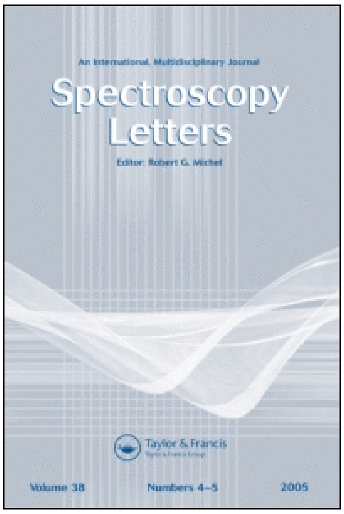

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Photoacoustic Spectroscopy Studies on DL-β-Phenylalanine and Pd(Phe)2·H_2O Complex

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PHOTOACOUSTIC SPECTROSCOPY STUDIES ON DL-β-PHENYLALANINE AND $Pd(Phe)_2 \cdot H_2O$ COMPLEX

Key words: PA spectrum, phase and amplitude, complex nonradiative relaxation.

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ABSTRACT

The complex crystal of $Pd(Phe)_2 \cdot H_2O$ was synthesized and its PA spectra (with DL-β-Phenylalanine) were also determined in the range of 280--780nm at room temperature and explained. A method used to resolve the PA amplitude spectrum was suggested. With the phase spectrum of complex, the PA absorption peaks were resolved by this method, and the nonradiative relaxation time of all absorption bands were calculated.

INTRODUCTION

The complexes system of the type metal-amino acids, peptide or nucleoside, therefore, constitute the simplest models for the study of the more complex DNA-protein interactions. For the essential significance in biological system, the transition metal-amino acids complexes have been widely studied by chemists and biochemists[1,2]. As the interested in palladium-amino acid complexes, their structures have been widely studied[3] and some investigators had also studied their synthesis[4], spectral and some other properties[5]. In this work, the complex crystal $Pd(Phe)_2 \cdot H_2O$ was synthesized, and the PA spectra of complex and amino acid Phenylalanine were determined and studied.

Recently, the photoacoustic measurement have been widely used to investigate the chemical and physical properties of almost all kinds of samples[6]. The PA spectroscopy enables to obtain spectra on any type of solid, whether it be crystalline, powder or gel, and it be a direct monitor of energy gap and the nonradiative relaxation channel, the complement of absorption and photoluminscence spectroscopic technique[7]. In complex system, besides the uv-vis PA spectrum, the phase spectrum has a very important significance to the study of electronic structure, and it will be discussed in this work.

EXPERIMENT

(I) Preparation of complexes

The complex crystal was prepared by the dissolving 1mmol $PdCl_2$ in hot HCl solution with constant stirring, and 2mmol Phenylalanine dissolved in a little distilled water was added to the former solution, adjusting the PH value of the mixture solution to 7 with NaOH solution. Slowly evaporated at room temperature and the orange crystals were obtained in seven days. The results of elemental analysis of $Pd(Phe)_2 \cdot H_2O$ crystal were: exp. C 44.47, H 4.48, N 5.57; clac. C 44.54, H 4.54, N 5.77%.

(II) Characterization

The IR spectral measurements were made as reflectance spectra using KBr as the diluent on a IR instrument under standard operating conditions.

The photoacoustic spectra (amplitude and phase spectra) were recorded in the region of 300--800nm at room temperature. The excitation source was a 500W xenon lamp. The light source was modulated by a variable speed mechanical chopper at a frequency of 12Hz. The acoustic signal was detected with the sample placed in a locally built photoacoustic cell fitted with an ERM 10 electret microphone. The output signal was normalized for changes in lamp intensity using a carbon-black reference.

RESULTS AND DISCUSSION

Of the various vibratory models of the amino acids, the carboxyl stretching frequencies which are usually identified with certainly and the most sensitive to a change in the strength of the metal-oxygen interaction have been widely discussed[8]. In amino acid compound, the carboxylic acid exists in amphoteric ion $-C(NH_3^+)-COO^-$, and its carboxyl stretching frequencies are decreased at 1580 and 1420 cm^{-1}. The IR spectrum of $Pd(Phe)_2\cdot H_2O$ show that the carboxyl stretching frequencies are observed at 1610 and 1380 cm^{-1}. Comparing to the amino acids, the antisymmetric carboxyl stretching of $Pd(Phe)_2\cdot H_2O$ complex has a violet shift, $\Delta\nu=30$ cm^{-1}, and the symmetric carboxyl stretching of complex crystal has a red shift, $\Delta\nu=40$ cm^{-1}. For this reason, it is seen to be that the metal-oxygen bond of $Pd(Phe)_2\cdot H_2O$ complex is in this formula[9]:  $(M - \genfrac{}{}{0pt}{}{O}{O}\!>C-)$. And it is said that the coordinative effect is very strong in this complex.

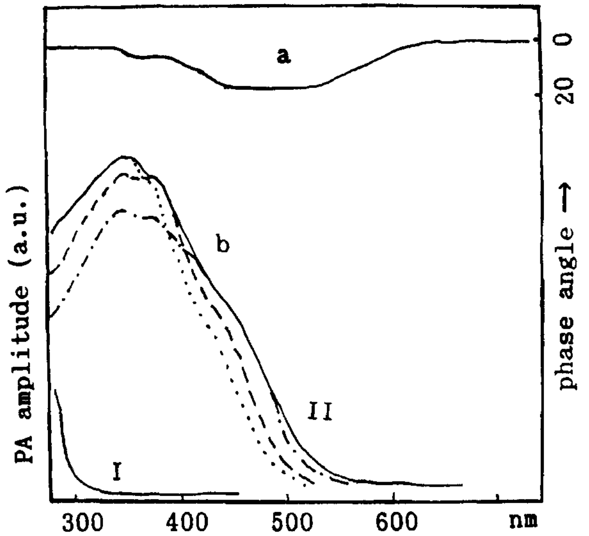

Fig. 1. The PA spectra of Phenylalanine and $Pd(Phe)_2\cdot H_2O$ crystal
I: DL-β-Phenylalanine; II: $Pd(Phe)_2\cdot H_2O$
a: phase spectrum; b: amplitude spectrum.
•••••• phase angle 5°, - - - 7°, -•-•- 17°.

Figure 1 is the photoacoustic amplitude and phase spectra of $Pd(Phe)_2\cdot H_2O$ and DL-β-Phenylalanine compounds. It is seen to be that the PA spectrum of $Pd(Phe)_2\cdot H_2O$ complex is overlapping. Connected with the phase spectrum, we see that the different absorption peak of amplitude spectrum has a different phase angles. With the phase spectrum, the amplitude spectrum can be resolved.

As to a complex system, the absorption of different energy levels have different PA phase angles. So, we can calculated the fraction PA signal in different phase angles. If the PA signal gets a maximum value at one phase angle Φ_1, then the absorption peak may be observed at the position where the

Table 1

The PA absorptions and their relaxation times of $Pd(Phe)_2 \cdot H_2O$ complex (nm).

assignment	absorption bands	phase angles	time(ms)
$^1A_1 - - ^1E$	340	5	1.2
$^1A_1 - - ^1B_2$	370	7	1.6
$^1A_1 - - ^1B_1$	470	17	4.1

maximum value is and the phase angle of this absorption band is Φ_1[10]. As see Fig.1, the phase spectrum of $Pd(Phe)_2 \cdot H_2O$ shows the phase angles of different absorption may be 5,7, 17 degree. Calculate the fraction PA signal with phase angle 5, 7, 17 degree respectively, by the equation:

$$P_i = P_o(\mathrm{Cos}\Phi)^n \qquad (I)$$

where n usually takes 1. If the changes of phase angle are too small, we can take n large than 1 to get clear results. In Fig.1, we see the maximum value position of different phase angles are at 340, 370, 470 nm. It is said that there exist absorption peaks at 340, 370, 470nm with the phase angles 5, 7, 17 degree respectively. So, with the phase resolved method of PA spectrum, the transitions of different energy levels can be calculated.

The PA spectrum of Phenylalanine shows a absorption band at the range of <280nm which may be assigned as $L--L^*$ transition[11]. In PA spectrum of $Pd(Phe)_2 \cdot H_2O$ complex, the resolved PA absorption peaks at 340, 370, 470nm. And the absorption bands observed at 340, 370, 470nm may be assigned as the d-d transitions of $^1A_1 - - ^1E$, $^1A_1 - - ^1B_2$, and $^1A_1 - - ^1B_1$ respectively[12], see Table 1.

In PA theory, two absorption bands at a absorbing center at different wavelength λ_a, λ_b will have respective nonradiative relaxation times τ_a, τ_b. At a fixed modulation frequency, the heat generated at the absorption center takes a finite time to diffuse to the sample surface (sample-air interface) and generate the acoustic signal. This time delay is a function of the optical-absorption coefficient, the nonradiative relaxation time (the time the center takes to generate the heat), and the sample thermal-diffusion time. According to R-G theory[13], the time may be calculated from the phase angle Φ of respective energy levels:

$$\tau = \mathrm{tg}\Phi \ / \ 2\pi\omega \qquad \text{(II)}$$

where ω is the modulated frequency. In this work, ω is 12Hz.

In PA spectrum of $Pd(Phe)_2 \cdot H_2O$ complex, the phase angle of different energy levels are 5, 7, 17 degree respectively. And the time delay are calculated by equation(II): τ_1 = 1.2, τ_2 = 1.6, τ_3 = 4.1ms, see Table 1. However, the nonradiative relaxation time is usually in the range of 10^{-9}--10^{-12} second. It is much more small than this time delay. So, we can say that the time delay from the generating of heat to the generating of PA signal is dominantly controlled by the time of thermal-diffusion and generating the acoustic signal, and it is affected by the optical-absorption coefficient.

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