Low-lying electronically excited states of C_{60} and C_{70} and measurement of their picosecond transient absorption in solution

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Low-lying electronically excited states of C_{60} and C_{70} were identified in picosecond transient absorption measurements extending in wavelength down to 1000 nm. Spectral features in the near-infrared region were found to be significantly different from the results of previous studies. The lifetimes for S₁ states of C₆₀ and C₇₀ were determined to be 1.3 ± 0.2 ns and 0.7 ± 0.05 ns, respectively. A simple energy diagram for electronic states of C₆₀ and C₇₀ is presented.

1. Introduction

The recent development of a method of mass production [1,2] of C_{60} and its kindred fullerenes prompted intense research efforts in studying many basic properties of this unique class of molecules. Photophysical properties of C₆₀ have been investigated in UV-visible absorption studies at cryogenic [3-5], and room temperatures [3,6,7]. Emission study of C₆₀ has been possible only in low-temperature solids [4,8], but a very weak fluorescence emission from room-temperature solutions was also observed recently [9]. Similarly, C₇₀ has been studied by UV-visible absorption [3,6,7], and also by fluorescence emission at cryogenic temperatures [8,10], and in room-temperature solutions [9,10]. Excited-state properties have also been studied. Transient absorption studies of C₆₀ and C₇₀ have revealed a fast decrease in the population of the first

excited singlet (S₁) state and a corresponding increase in the population of the lowest triplet (T_1) state, suggesting a rapid intersystem crossing between S_1 and T_1 states. Generally, features of transient absorption spectra agree among them, but there are some discrepancies in the lifetimes of S_1 states of C_{60} and C_{70} . The singlet-state lifetime for C_{60} has been reported to be 0.65 ns [11], or 1.2 ns [12], and that for C_{70} is 0.67 ns [13]. Lifetimes as short as 33 ps for C₆₀ and 110 ps for C₇₀ have also been suggested [14]. The time-correlated single-photon counting technique has revealed a lifetime of 1.17 ns for C_{60} and 0.66 ns for C_{70} through the measurement of fluorescence decay [9]. An interesting, and potentially useful, application of the rapid intersystem crossing in fullerenes is the optical limiting property, recently found for both C_{60} and C_{70} in solutions [15]. In this study, transmission of visible light through solutions of fullerenes was shown to reach a plateau after initially conforming to Beer's law. This limiting behavior was interpreted as due to the rapid $S_1 \rightarrow T_1$ intersystem crossing, in addition to the large cross section for $T_1 \rightarrow T_n$ absorption. Study of optical transition from S_1 or T_1 states to higher excited states is

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important both scientifically and in terms of application. The present study aims to identify the lowlying electronically excited states of C_{60} and C_{70} by extending the wavelength region of transient absorption spectra down to 1000 nm. Our spectra reveal transitions to states lower in energy than those known from any previous studies.

2. Experimental

The fullerenes were produced by the contact-arc method [1,2] and purified by standard procedures [16]. Briefly, two graphite rods of $\frac{1}{4}$ inch diameter (99.9%, Poco Graphite) were positioned against each other and a contact-arc was produced by flowing 100-200 A of current at 20 V ac under 150 Torr helium atmosphere. Soxhlet extraction was carried out for the resulting soot, first with diethyl ether for 3 h to wash out hydrocarbons, and then with benzene or toluene for 24 h. Dry column chromatography on neutral alumina with n-hexane as eluent was used to separate C_{60} . Solvent was then evaporated and the remaining powder was baked at 200°C (in vacuo) to remove saturated long-chain hydrocarbons. C₇₀ was separated from the mixture with C₆₀ by secondary column chromatography with n-hexane. UV-visible absorption, FT-IR, Raman, ¹³C NMR spectroscopy as well as HPLC and mass spectrometry were employed to identify the species. For C₆₀, the sample purity was estimated to be 99.5% or higher from mass spectrometric measurement. The purity of C70 sample was also very high \approx 98%, and the only detectable impurity was C₆₀.

Transient absorption data on a picosecond to 5 ns time scale with a 2 mm pathlength flowing cell were recorded by first exciting the sample with 20 Hz, 0.8 ps, 0.3 mJ pulses at 587 nm, and then probing with a continuum pulse generated by focusing the same laser pulses into a 1 cm×1 cm cell containing water [17]. These laser pulses were obtained from a combination system of cw mode-locked Nd: YAG laser, hybridly mode-locked synchronously pumped dye laser, Nd: YAG regenerative amplifier, and tunable picosecond dye amplifier. Concentrations of C_{60} and C_{70} solutions in toluene were 1×10^{-3} and 1×10^{-4} M, respectively.

3. Results and discussion

Fig. 1 presents the transient absorption spectra measured at 20, 153 ps, 0.8, 1.8 and 3.1 ns after the picosecond laser pulse excitation of C₆₀ in toluene at 587 nm. The transient absorption spectrum at 3.1 ns delay time is in general accord with the previously reported $T_1 - T_n$ absorption spectrum with a peak at 747 nm, accompanied by a broad shoulder in the shorter wavelength region [11,12,18]. At longer than 3.1 ns delay time, up to 5 ns, the overall spectral features remain unchanged, indicating that the excited molecule in the singlet S₁ state decays to the triplet T_1 state almost completely at 3.1 ns via intersystem crossing. On the other hand, the transient absorption spectrum at 20 ps delay time clearly shows a different feature from the one reported by Ebbesen et al. [12], especially in the near-infrared region. The spectrum at 20 ps delay time is attributed to mostly $S_1 - S_n$ absorption due to the reported lifetimes of the S_1 state of C_{60} in solution [9,11,12]. Ebbesen et al. reported the lowest S_1 - S_n absorption band at 887 nm [12], while our spectrum shows broad transient absorption centered at 920 nm with a broad absorption bandwidth (about 160 nm). The lifetime of the excited singlet state was determined from the rate of



Fig. 1. Transient absorption spectra of C_{60} in toluene obtained for delay times of 20, 153 ps, 0.8, 1.8, and 3.1 ns. The pump wavelength was 587 nm. The arrows \uparrow and \downarrow indicate the increase and decrease of the transient absorption intensity, respectively, with an increase in delay time.

decrease of S_1 - S_n absorption as well as that of increase of T_1 - T_n absorption with an increase in delay time. The estimated lifetime is 1.3 ± 0.2 ns, which agrees well, within experimental error, with the fluorescence lifetime [9]. From the molar absorption coefficient of 15000 M⁻¹ cm⁻¹ for the triplet state at 747 nm [12], it is estimated that the molar absorption coefficient for the singlet state at 920 nm is 8000 M⁻¹ cm⁻¹.

Fig. 2 shows transient absorption spectra at 20, 153 ps, 0.8 and 1.8 ns delay times of C_{70} in toluene with excitation at 587 nm. The 20 ps delay time spectrum mostly due to S_1 - S_n absorption is somewhat different from the previously reported S_1-S_n absorption spectrum [13]. Our wavelength coverage down to 1020 nm reveals spectral features which have not been observed previously. First, the spectrum at 20 ps delay time clearly indicates absorption peaks not only at 675 nm as reported but around 840 nm with a broad absorption bandwidth, extended to the near infrared region. In addition, the 1.8 ns delay time spectrum mainly due to $T_1 - T_n$ absorption shows a maximum peak at 960 nm. The lifetime for the excited singlet state of C₇₀ was determined to be 0.7 ± 0.05 ns from the rate of decrease of absorption at 675 nm and also from that of increase of absorp-



Fig. 2. Transient absorption spectra of C_{70} in toluene obtained for delay times of 20, 153 ps, 0.8, 1.8 ns. The pump wavelength was 587 nm. The arrow \uparrow and \downarrow indicate the increase and decrease of transient absorption intensity, respectively, with an increase in delay time.

tion at 960 nm. This is in good agreement with the fluorescence lifetime [9]. The reported molar absorption coefficient of 3800 M^{-1} cm⁻¹ at 675 nm for the singlet state [13] provides an estimated value of that for the triplet state as 2000 M^{-1} cm⁻¹ at 960 nm. The molar absorption coefficient for the T₁ state of C₆₀ is significantly larger than that of C₇₀, while the ground state absorption cross section in the visible range is much larger for C₇₀ than for C₆₀. It is thus expected that the optical limiting capability of C₆₀ should be higher than that of C₇₀, as found experimentally [15].

An energy diagram for electronic states of C_{60} and C₇₀, based on the previous results on photophysical properties [3-14,18,19] and transient absorption spectra given here, is presented in fig. 3. As for C_{60} , the (0, 0) transition energy between S₀ and S₁ states was suggested as 16100 cm⁻¹ based on the lowest energy absorbance maximum [19]. The (0, 0) energy difference between S_0 and T_1 states was estimated to be around 13100 cm⁻¹ by Arbogast et al. [19]. Also a gas phase R2PI study estimated this energy to be 13700 cm⁻¹ [20]. Since no phosphorescence has yet been observed in C_{60} , we have a relatively large uncertainty in this estimate. The energy of the next higher singlet state above S₁ was calculated as 27000 cm^{-1} (from S₀ level) through S₁-S_n absorption of C₆₀ at 920 nm. Although our transient absorption measurements were carried out into the near-infrared region, it is not yet conclusive to assign the upper singlet and triplet states as S₂ and T₂, respectively, until it is theoretically or experimentally established that no other lower energy transitions from S_1 or T_1 state exist past 1000 nm. Thus, all the assignments of the next higher singlet or triplet states above the S_1 or T_1 state are based on our transient absorption measurements down to 1000 nm. The energy of the next higher triplet state above T_1 state is estimated by T_1-T_n absorption centered at 747 nm.

As for C_{70} , the (0, 0) transition energy between S_0 and S_1 states was suggested as 15400 cm⁻¹ following the comparison between absorption and 77 K fluorescence spectra of C_{70} [10]. Other estimates range from 15012 cm⁻¹ [8] to 15699 cm⁻¹ [6]. The phosphorescence of C_{70} in low temperature organic glass had a broad band from 790 to 870 nm with double peaks at 810 and 840 nm [14] which gives the energy of the (0, 0) transition between S_0 and T_1



Fig. 3. Energy diagrams for electronic states of C_{60} and C_{70} based on previously determined photophysical properties and transient absorption spectra given in this Letter. Triplet-state quantum yields and triplet-state lifetimes for C_{60} and C_{70} are from refs. [10,19]. The phosphorescence quantum yield and the fluorescence quantum yield for C_{70} are from refs. [10,14], respectively. The wiggly and straight lines indicate the nonradiative and radiative decay channels, respectively. The thick arrow lines indicate the possible transitions to the upper S_n or T_n state from the S₁ or T₁ state presented in figs. 1 and 2.

states as 12400 cm⁻¹. In another study of low-temperature glassy solution, the (0, 0) transition energy was estimated to be 12614 cm⁻¹ [8]. A gas-phase R2PI study estimated this energy to be 12900 cm⁻¹ [20]. These results are all in good agreement with the estimate of Arbogast and Foote [10]. The next higher singlet state above S₁ for C₇₀ is expected to lie at 27300 cm⁻¹ based on broad S₁-S_n absorption centered around 840 nm. The energy of another higher state is suggested as 30200 cm⁻¹ due to the relatively strong S₁-S_n absorption at 675 nm. The location of the next higher state above T₁ for C₇₀ was assigned as 22800 cm⁻¹ due to T₁-T_n absorption at 960 nm.

A small S_1-T_1 splitting (about 3000 cm⁻¹) in both C_{60} and C_{70} is viewed as a result of the large diameter of the molecule and the resulting small electronelectron repulsion energy [10]. Although the S_1-T_1 splitting is similar for C_{60} and C_{70} , the lifetimes of the singlet states for C_{60} and C_{70} are different from each other by nearly a factor of 2. The large diameter and the reduced symmetry of C_{70} compared with C_{60} would provide an effective channel for the intersystem crossing between S_1 and T_1 states. On the other hand, the lifetime for the triplet state of C_{70} [10] is longer than that of C_{60} [19], even though the energy differences between T₁ states of C_{60} and C_{70} are small ($\approx 900 \text{ cm}^{-1}$). As described above, the energies of the higher dipole-allowed transitions from S₁ or T₁ states for C_{60} and C_{70} are quite different from each other. Thus, although C_{60} and C_{70} have excited state properties in many ways similar to other aromatic molecules, the properties of C_{70} are quite different from C_{60} , probably resulting from the change in electronic structure caused by strain and reduced symmetry.

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