

Determination of the Triplet State Lifetime of C₆₀ / Toluene Solution and C₆₀ Thin Films by Pump-Probe Method

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Abstract

Excited state lifetimes of C₆₀/toluene solution and C₆₀ films macromolecular were measured by pump-probe method. Relation between optical switching effect of material and pulse width of pumping field is briefly described. It is found that the faster switching speed of light is, the triplet state lifetime is shorter. A He-Ne laser, as a probe, passed through the sample in the pump-probe experiment. All-optical switching effect was realized. Changing the optical power of the pumping field, switching response of the sample and modulation depth were investigated. In certain experimental conditions, relation between transmission through the sample and response were measured by an oscilloscope. Triple state lifetime of the molecule is speculated. The result showed that C₆₀/toluene solution and C₆₀ film have a fast response time. They would be utilized in some applications, such as optical switches, photonic devices.

Keywords: Excited State Lifetimes, All-Optical Switching, Fullerenes

1. Introduction

The nonlinearities of C₆₀ have been paid considerable attention for their promising use in the applications of photonic devices due to its unique opto-electronic properties, its reverse saturable absorption phenomenon was found by Guiliano and Hess [1]. In recent years, the potential applications of RSA materials in optical limiting and switching have attracted more interests because of the growing needs for laser protection [2]. RSA behaviours have been successively investigated in numerous materials.

The C₆₀ shows a strong and broad spectrum absorption induced in the visible domain. As an view of application, this makes C₆₀ an interesting candidate for optical power limiting purposes [3-7]. On the other hand there exist a multitude of studies concerning the relaxation dynamics following a photo excitation of C₆₀ in liquid solutions and in thin films. In this paper, we compared with functionalized fullerene solutions, scattering contributions to the observed limiting performance, and possible limiting in the near infrared region, we got a clear picture of optical switching properties of liquid C₆₀/toluene solution and solid C₆₀ thin films.

2. Experiment and Theory

The mechanism of optical switch of excited state absorption is that the molecules at excited states pumped by laser strongly absorbs photons at some wavelength, while the ground state absorption is very weak. So when the pump field stimulated the medium, the probe light is strongly absorbed, the output is in low state (in the closed state); on the contrary, when no pump exists, molecules in the ground state, probe light is not absorbed (or little absorbed), output in highly excited state (the switch turned on).

The experimental arrangement is shown in **Figure 1**. A doubled-frequency Nd: YAG laser with repetition rate of 10 Hz, at 532 nm, is employed to provide exciting pulse, and its pulse width is 10 ns. The laser beam first through the beam splitters 1 (BS1), part of the beam splitted was detected by detector D₁, which is used as the trigger pulse for the oscilloscopes. The other part of the laser, which is used as the pump beam, passed through the beam splitters 2 (BS2), was focused on the sample by a lens ($f = 300$ mm). A He-Ne laser at 632.8 nm is used as the probe light. The probe beam first through the sam-

ple, then focused by the lens, splitted by BS2. And at last the probe beam is detected by D_2 , then is recorded on a digital oscilloscope.

Figure 2 is the energy level diagram of C_{60} molecules in the laser irradiation, the ground state molecule absorbs photon and transits to the first singlet excited state vibrational level S_1 , then rapidly relaxes through the intersystem crossing transition to the first excited triplet state T_1 , molecules of the excited state T_1 absorbs photon can transition to a higher excited level T_n , then return to the energy levels of T_1 . Molecules of the level T_1 may have a longer lifetime, and can be back to the ground state in the form of non-radiative transition.

Considering the role of the pump light, the rate equations take the following:

$$\frac{dN_0}{dt} = -\frac{\sigma_0 I_L(t)}{h\gamma_l} N_0 + \frac{1}{\tau_{SO}} N_S + \frac{1}{\tau_{TO}} N_T \quad (1)$$

$$\frac{dN_S}{dt} = \frac{\sigma_0 I_L(t)}{h\gamma_l} N_0 - \frac{1}{\tau_{SO}} N_S - \frac{1}{\tau_{ST}} N_T \quad (2)$$

$$\frac{dN_T}{dt} = \frac{1}{\tau_{ST}} N_S - \frac{1}{\tau_{TO}} N_T \quad (3)$$

Boundary conditions:

$$\begin{aligned} N_0(t = -\infty, z) &= N \\ N_S(t = -\infty, z) &= N_T(t = -\infty, z) = 0 \\ I_L(t, z) &= I_0 f(t) \end{aligned} \quad (4)$$

where N_0 , N_S and N_T represent the number densities of states S_0 , S_1 and T_1 , respectively. N is the total number density of the molecules, γ_l is the pump frequency, $f(t) = \exp[-c(t/\Delta t)]$ is described time function of pump pulse shape ($c = 2$). Through the medium of the probe light can be expressed as:

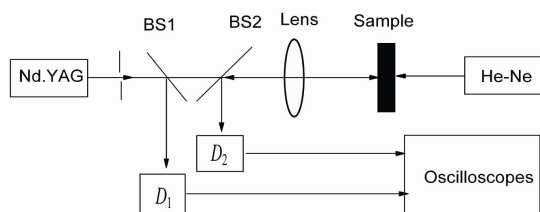


Figure 1. The experimental setup.

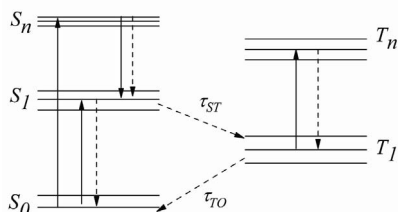


Figure 2. The five-energy-level diagram showing optical excitation.

$$\frac{dI_p}{dz} = -\sigma_T(p) N_T(t) I_p(t) \quad (5)$$

Boundary conditions: $I_p(t =, z = 0) = I_{p0}$

where $\sigma_T(p)$ is the absorption cross sections for the probe light of T_1 state. I_{p0} is the optical power density of incident to the sample surface for the detection.

The change of population along with time in the first triplet state are described by solving Equations (1) - (5). We obtain simulated transmission as shown in **Figure 3**.

3. Results and Discussion

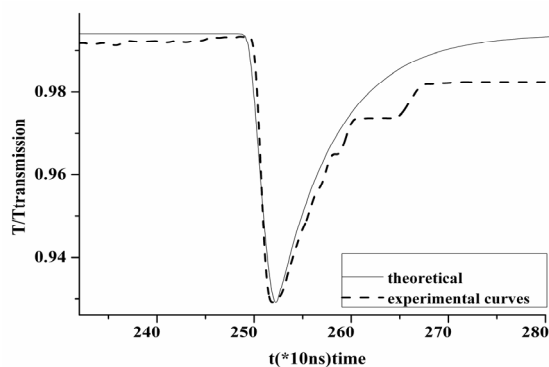
The numerical result for the case of solutions is in good agreement with published results summarized in **Table 1**.

The data for σ_i of the C_{60} /toluene is taken from Ref. [8-10], σ_{S1} and σ_{T1} is the S_1 and T_1 state absorption cross sections. The higher excited states S_n and T_n are assumed to have a very short lifetime [11-13] compared to our pulse duration, such that they can always be considered to be empty. Electrons relax back to the S_1 state almost immediately and the first excited triplet state T_1 is populated via intersystem crossing with a time constant τ_{ST} . The lifetime of the T_1 state τ_{T0} of the investigated compounds have been reported previously and ranged between 100 ns and 300 μ s.

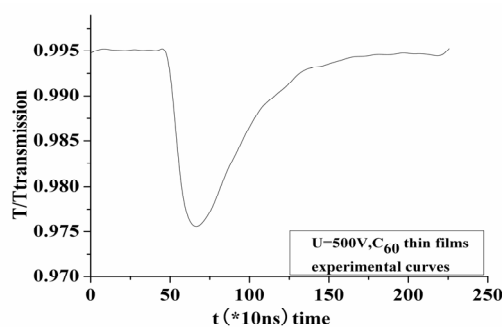
In the pumping processing, the pumping field excites molecules at ground state to the excited states. The absorption of excited state leads to the decrease of probe field energy. When molecule returns to ground state from excited states. The absorption at excited states disappears. The probing power resumes the initial value. The time corresponding this process is considered as the lifetime of the excited state, which is equal to the closing time. We implemented similar measurement on C_{60} toluene solutions in thin quartz cells. The result of the pump-probe experiment on C_{60} /toluene solutions is shown in **Figure 3(a)**. It is shown that the triplet state lifetime in our samples is 0.28 μ s. The parameters of interest are summarized in **Table 1**. The experimental results agree well with theoretical analyses. The output of the digital oscilloscope in our pump-probe experiment for a C_{60} thin film is shown in **Figure 3(b)**. The results show that the triplet state lifetime in the samples is 0.98 μ s. The numerical value of lifetime is between the two values of 100ns or 300 μ s [14]. One difference in our experimental conditions is the fact that we used film as toluene solvent, which leading to a longer lifetime of these states.

Table 1. The input data for simulations.

Parameters	Datas
σ_{S0} (cm ²)	1.24×10^{-18} cm ²
σ_{S1} (cm ²)	6.81×10^{-18} cm ²
σ_{T0} (cm ²)	4.0×10^{-18} cm ²
σ_T (cm ²)	2.48×10^{-17} cm ²
I_0 (W/cm ²)	1.34×10^5 W/cm ²
c (mol/L)	4.0×10^{-4} mol/L
l (mm)	1 mm



(a)



(b)

Figure 3. Transmission changes during a pump—probe experiment for a C₆₀ thin film.

Under identical conditions, increasing the concentration and the thickness of the sample, the switching time is not changed and the contrast ratio is increased. These are essential characteristics of an RSA process involving a long-lived excited state. Our experimental method is well adapted to the determination of these important parameters by a purely optical method.

4. Conclusions

We studied the triplet state lifetime of C₆₀/toluene solution and C₆₀ thin films. From the experimental results we conclude following conclusion: The lifetime of the excited state is about 0.28 μs and 0.98 μs of C₆₀/toluene solution and C₆₀ thin films, respectively. The theoretical fits are in good agreement with experimental results. This is of advantage for RSA materials used as optical limiting. The absorption cross section of the excited state is larger than that of the ground state at both 532 nm and 632.8 nm. Furthermore, we showed with pump-probe experiments, that the T₁ state of C₆₀ decays exponentially with a time constant which depends on the vibrational excitation energy of the molecule. This also allowed us to find the unambiguous assignment of the number of absorbed photons associated with a specific lifetime.

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