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Observation and analysis of abnormal absorption signals in laser flash photolysis measurement

Wen Li [a],*, Yao-feng Yuan [b], Xiao-lin Li [c], Xiao-long Su [b], Wen-hua Sun [d]

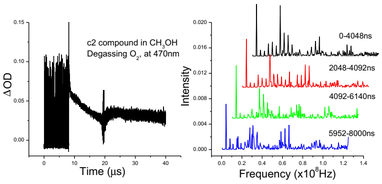
[a] *Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, China*
[b] *College of Chemistry and Chemical Engineering, Fuzhou University, Fuzhou, China*
[c] *Institute of Ferrous Metallurgy, RWTH Aachen, Aachen, Germany*
[d] *Key Laboratory of Engineering Plastics, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China*

HIGHLIGHTS

- ▶ Tentative analysis of abnormal signals concomitant with transient absorption decays.
- ▶ Fourier Transform between noise-like time-domain signal and frequency domain signal.
- ▶ An origin of noise-like signals may be attributed to nuclear optical resonance.

GRAPHICAL ABSTRACT

FFT results of the abnormal time-domain signals appearing transient absorption decay show a kind of a novel spectrum, which may be attributed to nuclear optical resonance, similar to the NMR spectrum.



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ABSTRACT

In order to investigate a noise-like signal appearing in dynamic mode measurement during laser flash photolysis experiments, five compounds were chosen which show this abnormal phenomenon. The reproducibility of this phenomenon was done repeatedly, indicating that it originates from each molecular structural property. Also their two regulation pattern or features were found by our analysis. One is a U-shaped curve of main frequency intensity with time and it seems to be directly related to the concentration of the T_1 excited state. The other is a high damping oscillation curve of the frequency shift with time and this curve seems to be indicating an energy transportation process from light into chemical energy. Finally, a possible origin of hydrogen nuclear optical resonance was proposed for the abnormal signal.

Introduction

Laser flash photolysis (LFP) is a technique developed in the late 1960s [1], which can be used to measure transient absorption spectra usually in ultraviolet and visible region. For nearly half a century, it has proven to be one of the most important tools to detect short-lived intermediates in reactions and has been applied to elucidate reaction mechanisms [2–4]. In the time resolution aspect, the nanosecond (ns) LFP is often used for photochemical research despite of the fact that femtosecond laser sources are also available [5]. The detection technology ranges from densitometry of photographic plates to the manual analysis of oscilloscope photographs and to the digitization of the photomultiplier tube output. Especially the digital oscilloscope has been greatly advanced, such as the 500 MHz digital oscilloscope. In our laboratory, the minimum time interval of the currently used the digital oscilloscope Tektronix 100 MHz TDS3012B capturing experimental data can be down to 0.1 ns using the commercially available spectrometer LP920 [6]. Hence, it can be expected that more spectral details of a spectral signal from the same sample could be depicted with the improving ability to capture signals. In other words, previously reported spectra using other techniques may lack some details and/or concomitant other information that can be detected from the same sample by an ns LFP setup equipped with a modern digital oscilloscope, such as the Tektronix 100 MHz TDS3012B. For data collection and storage

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* Corresponding author. Tel.: +86 10 82543558; fax: +86 10 62554670.
E-mail address: liwen@mail.ipc.ac.cn (W. Li).

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way, there are two modes with spectrographic and kinetic detection systems, but most ns LFP systems operate in the kinetic mode, where the transition absorption is monitored at a single wavelength as a function of time. According to the preset step size, continual different wavelength kinetic decays are detected from low end to high end of a spectral band. Before the year 2000, only 512 digital values could be obtained for a kinetic curve in our laboratory using previous generation digital oscilloscope, with the same ns laser excitation source in use. Of course, in our previous measurement, the abnormal phenomenon said above was indeed never encountered.

However, with the detective device development, the digital oscilloscope with a much higher digitalizing capability is used in the ns LFP system. Since the year 2001, the type LP920, made by the Edinburgh Instrument Company in the United Kingdom, has been used in our laboratory, which is the equipment that is similarly configured, except for the digital oscilloscope Tektronix 100 MHz TDS3012B. This instrument can be used to measure transient absorption signals, with 10,000 numerous data being recorded through 10,000 time channels within more than 1 microsecond (μs). Clearly, the number of data has nearly increased by 20 folds, compared to 512 figure points. Therefore, it should not be surprising that more details of the transient absorption signal can appear for the detection of LFP.

In fact, just as we expect, since the LP920 has been used to measure transient absorption spectra in our laboratory, we often meet an exotic signal together with conventional signals for a few wavelength decays by using the kinetic mode. Here perhaps it may be thought of as a kind of shock wave due to intense laser [7]. Indeed, in case of very high laser intensity and large absorbance of the sample, a shock wave together with the *T*–*T* absorption signal could often be found with undoubtedly damping attenuation and much smaller frequency, in comparison to the frequency of the noise-like signal. The two cases are easily distinguished for anyone with short time's measuring experience. Since this abnormal phenomenon is quite commonly observed in the measurement of organic compounds, we reported this in 2006 [8], where a few examples and a basic analysis were presented. In the previous work, the noise-like signal can be conjectured that the signal seems to have a close relation with proton spins. According to the analysis of the time-domain signals transforming into the frequency-domain signals, the presented four molecules can be classified into two cases: the two molecules containing oxygen atoms showed that during their excited states there exist tautomeric phenomena but the other molecules that only consist of hydrogen, carbon and nitrogen elements only stabilized at the excited triplet states. Of course, since this is a novel signal, whether those spectra can be attributed to the corresponding possible tautomers still needs further investigation. The observations currently lack theoretical foundation, but the signal synchronizing conventional transient absorption kinetic spectra is a reproducible experimental fact, which is worth exploring further theoretically and experimentally. In this study, we shall analyze further some examples and try to draw some possible conclusions on the basis of the experimental data.

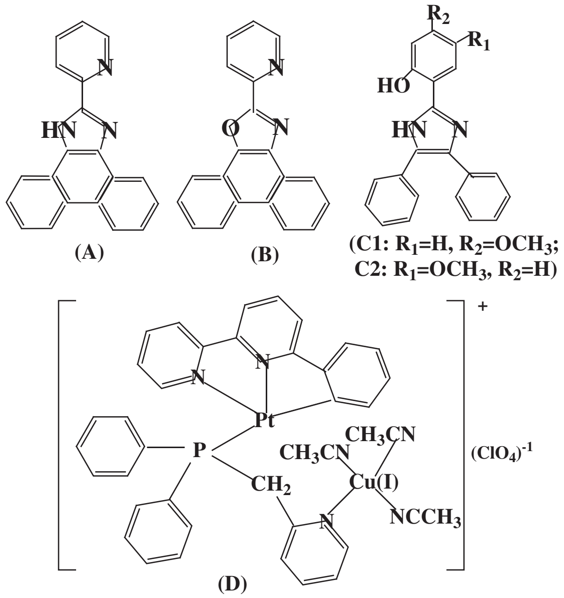

Fig. 1. The molecular structures of the chosen five compounds.

Experimental

Materials

The compounds of 2-(pyridine-2-yl)-1H-phenanthro[9,10-d]imidazole (A) and 2-(pyridine-2-yl)-1H-phenanthro[9,10-d]oxazole (B) were synthesized following the previously reported procedure [9]. A simple description of the procedure is given below. Phenanthrene-quinone and the corresponding aldehyde (1 M equiv.) were refluxed for 3 h in the presence of ammonium acetate (10 M equiv.) and glacial acid (0.5–1.0 mL) as catalyst. The reaction solution was cooled and stirred with a few drops of concentrated aqueous ammonia at room temperature to neutralize the residual acid. The mixture was extracted twice with CH_2Cl_2 (60 mL and 20 mL) and purified on a silica gel column using petroleum ether/dichloromethane (1:4) as eluent. The eluent portions containing the respective products were collected and concentrated under vacuum. Addition of petroleum ether precipitated the products which were filtered, washed with petroleum ether and dried under vacuum at 60 °C. The compounds were characterized by element analysis, IR and NMR (here we omitted those data). 5-Methoxy-2-(4,5-diphenyl-1H-imidazol-2-yl)phenol (C1) and 4-Methoxy-2-(4,5-diphenyl-1H-imidazol-2-yl) phenol (C2) were synthesized repeatedly in case of need. The detailed procedures can also be seen in our previous publication [10]. The fifth compound chosen is an organometallic compound that was synthesized by Yong Chen (a doctoral student) in our institute in 2006, with the molecular formula being [(6-phenyl-2,2-bipyridine)Pt(biphenyl-2-CH_2-pyridine-phosphine)Cu($CH_3CN)_3$] (ClO_4) (D). The molecular structures of these compounds are shown in Fig. 1.

In the LFP experiment, the solutions to be measured were prepared by dissolving the imidazole (A) and oxazole (B) derivatives into CH_2Cl_2, respectively, and the solution with a concentration of about 4×10^{-5} Mol/L was prepared. The compounds C1 and C2 were dissolved in methanol with about the same concentration above, respectively. The same concentration as for the organometallic compound was prepared in acetonitrile. The three solvents were all used in spectral grade. Before measurement the sample was deoxygenated for 30 min by bubbling high purity nitrogen gas (99.999%) through the solution.

Instruments and method

In the measurement, the used instrument is the conventional laser flash photolysis equipment named as LP920 by Edinburgh Instrument Ltd. (England, UK). A ns Nd:YAG laser system was used for sample excitation (Surelite Continuum Laser, pulse width 6–8 ns) and a Xe lamp with 450 W was used as the probe light. The conversion of light to electricity was completed with a HAMAMATSU PMT R955. Laser light was inducted into a sample quartz cell (1 cm × 1 cm × 4 cm) from a right angle direction with the probe light on the plane of the optical table, and finally the signals were recorded using a digital oscilloscope Tektronix 100 MHz