sup> are often intermixed and the relaxation process undergoes a nonradiative channel most readily. The relaxation process of Nd<sup>3+</sup> is very fast,  $\tau \rightarrow 0$ , which means that the Eq. (5) is available. When the chopping frequency is chosen,  $\mu_s$  keeps constant, and  $\beta$  varies directly with the PA amplitude (*A*), so  $\beta \mu_s$ can be written as the form of *KA*. Eq. (5) were rewritten as

$$\phi_{E(\lambda)} = \phi_0 + \tan^{-1} \left( 1 + \frac{2}{KA_{(\lambda)}} \right) \tag{7}$$

with  $\lambda$ , the wavelength of PAS peaks of central ion. Based on Eq. (7), PA information about Nd<sup>3+</sup> at 530 nm and 584 nm were collected to calculate  $\varphi_0$  in different chopping frequency. The results of  $\varphi_0$  were shown in Table 1 and Fig. 5.

There are two methods to acquire the  $\tau_{(AA)}$ . One is method of calculating, and the other is method of plot-comparing, as described below.

#### 4.2.1. Method of calculating

Because  $\varphi_{E(330 \text{ nm})}$  is obtained directly from experiment,  $\tau_{(AA)}$  can be acquired based upon Eq. (6) and the value of  $\varphi_0$  in Table 1.

Table 1  $\varphi_0$ , the instrumental contribution to phase angle in different chopping frequency

f(Hz)	$arphi_0$ (°)	$f(\mathrm{Hz})$	$arphi_0$ (°)
12	-141.1	180	190.3
22	-64	200	228.5
31	-29	220	221.2
39	-7.7	240	237.7
55	15.5	260	244
59	33.4	280	245.3
69	42.9	310	254.7
70	47.1	370	266.7
80	71.4	420	270.9
100	112	470	269.4
160	181.0		



Fig. 3.  $\tan^{-1}(\omega\tau)$  of a series  $\tau$  vs. chopping frequency.

## 4.2.2. Method of plot-comparing

Since the lifetime of triplet state is about  $10^{-3}$  s, it is logical to evaluate  $\tau$  to be from  $10^{-3}$  to  $20 \times 10^{-3}$  s. Fig. 3 is the plot of  $\tan^{-1}(\omega\tau)$  versus chopping frequency at eight values of  $\tau$ . The value of  $\tan^{-1}(\omega\tau)$  closes to  $\pi/2$  along with the increase of frequency. The same trend is presented in the plot of  $\varphi_0$  versus frequency at different  $\tau$  (Fig. 4).  $\varphi_0$  can be also acquired from Eq. (6) instead of calculating from Eq. (7) as mentioned before.  $\varphi_0$  obtained in this way is defined as  $\varphi_0^*$ 

$$\phi_0^* = \phi_{\rm E(330\,nm)} - \frac{\pi}{4} - \tan^{-1}(\omega\tau_{\rm (AA)}) \tag{8}$$

When f = 12 Hz,  $\varphi_0^{\circ}$  covers from  $-343.6^{\circ}$  to  $-291.5^{\circ}$  corresponding to different  $\tau$ , with the shift extent of  $52^{\circ}$ . While f = 470 Hz,  $\varphi_0^{*}$  is from  $70.9^{\circ}$  to  $88.3^{\circ}$ , with the shift being only  $17.4^{\circ}$ . It is difficult to distinguish the dots from each other in high frequency region for they gather tightly, while in the low frequency region, they can be resolved clearly.



Fig. 4.  $\varphi_0$  at a series of  $\tau$  vs. chopping frequency.



Fig. 5. Method of curve-comparing to obtain  $\tau_{(AA)}$ .

It is explained that the contributions from different triplet state lifetime to the value of phase angle become closer and closer to each other along with the increase of chopping frequency.

Compare the  $\varphi_0$  in Table 1 with the data in Fig. 4. The dots in Fig. 4 who match the curve of  $\varphi_0$  best should be regarded as compatible theoretical results, and the  $\tau$  described by those dots is regarded as the value of triplet lifetime of AA. There is one point should be noticed that the values of PA angle during the processes of different calculations may shift with one period, which is 180°.

#### 4.3. Discussion and application of the method

It is clear that the curve representing  $\tau_{(AA)}$  matches those dots corresponding to  $\tau = 0.009$  s and 0.007 s well in low frequency region while is much closer to dots corresponding to  $\tau = 0.001$  s in high frequency (Fig. 5). It is believed that the simplifying method of Eq. (1) to (2) and (4) has no good adaptability in high frequency region. Although the  $\tau_{\beta}$  in Eq. (1) is a small value, the section of  $\tan^{-1}(-\omega\tau_{\beta})$  is neglected reasonably only when  $\omega$  is not high. With the increase of  $\omega$ ,  $\tan^{-1}(-\omega\tau_{\beta})$  begins to show its influence to the process of calculating  $\varphi_0$ , and further more to that of  $\tau_{(AA)}$ . Being lacking one positive section,  $\varphi_0^*$  gotten from Eq. (8) becomes smaller than should be, especially in high frequency region.

It is also proved by the  $\tau_{(AA)}$  acquired from method of calculating.

Fig. 6 shows that  $\tau_{(AA)}$  decreases with the increase of frequency. When the frequency is in the region below 30 Hz,  $\tau_{(AA)}$  gathers around 0.007–0.009 s. When the frequency is enhanced above 200 Hz,  $\tau_{(AA)}$  begins to close to 0.001 s, which accords with the method of plot-comparing.

To obtain the value of  $\tau_{(AA)}$ , chopping frequency was controlled in low region and measurements were done again. The results are shown in Table 2. In this frequency region,  $\varphi_0$  has a good linear relationship with *f*. It is also evident that the



Fig. 6. Method of calculating to obtain  $\tau_{(AA)}$ .

Table 2  $\varphi_0$  and  $\tau_{(AA)}$  in different chopping frequency

f(Hz)	$arphi_0$ (°)	$\tau$ (AA) (S)
9	-178.8	0.0070
12	-140.1	0.0083
15	-102.0	0.0075
18	-73.3	0.0067
21	-51.3	0.0083
24	-29.5	0.0055

results of  $\tau_{(AA)}$  keep consistent very well. It explains that only in a limited region the frequency has hardly any influence to the calculation of triplet state lifetime. And in the same region,  $\varphi_0$  is linear with chopping frequency, which makes  $\varphi_0$  the parameter representing the instrumental measurement conditions.

#### 5. Conclusions

Instrumental contribution to PA phase angle is not always the constant and has an irregular relationship with chopping frequency, which is linear in the low frequency region. For optically opaque and thermally thick samples, instrumental contribution is independent of samples and is one of parameters representing the situations of instruments and measurement. Instrumental contribution can be applied to acquired the triplet state lifetime of ligand in complex, and the lifetime is also influenced by chopping frequency, because the simplified model of PA is not always available in whole frequency region. It is helpful to select proper chopping frequency region to study the lifetime by PAS. When the chopping frequency is in the region where the triplet state lifetime keeps constant, it is efficient to investigate the instrumental contribution to phase angle, the relaxation process of complex and calculate the lifetime of ligand.

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