Transient absorption, lifetime and relaxation of C_{60} in the triplet state

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Transient absorption and time-resolved thermal lensing techniques have been used to study the photophysical behavior of C_{60} in benzene solution at room temperature. After the photoexcitation with a 308 nm XeCl excimer laser, the triplet state was the only transient species detectable with the 10 ns time-resolution. The triplet–triplet absorption spectrum with apparent band peaks at 330 and 745 nm covers the whole spectral range of 290–850 nm. The triplet lifetime in air-free benzene is 49 ± 1 µs and essentially all the photon energy absorbed is released as heat, predominantly through the triplet state.

1. Introduction

Extensive attention has been attracted to a soccer-ball molecule (C_{60}, buckminsterfullerene), since its discovery by Smalley's group [1,2] in a carbon-cluster beam. This molecule, whose existence was predicted by Osawa [3] in 1970, has become widely available for experimental scientists after Krätschmer et al. [4] developed a simple and efficient method to synthesize C_{60}. A more efficient production is described by Haufler et al. [5]. The soccer-ball structure of solid C_{60} has recently been confirmed by X-ray diffraction [4] and scanning-tunneling microscope images [6,7]. Spectroscopic data are available in the infrared [4,5,8,9] and ultraviolet–visible [4,8,10] regions. The electronic spectrum has also been simulated by the CNDO/S calculation [11]. The ionization potential is estimated to be 7.6 ± 0.2 eV from the photoelectron spectrum of C_{60} [12] and the electron affinity to be 2.7 ± 0.1 eV from that of C_{60}^- [13].

The photophysical properties of C_{60} have been measured and summarized by Arbogast et al. [14]. We have been examining the photophysical behavior of C_{60} independently by using transient absorption and time-resolved thermal-lensing (TRTL) techniques. This paper describes the transient absorption, lifetime and relaxation of triplet C_{60} in benzene at room temperature.

2. Experimental

2.1. Apparatus

The setup for laser-flash photolysis has been reported [15]. A XeCl excimer laser (Lambda Physics LPX105) was used as a light source. A Xe flash lamp was synchronously fired with the laser. A monochromator/photomultiplier combination was used to obtain transient absorption spectra with a spectral resolution of 2 nm. The transient spectra were measured by a digital memory (Iwatsu DM901) on-line with a personal computer and were averaged over a few tens of shots.

In the setup for TRTL [16], a He–Ne laser aligned to overlap the excitation laser beam in a sample cuvette was used to probe the thermal-lensing effect. The He–Ne laser beam was detected through a pinhole with a photomultiplier tube. The excitation of the sample causes defocusing of the He–Ne laser which results in the decrement of the irradiance of the probe laser and gives the TRTL signal. Data handling was similar to that for the flash photolysis.

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2.2. *Material*

The sample of C_{60} was prepared by a method similar to that described by Krätschmer et al. [4]. A graphite rod of a 6 mm outer diameter was evaporated by arc discharge (typical current of about 60–80 A) under helium gas of 100 Torr. A soot-like material was collected and extracted with benzene. The powder obtained after drying consisted of C_{60} and C_{70} with a ratio of about 10:1. Each component was separated by column chromatography on neutral alumina with hexane. C_{60} was separated completely from C_{70}. Pyridazine (Tokyo Kasei) was purified by repeated trap-to-trap distillation under vacuum. Benzene (Merck Uvasol) was used as received. The samples for the transient absorption measurement were degassed by freeze–pump–thaw cycles on a vacuum line. For the TRTL measurement, the samples were deaerated by bubbling Ar for half-an-hour before use. Absorption spectra were measured by a spectrophotometer (Shimadzu UV 2200).

3. Results and discussion

3.1. *Transient absorption spectra*

Fig. 1 shows the transient absorption spectra measured at four different delay times after the laser-pulse excitation of C_{60} in degassed benzene at 308 nm. These spectra exhibit an intense bleaching around 330 nm where C_{60} has the first strong absorption [10]. Therefore, this bleaching is understood as the depletion of C_{60} in the ground state. At both tails of the bleaching negative band, one can recognize two positive peaks at 300 and 360 nm, which indicate the existence of a strong and broader transient absorption located at the same spectral position as the 330 nm absorption of the ground state. There exists another absorption band peaking at 745 nm, accompanied with a shoulder around 650 nm.

The absorbance measured in the whole spectral region of fig. 1 decays and recovers by the first-order kinetics with a lifetime of 49 ± 1 μs. Therefore, the intermediate responsible for the transient absorption shown in fig. 1 should be a single species. This value is comparable with the lifetime of 40 ± 4 μs measured in the weak absorption region by Arbogast et al. [14]. The lifetime of this transient decreases in the presence of oxygen. Thus, this transient is concluded to be C_{60} in the triplet state. The transient absorption disappears completely at a delay time around 400 μs and the initial absorption of C_{60} in the ground state recovers. The C_{60} molecule seems to relax efficiently from the triplet state to the ground state and to be photochemically very stable. The rise

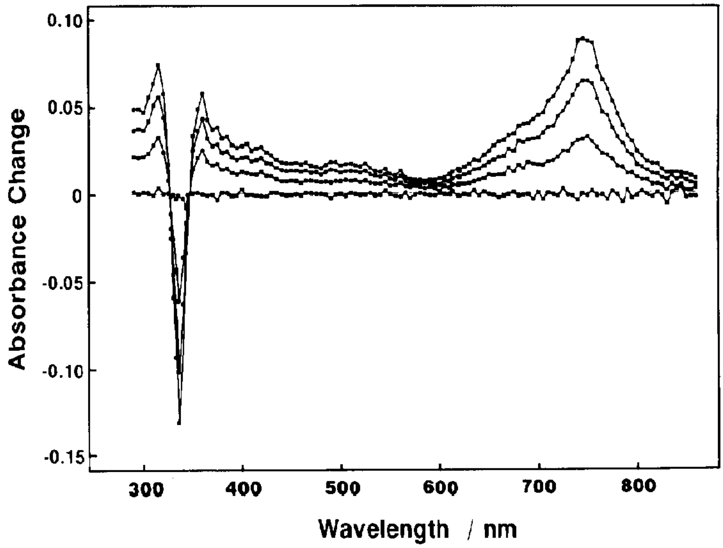

Fig. 1. The transient absorption spectra of C_{60} in degassed benzene at 0, 10, 35 and 400 μs after the laser pulse, with signal intensities decreasing with time.

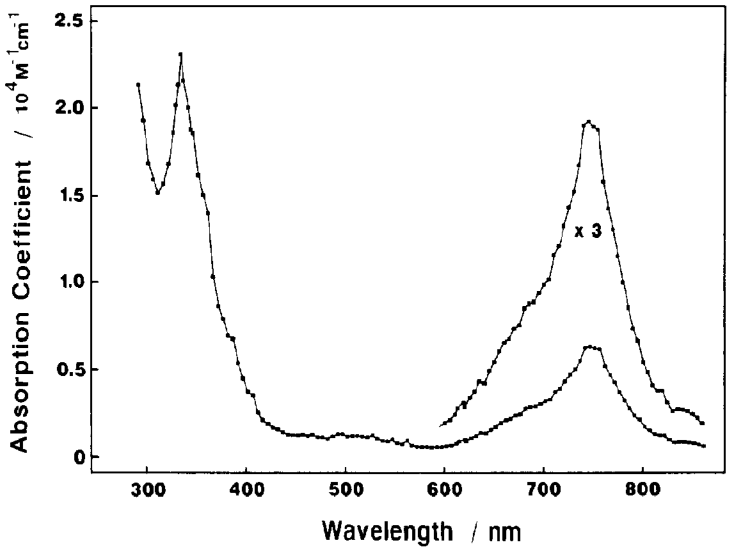

Fig. 2. The corrected T–T absorption spectrum.

of the transient absorption is measured with a fast digital-storage oscilloscope (Gould 4074). The lifetime of the excited singlet state is estimated to be shorter than 1 ns, because the rise curve is described as a convoluted profile of the laser-pulse function.

The T–T absorption spectrum of C_{60} was obtained by a method similar to that reported by Hadley and Keller [17]. The absorption coefficient, ϵ_T, is estimated from the absorbance change, ΔA, in fig. 1 by

$$\epsilon_T = \epsilon_S + \Delta A/[T] ,$$

where ϵ_S is the absorption coefficient of C_{60} in the ground state and [T] is the concentration of the triplet state. The T–T absorption spectrum was reproduced by using [T] as a parameter to compensate for the depletion at 330 nm. The spectrum shown in fig. 2 gives the lower limit of ϵ_T. The absorption coefficient $(3 \pm 1) \times 10^4$ M^{-1} cm^{-1} of the ground state at 330 nm [#1] determines the upper limit, which is 1.5 times the values shown in fig. 2. The T–T absorption spectrum reported by Arbogast et al. [14] covers only the wavelength region of 400–550 nm where the absorption is weak. It is clear that there are strong ultraviolet bands peaking at <290 and 330 nm, and a weak red band peaking at 745 nm with a shoulder around 650 nm. It is worth noting that this spectral feature is similar to that in the electronic absorption spectrum of the radical cation, C_{60}^+, measured and calculated by Kato et al. [19]. The UV and red/IR bands of C_{60}^+ are assigned under the assumption of a truncated icosahedral (I_h) structure to the ($h_u \rightarrow t_{1g}$) and ($g_g \rightarrow h_u$, $h_g \rightarrow h_u$) transitions, respectively [19].

Fig. 3 shows the logarithmic plots of the triplet-state decay under several laser powers. Although the triplet state decays single exponentially at the lowest laser power (1.06 mJ cm^{-2}), the logarithmic plots of the decay profile under higher laser powers deviate from a straight line. These curves are well fitted by a least-squares method with a sum of the first- and second-order decay functions. The second-order component must be due to the T–T annihilation. The resultant rate of the second-order term is determined to be $(6 \pm 2) \times 10^9$ M^{-1} s^{-1}, which nearly corresponds to a diffusion rate. The observation of the T–T annihilation process indicates the high quantum yield of the triplet formation.

3.2. Relaxation processes

We employed the TRTL method to determine the quantum yield of nonradiative relaxation processes

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[#1] The absorption coefficient of C_{60} employed is $(3 \pm 1) \times 10^4$ M^{-1} cm^{-1} at 330 nm [18].

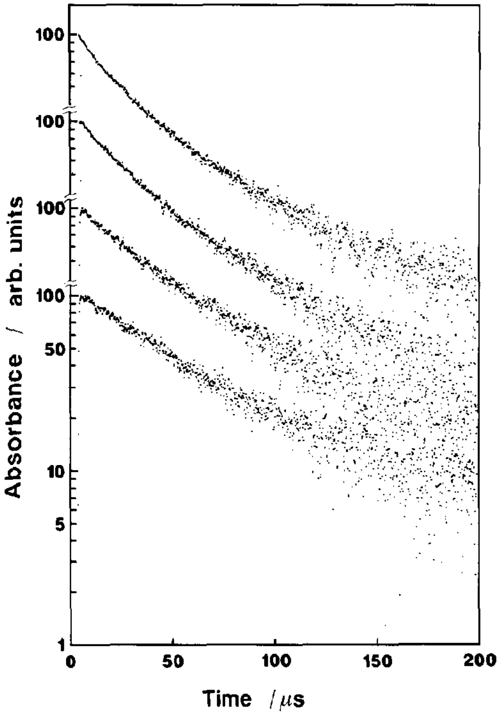

Fig. 3. Decay curves of the transient absorption of C_{60} monitored at 745 nm at four different laser powers, 1.1, 3.5, 14.3 and 41.3 mJ cm^{-2} from the bottom. Curves are displayed in the same scale but shifted for clarity.

of C_{60} in degassed benzene. The heat conversion efficiency α, a fraction of the absorbed photon energy emitted as heat, was first determined. Since the heat released to the solvent is proportional to α and the number of photoexcited molecules, the heat U measured can be described as

$$U = K\alpha I_L(1-10^{-A}),$$

where K is an instrumental factor including the thermal properties of the solvent, I_L the laser energy, and A the absorbance of the sample. Pyridazine was used as a calorimetric reference; $\alpha = 1$ for the 308 nm excitation in order to eliminate the K factor [16]. Since C_{60} in the triplet state disappeared entirely at 400 μs after the laser irradiation, the total heat released during the initial 400 μs period was measured as the TRTL signal. Fig. 4a plots the signals measured at several C_{60} concentrations as a function of the laser power. A linear relation holds for laser powers below 30 μJ. Therefore, the multiphoton process is negligible in this laser-power range, although the T–T absorption gives a relatively high coefficient in the UV region. The solid lines in fig. 4a show the least-squares fits of the data to a linear relation. Fig. 4b shows the TRTL signals of pyridazine measured carefully under the same experimental conditions as those for

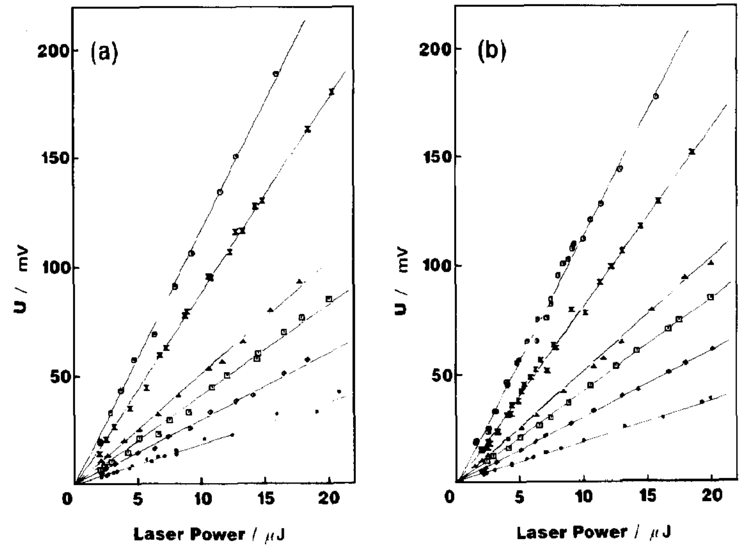

Fig. 4. (a) Plots of TRTL signal intensity of C_{60} in deaerated benzene versus laser power. The absorbances, A, corresponding to the concentration of C_{60} are 0.766 (Φ), 0.402 (x), 0.202 (▲), 0.143 (□), 0.100 (◇), and 0.060 (●). (b) Plots of the TRTL signal intensity of pyridazine in deaerated benzene versus laser power. The absorbances, A, corresponding to the concentration of pyridazine are 0.730 (Φ), 0.400 (x), 0.201 (▲), 0.143 (□), 0.101 (◇) and 0.059 (●).

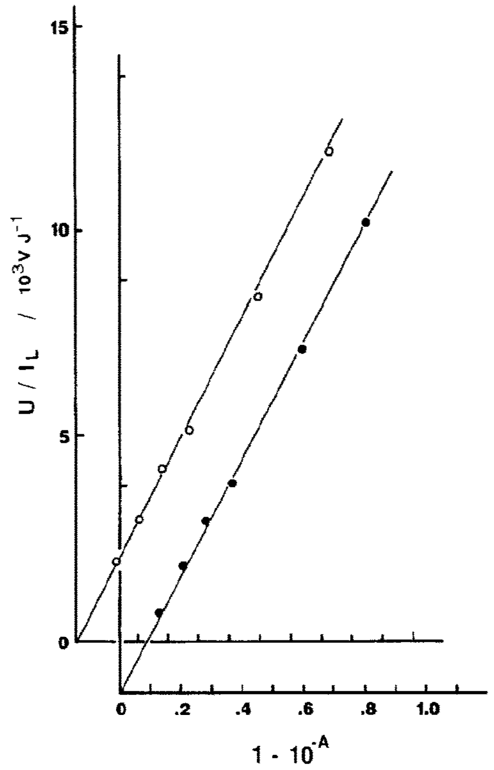

Fig. 5. Plots of U/I_L versus $1-10^{-A}$. Data are fitted to a linear relation: (○) C_{60} and (●) pyridazine.

C_{60}. Fig. 5 plots the slopes, U/I_L, of fig. 4 against $1-10^{-A}$. The α value for C_{60} is determined to be 0.98 ± 0.03 by comparing the two slopes shown in fig. 5. The unit value of α strongly suggests that the nonradiative heat-resulting process is the major deactivation process of the photoexcited C_{60} molecules in solution. This nonradiative process is concluded to proceed predominantly through the triplet state, judging from the large triplet yield, the absence of fluorescence [14] and the fast rise of the T_1 state (< 1 ns).

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