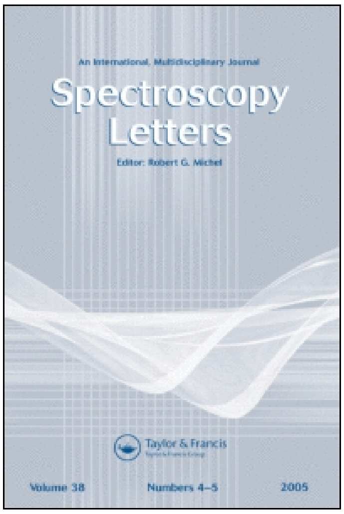

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C_{60} THERMAL LENS SPECTRA AND ITS THEORETICAL EXPLANATION

Key words: C_{60}; time-resolved; thermal lens spectra; theoretical explanation

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Abstract

We presented the time-resolved thermal lens spectra of C_{60}-benzene system under nitrogen-saturated condition. The theoretical explanation for C_{60} thermal lens spectra was indicated and in agreement with the experimental data. The theoretical model for C_{60} thermal lens spectra and the lifetime of triplet C_{60} (τ_T=10.2μs) were also given.

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I INTRODUCTION

Since the technique reported by **Kratchmer** and his co-workers for preparing and isolating macroscopic quantities of C_{60} "a new formation of carbon " [1], the extensive attraction has been focused on this type cluster. This breakthrough virtually ensured very rapid development in understanding the physical and chemical properties of C_{60}. Therefore in particular, the lifetime of the triplet C_{60} is still hard to be sure of. The triplet state lifetime of C_{60} ranged from 10μs to 300μs using different determination methods [2-6]. The determination of the C_{60} triplet state lifetime by using the time-resolved thermal lens (TL) spectra is an extremely sensitive method since the non-radiation process takes the main place and the fluorescence and phosphorescence of excited C_{60} is very faint which can be ignored in room temperature. But the TL spectra would be complex with the T-T absorption of triplet C_{60}. It's difficult to get the lifetime of triplet C_{60} without theoretical explanation. The paper focused on the theoretical explanation and mathematical model of C_{60} TL spectra. The lifetime of triplet C_{60} was also obtained through the theoretical explanation of C_{60} TL spectra.

II EXPERIMENTAL SECTION

C_{60} was purchased in finished product, its purity was monitored by IR spectrum. Benzene was washed with concentrated H_2SO_4, water,K_2CO_3 in proper order, dehydrated with P_2O_5 and distilled three times.

The time-resolved TL apparatus is shown in FIG.1. A pulsed N_2 laser with output energy of about 1mJ/pulsed was carried out to excite sample molecules (λ=337.1nm). The laser beam was focused inside the sample cell. A CW He-Ne laser with output energy of about 2mW (λ=632.8nm) was made collinear with the excited laser beam to probe the change of refractive index resulting from the non-radiative transition of the sample. The transmitted light through a pinhole and a filter to remove scattered light entered a

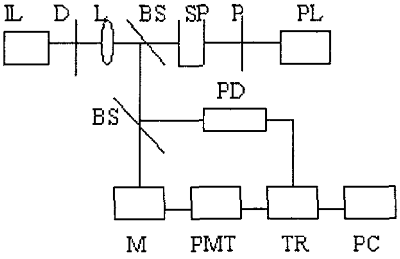

FIG.1. Diagram of TL experimental apparatus

IL: irradiation laser; D: diaphragm; L: lens; BS: beam splitter;

SP: sample cell; P: pinhole; PD: probe laser; M: monochromator;

PMT: photomultiplier tube; TR: transient recorder; PC: personal computer

monochromator equipped with a photomultiplier (Hamamatsu R955). Without being amplified, signal was gathered by a 100MHz transient recorder and processed with an IBM/AT computer.

III RESULTS AND DISCUSSION

The solution containing about 10^{-4} mol $\cdot L^{-1}$ C_{60} in benzene was bubbled by extra high pure N_2 for at least 30 min. in a quartz cell before use.

The time-resolved TL spectra of C_{60} - benzene solution saturated with nitrogen was obtained as follows::

The energy transfer processes of C_{60} - benzene system under nitrogen-saturated condition was investigated as:

(1) $C_{60}(S_0) + h\nu_i \rightarrow C_{60}(S_n)$ laser excited process

(2) $C_{60}(S_n) \rightarrow C_{60}(S_1)$ IC process

(3) $C_{60}(S_1) \rightarrow C_{60}(S_0) + h\nu_f$ fluorescence process

(4) $C_{60}(S_1) \rightarrow C_{60}(T_1)$ ISC process

(5) $C_{60}(T_1) + h\nu_s \rightarrow C_{60}(T_n)$ T-T absorption process

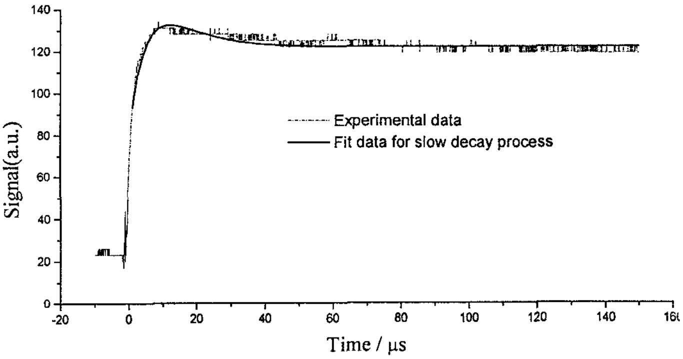

FIG.2. The TL signal of C_{60} in benzene solution saturated with nitrogen

(6) $C_{60}(T_n) \rightarrow C_{60}(T_1)$ IC process

(7) $C_{60}(T_1) \rightarrow C_{60}(S_0)$ ISC process (non-radiative transition)

(8) $C_{60}(T_1) \rightarrow C_{60}(S_0) + h\nu_p$ phosphorescence process

Here $h\nu_i$, $h\nu_s$ expressed irradiation and probe laser respectively.

The TL spectra of C_{60} - benzene system under nitrogen- saturated condition in our experiment was different to Terazima 's[4]. T-T absorption of triplet C_{60} would lead to the following two results based on the TL effect principle and the energy transfer processes of C_{60} - benzene system under nitrogen-saturated condition.

Result 1: the energy from the T-T absorption of triplet C_{60} was released in the fast-rising process in the form of vibrational relaxation.

Result 2: probe beam intensity decreased and was indicated in the TL spectra slow-decay component.

Process (7) was the slow process for the spin-forbidden principle; process (5), (6) were the fast process in the form of T-T absorption and internal conversion. Since the irradiation light was pulsed laser and the probe light was CW laser, process (5), (6) were continuously excited during the process (7). In the theoretical explanation of experimental C_{60} TL spectra, process (5), (6), (7) should be considered together. Process (8) was the slow process too, but it can be ignored since phosphorescence of excited C_{60} is very faint in room temperature.

The theoretical explanation of the fast-rising part of C_{60} TL spectra under nitrogen- saturated conditionwas the same asTerazima 's[4]. But the theoretical explanation of the slow-rising and slow-decay part was different one as follows:

Because process (5), (6), (7) have occurred at the same time and influenced each other, the mathematical expression of process (5), (6), (7) couldn't be separated.

According to Beer-Lambert law:

$$I_t = I_0 \bullet EXP(-\sigma Nl) \qquad [1]$$

Where I_t, I_0 is the passable and initial light intensity respectively; σ is the absorption coefficient; N is the molecular number of sample; l is the length of sample cell.

When $EXP(-\sigma Nl) << 1$, then $I_t = I_0 \bullet (1-\sigma Nl)$ [2]

For Process (5), $I_{st}(t) = I_{s0}\,(1-\sigma_{TT}N_{T1}(t)l\,)$ [3]

Where $I_{st}(t)$ is the passable probe light intensity with C_{60} T-T absorption which changed with time; I_{s0} is the probe light intensity without C_{60} T-T absorption; σ_{TT} is the absorption coefficient of C_{60} T-T absorption; $N_{T1}(t)$, the particle number of the first triplet C_{60} is changed with time.

$$N_{T1}(t) = N_{T0}\,EXP(-k_T t) \qquad [4]$$

Where N_{T0} is the initial particle number of the first triplet C_{60} which is equal to $\alpha\, I_i\, \Phi_{isc}$ (α is the absorption proportion factor; I_i is the irradiation light intensity; Φ_{isc} is the quantum yield of process (4)), k_T is the rate constant of process(7).

From [3] and [4], it can be obtained as:

$I_{st}(t) = (1\text{-}\alpha\ I_i\ \Phi_{isc}\ EXP(\text{-}k_T t)\ \sigma_{TT}\ l)$ [5]

According to the TL principle, the $I_{TL}(t)$ which presents TL effect is proportional to probe light intensity ($I_s(t)$) and energy difference (ΔE):

$I_{TL}(t) \propto I_s(t)\ \Delta E$ [6]

Process (7) can be expressed as:

$I_{(7)}(t) = B\ I_{st}(t)\ \Delta E$ [7]

Where B is the constant that reflected the sensitivity of the TL signal detection; Q is equal to $N_{T1\text{-}S0}(t)\ E_T$; $N_{T1\text{-}S0}(t)$ is the particle number of process(7) which changed with time; E_T is the energy difference of singlet C_{60} and triplet C_{60}.

$N_{T1\text{-}S0}(t) = \alpha\ (I_i\ \Phi_{isc} - I_i\ \Phi_{isc}\ EXP(\text{-}k_T t))$ [8]

From [7] and [8], it can be derived as:

$I_{(7)}(t) = \alpha\ B\ I_i\ \Phi_{isc}\ (1\text{-}EXP(\text{-}k_T t))\ I_{st}(t) E_T$ [9]

Process (6) can be similarly expressed as follows:

$I_{(6)}(t) = B\ N_{Tn\text{-}T1}(t)\ I_{st}(t)\ \Delta E$ [10]

Where $N_{Tn\text{-}T1}(t)$ is the particle number of process(6).

$N_{Tn\text{-}T1}(t) = \Phi_{ic}\ N_{Tn}(t) = \gamma\ \Phi_{ic}\ N_{T1}(t) = \alpha\ \gamma\ I_i\ \Phi_{ic}\ \Phi_{isc}\ EXP(\text{-}k_T t)$ [11]

Where Φ_{ic} is the quantum yield of process($C_{60}(T_n) \rightarrow C_{60}(T_1)$); γ is the absorption proportion factor of process($C_{60}(T_1) \rightarrow C_{60}(T_n)$); ΔE is the energy difference between the triplet state energy levels($\Delta E = h\nu_s$).

From [10] and [11], it can be derived as:

$I_{(6)}(t) = \alpha\ \gamma\ B\ I_i\ \Phi_{ic}\ \Phi_{isc}\ EXP(\text{-}k_T t)\ I_{st}(t) h\nu_s$ [12]

Considering processes (5), (6), (7) together, the probe light intensity could be expressed as:

$$\begin{aligned} I_{slow}(t) = {} & \alpha\ B\ I_i\ \Phi_{isc}\ (1\text{-}EXP(\text{-}k_T t))\ I_{s0}\ (1\text{-}\alpha\ I_i\ \Phi_{isc}\ EXP(\text{-}k_T t)\ \sigma_{TT} l) E_T + \\ & \alpha\ \gamma\ B\ I_i\ \Phi_{ic}\ \Phi_{isc}\ EXP(\text{-}k_T t)\ I_{s0}\ (1\text{-}\alpha\ I_i\ \Phi_{isc}\ EXP(\text{-}k_T t)\ \sigma_{TT} l)\ h\nu_s] \\ = {} & \alpha\ B\ I_i\ \Phi_{isc}\ I_{s0}\ (1\text{-}\alpha\ I_i\ \Phi_{isc}\ EXP(\text{-}k_T t)\ \sigma_{TT} l)(E_T + (\ \gamma\Phi_{ic}\ h\nu_s\text{-} \\ & E_T) EXP(\text{-}k_T t)) \end{aligned}$$

$$= X(1-Y \bullet EXP(-k_Tt))(1+Z \bullet EXP(-k_Tt))$$

$$= X + X(Z-Y) \bullet EXP(-k_Tt) - XYZ \bullet EXP(-2k_Tt)$$

$$= A_0 + A_1 \bullet EXP(-k_Tt) + A_2 \bullet EXP(-2k_Tt) \qquad [13]$$

Where $X = \alpha\ B\ I_i\ \Phi_{isc}\ I_{s0}\ E_T; Y = \alpha\ I_i\ \Phi_{isc}\ \sigma_{TT}; Z = (\ \gamma\Phi_{ic}h\nu_s / E_T-1\ );$

And defined as: $A_0 = X$; $A_1 = X(Z-Y)$; $A_2 = -XYZ$

The fit curve for the slow component of TL spectra in FIG.2. is in agreement with the theoretical model.

The lifetime of C_{60} triplet state in benzene solution ($\tau_T = 1/k_T = 10.2\mu s$) which keeps accord with our former data [6] ($\tau_T = 9.7\mu s$) is also given in the fit function.

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