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The observation of abnormal signals in laser flash photolysis: A type of probable synchronized nuclear spin signals

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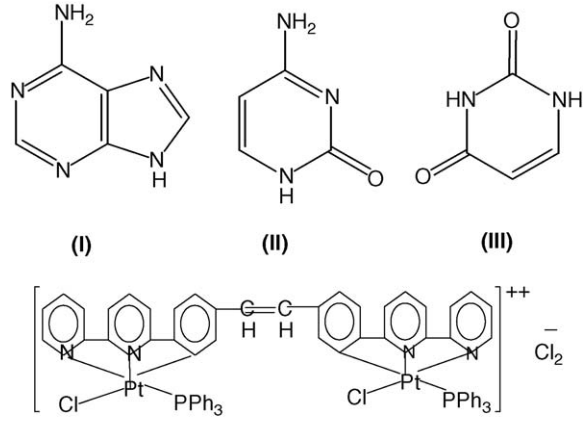
Abstract

In laser flash photolysis (LFP) work, noise-like signals were observed together with transient absorption decay spectra in time domain. Analyzed results show that it is a valuable resonance spectrum of excited state molecules, in which four molecular cases are given here. We proposed that this kind signal might originate from nuclear or nuclear and electron spin resonance features in the excited molecules based on radio wave frequency spectrum levels and the significant interaction with static magnetic field.

Keywords: Laser flash photolysis; Transient absorption spectra; Hydrogen nuclear spin

1. Introduction

Recent years, in our experimental work we have frequently found that some very strong or very significant noise-like signals presented in transient absorption decays. In practice, this unexpected phenomenon most appears in two or a few wavelength decays and these signals always ride on the decay curve of T–T absorption [1] signals. To show this point, four experimental examples chosen (adenine, cytosine, uracil and a platinum complex) were given in this work. And their molecular structures are illustrated in the molecular scheme. Here, the represent cases from the T–T absorption decay for adenine sensitized with $Ru(bpy)_3Cl_2$ (about which the experimental results will be published late) and $Pt_2[(C_{34}H_{22}N_4)(PPh_3)_2Cl_2]Cl_2$ [2] were given in Fig. 1. We can see clearly that there are many spikes on the definite time range of decay curves. And the intensity of these spikes was high in some cases, but it was not always. Meanwhile, those abnormal signals often have different distribution regions both at decay time and at wavelengths for different molecules. For instance, the noise-like signal phenomena occurred at the decays of 620 and 610 nm (the spikes centered on the top of curve at this wavelength) for adenine, and at the decays of 640 and 630 nm for the Pt complex, as shown in Fig. 1 where only 640 and 650 nm decays were illustrated for comparison. But the decay wavelength with the abnormal signals may have a red or blue shift due to sample temperature and other experimental conditions. However, it seems to show that the spikes could be detected during the whole time range of decays.



The scheme for molecular structures

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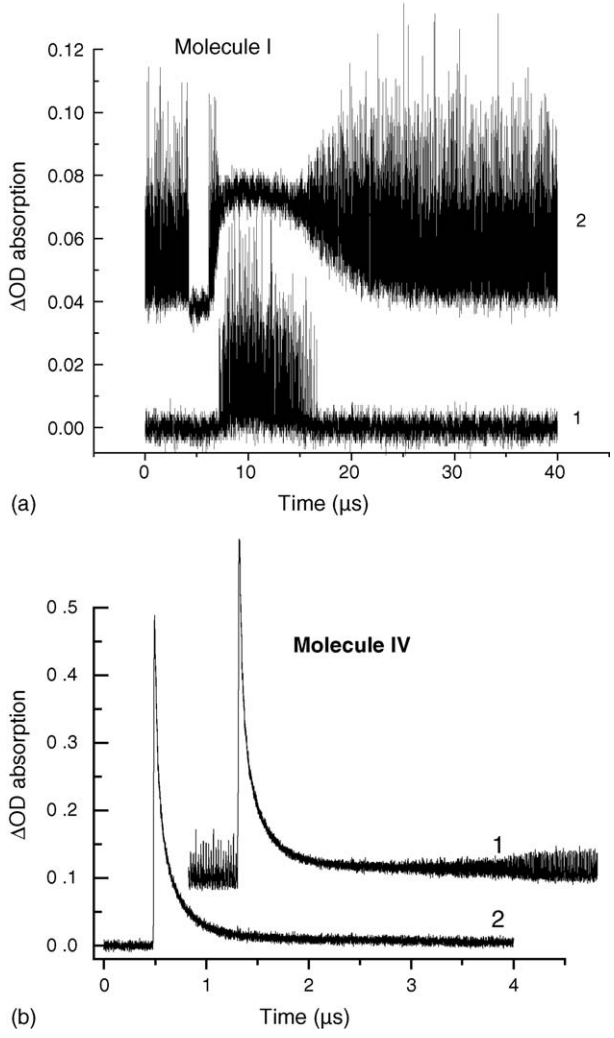

Fig. 1. The transient absorption decay curves of (above) adenine sensitized with $Ru(bpy)_3Cl_2$ at 610 nm (1) and 620 nm (2) in ethanol solvent and of (below) $Pt_2[(C_{34}H_{22}N_4)(PPh_3)_2Cl_2]Cl_2$ at 640 nm (1) with noise-like signals and 650 nm (2) without noise-like signal in $C_2H_4Cl_2$ solvent using 355 nm laser with about 80 mJ.

2. Experimental

In the experimental work, adenine, cytosine and uracil were used as received, which were purchased from Acros Organics (NJ, USA) and Fluka BioChemika, respectively. Their purity is more than 99% (HPLC) and >99%, respectively. AR grade alcohol was purified by adding magnesium turnings reacting with water, refluxing under boiling for 3 h and distilling before use. The concentration of all samples was about 2×10^{-5} M in alcohol. Before measurement each sample was deoxygenated for at least 30 min by bubbling through the solution with high purity nitrogen gas (99.999%). The sensitizer $Ru(bpy)_3Cl_2$ used for molecules I–III was a gift from a friend Dr. J.Y. Xu who is at Shanghai Institute of Organic Chemistry, The Chinese Academy of Sciences. The Pt compound and $C_2H_4Cl_2$ solvent were spectra grade.

In order to make the phenomenon more understandable, the scheme-measured is shown in Fig. 2, including permanent magnetic field case. And also the measurement system is described in detail here. It is a conventional LFP instrument set-up named as LP920 by Edinburgh Instruments Ltd. (England, UK). A ns Nd:YAG laser system was used for sample excitation (Surelite Continuum laser, pulse width 5–8 ns) and Xe lamp with 450 W was used as probe light. The conversion of light to electricity was completed with the HAMAMATSU PMT R955. Laser light was inducted into a sample quartz cell (1 cm × 1 cm × 4 cm) by right angle direction with probe light on the plane of the optical stable, and finally the signals were recorded with a Tektronix digital 100 MHz TDS3012B oscilloscope. The other point we should mention is the timing sequence in the LFP system different from other conventional LFP system. In the LP920 system all timing and delays were controlled relative to the probe light pulse, that is, exciting laser must superpose to an available platform of the Xe lamp pulse with about 4 ms time limit. The transient absorption signals were measured directly on the Xe lamp pulse platform as backgrounds and the correction of baselines was made automatically in the program. Here, a point we should keep in mind is that transient absorption signal rising may not be a start point of forming excited state due to different delays for the oscilloscope and Q-switch triggers. So, that is the reason why the noise-like signal can occur often before transient absorption signal appearing.

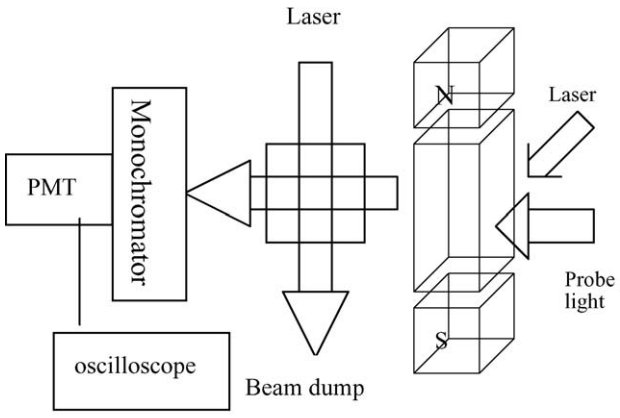

Fig. 2. The top view from sample cell in normal case and side view from sample cell with a permanent magnetic field in LFP.

3. Results and discussion

For the mentioned abnormal experimental cases above we are sure that those spikes should be a kind of signals from the studied sample. Moreover, the noise-like signal does not be an accidental phenomenon but it is always encountered in our LFP work so long as suitable conditions are maintained, such as sampling rates and laser intensity, sample temperature, etc. Hence, we attempted to analyze the unusual phenomenon, and we considered converting these data into frequency domain by fast Fourier transform (FFT) method [3] due to intuitional undiscerning of signals in time domain. The frequency range by FFT method is determined readily in terms of sampling rate [4] in an experimental work, such as 2.5×10^8 Hz. Due to the conjugative properties