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Absorption Spectra of C_{60}-Excited States in Various Solvents: Their Dependence on the Ionization Potential of Solvent Molecules

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Using a picosecond laser photolysis system, the absorption spectra of excited states of C_{60} in twelve solvents were measured in the 590—1190 nm wavelength range. The absorption spectra observed immediately after a 532 nm picosecond laser excitation and those in the late-time region depended upon the solvents. In particular, the former dependence was much larger than the latter one. Their spectral shapes did not correlate with either dielectric constant of the solvents or their refractive index, but with their ionization potential (I_p). The early-gated absorption spectra of C_{60} in solvents with a small I_p were extraordinary broad compared with those in solvents with a large I_p. In addition, the absorption changed to those observed in the late-time region both with a decay time constant of 1.2 ± 0.05 ns and with keeping the isosbestic points. This time constant was the same as the lifetime of the C_{60}-singlet excited state (${}^1C_{60}^*$) reported previously, and the presence of the isosbestic points was also the same as that observed during spectral evolution from $S_n \leftarrow S_1$ absorption of C_{60} to its $T_n \leftarrow T_1$ one. Combining the results of the resonance Raman spectra by Gallagher et al. with the present ones suggested that the solvent-dependent early-gated absorption spectra of the C_{60}-excited state are ascribed to ${}^1C_{60}^*$ with a distortion induced by specific interactions with solvents molecules through the donation of their π-electron density without forming obviously excited-state complexes. The transient absorption spectra observed immediately after the direct excitation of ground-state charge-transfer complexes formed between C_{60} and solvent molecules with a small I_p were not due to ionic species, but to ${}^1C_{60}^*$, suggesting that the photogenerated ionic species undergo a very rapid charge-recombination reaction to result in ${}^1C_{60}^*$ and the ground-state solvent molecule. The absorption spectra in the late-time region, which showed a slight dependence on I_p of the solvent molecules, as aforementioned, were assigned to the $T_n \leftarrow T_1$ absorption of C_{60}; the dependence was considered to be also ascribed to the same reason as that for ${}^1C_{60}^*$.

Fullerene (C_{60}) has attracted much attention owing to its highly symmetrical structure and its unique electronic structure; also, its photophysical, photochemical, and charge-transfer properties have been investigated. During the course of elucidating photoinduced electron-transfer processes of C_{60}, the absorption spectra of transient intermediates, such as the triplet excited state (${}^3C_{60}{}^*$) and the radical anion (C_{60}^{-}) of C_{60}, have been reported.[1,2] In these reports, the absorption spectra of ${}^3C_{60}{}^*$ and C_{60}^{-} show no variation from experiment to experiment. On the other hand, little attention has been paid to the absorption spectrum of the singlet excited state of C_{60} (${}^1C_{60}{}^*$) compared to the above-mentioned species, because experiments for the photoinduced electron-transfer reaction have been performed mainly for the triplet excited state. Firstly, the $S_n \leftarrow S_1$ absorption spectrum of C_{60} with peaks around 520 and 870 nm in toluene was reported as the result of a picosecond laser photolysis of C_{60} in the 400—960 nm wavelength range.[3] The spectrum, however, has not subsequently been reproduced. Lee et al. reported on the broad absorption spectrum of ${}^1C_{60}{}^*$ with a peak around 920 nm in the 620—1010 nm wavelength range, excited by a 587 nm picosecond laser.[4] From the time evolution of the time-resolved absorption spectra with an isosbestic point, they determined the lifetime of ${}^1C_{60}{}^*$ to be 1.3 ± 0.2 ns.[4] After that, the spectra of ${}^1C_{60}{}^*$ in poly(methyl methacrylate) (PMMA) and in polystyrene (PSt) films were measured using a 355 nm picosecond laser.[2,5] During the time evolution of the time-resolved spectra, the intersystem crossing process from ${}^1C_{60}{}^*$ to ${}^3C_{60}{}^*$ was demonstrated: with a time constant of 1.2 ns, both a decrement in the absorption intensity of ${}^1C_{60}{}^*$ and an increment in that of ${}^3C_{60}{}^*$ were observed with the isosbestic point at 770 and 790 nm for C_{60}–PMMA and –PSt films, respectively. However, the spectral shape of ${}^1C_{60}{}^*$ in the monitored wavelength region (700—980 nm) was not identical between these two C_{60}–doped polymer films. Recently, both using a probe beam based on broad-band optical parametric generation and using an InGaAs multichannnel detector, time-resolved absorption spectra of a C_{60}–benzene solution in the near-IR region from 700 to 1300 nm were measured, excited with a 532 nm picosecond pulse.[6] Although an isosbestic point was not observed clearly during the time evolution of their spectra, a broad absorption band of ${}^1C_{60}{}^*$ with a peak at 970 nm was observed, which was insisted to be the first observation of the absorption spectrum of ${}^1C_{60}{}^*$ including its absorption edge. More recently, the broad absorption band of ${}^1C_{60}{}^*$ with a peak around 900 nm was reported for a C_{60}–benzonitrile solution.[7] The lifetime of the S_1 state was estimated to be 1.16 ns from the growth rate of the triplet absorption, and the shape as well as the peak position of the $T_n \leftarrow T_1$ absorption of the solution were reported to be very similar to those in a decalin and benzene solution.

In order to reveal photoinduced electron-transfer processes in poly(*N*-vinylcarbazole) (PVCz) films doped with C_{60}, we measured the time-resolved absorption spectra of the films in the 590—1180 nm wavelength range, excited with a 532 nm picosecond laser.[8] In the spectrum observed immediately after excitation, the spectra of the PVCz cation ($PVCz^+$) and C_{60}^- were observed. While carrying out this investigation, we measured the time-resolved spectra of C_{60} in benzene and in inert poly(isopropyl methacrylate) (PIPMA) films as their reference spectra. The absorption band of $^1C_{60}^*$ was clearly observed immediately after excitation, and the time evolution of the spectra with isosbestic points to $^3C_{60}^*$ was observed with a time constant of 1.2 ns. Although the absorption spectra of $^1C_{60}^*$ with a peak around 975 nm in these media were similar to each other, they were slightly different from those in PMMA and PSt films.[2,5]

Unlike the absorption spectra of $^1C_{60}^*$, when the fluorescence spectra of C_{60} and their quantum yields in substituted benzenes were investigated using a near-IR-sensitive detector in detail, the fluorescence spectra in a given solvent observed by excitation on the first and second absorption bands were the same, and their fluorescence quantum yields were almost independent of the solvents.[9] In addition, even if the ground-state contact CT complex formed between C_{60} and naphthalene derivatives in toluene was excited, the fluorescence was reported to be the same as that for the C_{60}–toluene solution.[9]

It is indispensable to elucidate the details of the discrepancy among reported $^1C_{60}^*$-absorption spectral shapes and its origin not only for further investigation of photochemical and photophysical dynamics of C_{60}, but also for its application to photoconductive, photovoltaic, and photorefractive devices. Moreover, understanding them may help to better control the optical limiting properties of C_{60}-solutions.[11,12] In the present paper, we report on the transient absorption spectra of C_{60} in various solvents, measured in the 590—1190 nm wavelength range and in the 0 ps—6 ns time region, as well as their time evolution. Considering both the ground-state absorption spectra of C_{60} and its solubility, we employed twelve solvents for measuring them. It is widely known that the colors (the ground-state absorption spectra) of C_{60}-solutions depend on the solvents used.

Experimental

C_{60} (99.9%) was purchased from Shinku-yakin Co. and used without further purification. *trans*-Decalin (Tokyo-kasei, GR Grade) was purified through a silica-gel column. Anisole (Wako, Special Grade) was purified by removing impurities with H_2SO_4, drying it with $CaCl_2$, and distilling it under reduced pressure. Mesitylene (Wako, Special Grade) and 2-ethylnaphthalene (Tokyo-kasei, GR Grade) were distilled under reduced pressure. Benzene (Dotite Luminazol), chlorobenzene (Wako, Special Grade), toluene (Dotite Spectrosol), *o*-chlorobenzene (Tokyo-kasei, GR grade), *o*-xylene (Nacalai Tesque, Special Grade), 1,2,3,5-tetramethylbenzene (Aldrich, 80% and the remaining fractions being other isomers), veratrole (Tokyo-kasei, GR grade), and 1,4-dimethylnaphthalene (Tokyo-kasei, EP Grade) were used without further purification.

The ground-state absorption spectra were measured using a Shimadzu MPS-2000 multipurpose spectrometer at room temperature. Transient absorption spectra were measured using the apparatus described in a previous paper at 21±2 °C.[13] A second-harmonic pulse of a custom-built repetitive mode-locked Nd^{3+} : YAG laser (532 nm, 16 ps fwhm) was used as an excitation source. A picosecond laser pulse of 450 nm, obtained by optical parametric generation based on two KDP crystals pumped by a 355 nm third harmonic laser pulse, was also used.

All measurements were performed under an O_2-free condition.

Results and Discussion

Listed in Table 1 are the physical properties of the solvents employed: the ionization potential (I_p), dielectric constant (ε), and refractive index (n), where the solvents are listed in order of their I_p. Before describing and discussing the absorption spectra of the C_{60}-excited states, we discuss the ground-state absorption spectra of C_{60} in the present solvents.

Ground-State Absorption Spectra of C_{60}. Figure 1 shows the ground-state absorption spectra of C_{60} in twelve solvents. The spectra were normalized by the absorption intensity at 602.4 nm, and are shown in order of the I_p of the solvent molecules. The absorption spectra of C_{60} in PIPMA and PVCz films are also shown for a comparison.[8] Since there exists no specific interaction between C_{60} and PIPMA, the absorption spectrum of C_{60}–doped PIPMA films is ascribed to C_{60} molecules having no specific interaction with the environment. On the other hand, the absorption spectrum of C_{60}–doped PVCz films is different from it: The enhanced and broad absorption band in the 400—700 nm wavelength range was assigned to a ground-state CT complex formed between C_{60} and carbazolyl chromophore (Cz) by Wang and Kamat et al.[2,14,15] The assignment was also confirmed by the fact that the absorption spectra of the ionic species (C_{60}^- and $PVCz^+$) are observed for the spectra monitored immediately after a 532 nm picosecond laser excitation.[8]

The spectra of C_{60} in solvents are different from that of C_{60}–doped PVCz films. The spectrum of C_{60} in *trans*-decalin, having no π-electron, shows fine structures, which is similar to that of C_{60}–doped PIPMA films. This means no specific interaction between C_{60} and *trans*-decalin molecules. As shown in Fig. 1, the first absorption band in the 500—650 nm wavelength range is almost the same in all of the solvents except, for the fine structure of the *trans*-decalin solution, whereas a new absorption band is observed in the spectral valley between the first and second absorption bands for C_{60} in solvents with small I_p (2-ethylnaphthalene, veratrole, and 1,4-dimethylnaphthalene ((10), (11), and (12) in Fig. 1)). Although aggregates of C_{60} are known to show broad absorption around 450 nm,[16] the new band observed for these solutions is not ascribed to the C_{60} aggregates. Because the C_{60}–2-ethylnaphthalene solution diluted to one tenth of the concentration also showed new absorption, in addition C_{60} in mixed solvents of veratrole–*trans*-decalin or 1,4-dimethylnaphthalene–*trans*-decalin also showed the new one.

Table 1. Ionization Potential (I_p), Dielectric Constant (ε), and Refractive Index (n) of Solvents Used

No.	Solvents	I_p (eV)	ε g)	n g)
1	*trans*-Decalin	9.35 a)	2.172	1.467
2	*o*-Dichlorobenzene	9.24 b)	9.93	1.549
3	Benzene	9.23 c)	2.275	1.498
4	Chlorobenzene	9.07 d)	5.621	1.525
5	Toluene	8.82 c)	2.379	1.494
6	*o*-Xylene	8.56 c)	2.568	1.503
7	Mesitylene (1,3,5-Trimethylbenzene)	8.42 c)	2.279	1.497
8	Anisole (Methoxybenzene)	8.39 d)	4.33	1.514
9	1,2,3,5-Tetramethylbenzene	8.07 c)	(2.37) h)	1.513
10	2-Ethylnaphthalene	7.95 d)	(3.0) h)	1.5999
11	Veratrole (1,2-Dimethoxybenzene)	7.8 e)	4.09	1.532
12	1,4-Dimethylnaphthalene	7.82 ± 0.03 f)	(2.7) h)	1.6127

a) M. J. Dewar and S. D. Woriey, *J. Chem. Phys.*, **50**, 654 (1969). b) S. Jujisawa, I. Oonishi, S. Masuda, K. Ohno, and Y. Harada, *J. Phys. Chem.*, **95**, 4250 (1991). c) J. O. Howell, J. M. Goncalves, C. Amatore, L. Klasinc, R. M. Wightman, and J. K. Kochi, *J. Am. Chem. Soc.*, **106**, 3968 (1984). d) L. Klasins, B. Kovac, and H. Gusten, *Pure Appl. Chem.*, **55**, 289 (1983). e) L. N. Domelsmith and K. N. Houk, *NIDA Res. Monogr.* **22**, 423 (1978). f) E. Heibronner, T. Hoshi, J. L. von Rosenberg, and K. Hatner, *Nouv. J. Chim.*, **1**, 105 (1976). g) J. A. Riddick and W. B. Bunger, "Techniques of Chemistry, Vol. II: Organic Solvents," ed by A. Weissberger, Wiley-Interscience, New York (1970). h) Estimated values.

Colors of C_{60}-solutions are widely known to depend on the solvents.[9,17—22] Although the formation of CT complexes of C_{60} with aromatic amines was confirmed,[22] and it was reported that the absorption spectra of C_{60} in substituted benzenes should be analyzed in regard to any CT effects,[17] the formation of ground-state complexes between C_{60} and other aromatic molecules was unclear.[9,10,17,19,23] For example, Catalan showed that there are two patterns in the absorption spectra of C_{60} in eleven monosubstituted benzenes with variable electron-withdrawing and electron-donating ability:[19] one is spectra showing a broad band centered at 550 nm with a minimum at 440 nm; the other spectra do not show the minimum at 440 nm. These changes, however, were not ascribed to the formation of CT complexes in the ground state. Thus, he did not infer a single rationale for the spectral behavior of C_{60} in fifty-two solvents.[20] On the other hand, on the basis of the absorption spectra of C_{60} in fifteen solvents, Gallagher et al. considered that the spectral shift observed in benzene-derived aromatic solvents is responsible for solvent–solute π-staking resulting in the stabilization of C_{60} and $^1C_{60}{}^*$.[21] Since the solvent with the smallest I_p among aromatic solvents used by them was mesitylene (I_p = 8.42 eV), the new absorption band is unlikely to be observed between the first and second absorption bands. On the other hand, a ground-state contact CT complex between C_{60} and substituted naphthalenes was reported to be formed in toluene.[10] Recently, Ma and Sun examined the absorption and fluorescence spectra of C_{60} and its fluorescence quantum yields in ten solvents.[7] In a series of methyl-substituted benzenes, the second absorption band shifted to a longer wavelength along with an increase in the number of methyl substitutions; also the valley between the first and second absorption bands was observed, while the valley was not observed for 1-methylnaphthalene solution. Integrating these results with the absorption spectra of C_{60} in other solvents, they proposed that the unusual solvatochromism observed for the solvent series of methyl-substituted benzenes is more likely to be due to a result of specific interactions besides any ground-state complexes.

The observation of the red shift for methyl-substituted benzenes solutions shown in Fig. 1 is the same as the results of Ma and Sun.[9] As pointed out by Catalan et al.,[19] two kinds of absorption spectra are observed: the presence and absence of the minimum around 450 nm between the first and second absorption bands. Concerning the solvents that we employed, the latter type spectra were observed for solvents with small I_p, as aforementioned. In addition, for solvents with a smaller I_p than that of anisole, the tail of the second absorption band expands to long wavelengths with decreasing I_p of the solvent molecules. Furthermore, one can see that a new band showing a shoulder between the first and second absorption bands shifts to long wavelengths along with a decrease in the I_p of the solvent molecules. These results suggest the new absorption band observed for C_{60} in aromatic solvents with a small I_p is responsible for a transition with the CT character. This is similar to the fact that the maximum of the absorption (contact CT complex) observed for the toluene solution of C_{60} and naphthalene derivatives shifts to long wavelengths as the I_p of the naphthalene derivatives decreases.[10] Recently, CT complex formation of C_{60} with naphthalenes, phenanthrene, and pyrene in toluene has been reported.[10,23]

In the next part, the irradiation at 532 nm corresponds to the excitation of the first absorption band of C_{60}, but not to that of the new absorption band, as shown in Fig. 1. In the

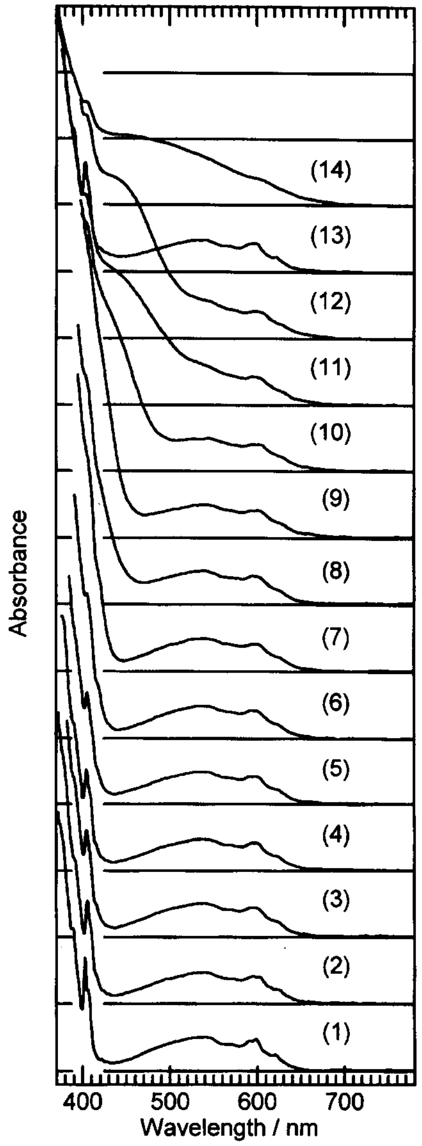

Fig. 1. Ground-state absorption spectra of C_{60} in solution: (1) *trans*-decalin (slightly less than saturated concentration), (2) *o*-dichlorobenzene (concentration: 9.7×10^{-4} mol dm^{-3}), (3) benzene (3.8×10^{-4} mol dm^{-3}), (4) chlorobenzene (7.2×10^{-4} mol dm^{-3}), (5) toluene (1.4×10^{-3} mol dm^{-3}), (6) *o*-xylene (1.3×10^{-3} mol dm^{-3}), (7) mesitylene (slightly less than saturated concentration), (8) anisole (1.7×10^{-4} mol dm^{-3}), (9) 1,2,3,5-tetramethylbenzene (1.3×10^{-3} mol dm^{-3}), (10) 2-ethylnaphthalene (6.5×10^{-4} mol dm^{-3}, (11) veratrole(slightly less than saturated concentration), and (12) 1,4-dimethylnaphthalene (9.0×10^{-4} mol dm^{-3}). The spectra are presented in order of I_p of solvents. Reference spectra: (13) PIPMA (5.5×10^{-2} mol dm^{-3}) and (14) PVCz (4.4×10^{-2} mol dm^{-3}) films. The concentrations of C_{60} in these films are one or two orders of magnitude larger than those in solution system.

subsequent part we discuss the transient absorption obtained by excitation upon the new absorption band.

Absorption Spectra of C_{60}-Excited State Observed Immediately after Excitation. Figure 2 exhibits the absorption spectra of C_{60} observed immediately after a 532 nm picosecond laser excitation, being in order of the I_p of solvent molecules.[24] The absorption spectra of C_{60}–doped PIPMA and –doped PVCz films are also shown for a comparison. In order to avoid a strong 1064 nm fundamental laser pulse entering the sample, the fundamental pulse was removed from the monitoring picosecond white light. As previously reported,[8] the transient absorption band with a

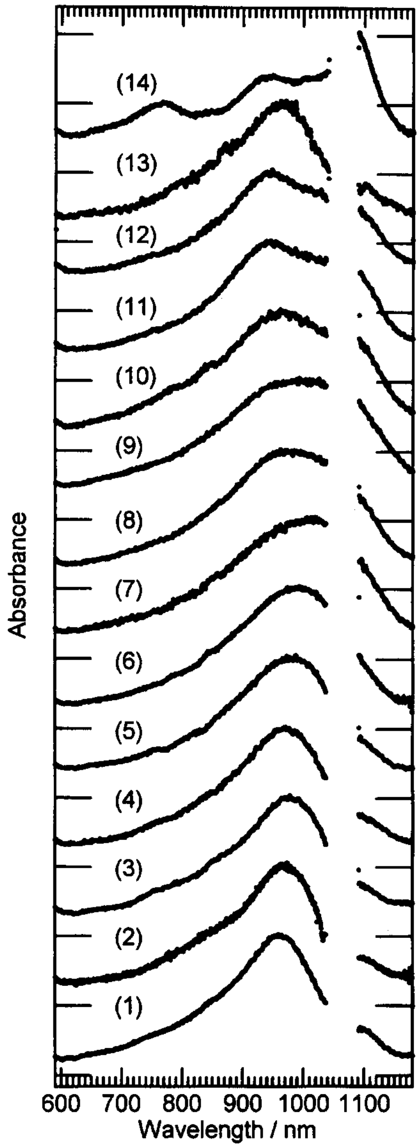

Fig. 2. Absorption spectra of C_{60}-excited states observed immediately after excitation: (1) *trans*-decalin, (2) *o*-dichlorobenzene, (3) benzene (1.5×10^{-3} mol dm^{-3}), (4) chlorobenzene, (5) toluene, (6) *o*-xylene, (7) mesitylene, (8) anisole (7.5×10^{-4} mol dm^{-3}), (9) 1,2,3,5-tetramethylbenzene, (10) 2-ethylnaphthalene, (11) veratrole, and (12) 1,4-dimethylnaphthalene. The spectra are presented in order of I_p of solvents. Unless specified otherwise, concentrations are the same as those in Fig. 1. These spectra were observed at 40 or 60 ps after excitation. Reference spectra: (13) PIPMA films and (14) the time-resolved absorption spectrum of C_{60}–doped PVCz films, which shows anion of C_{60} (C_{60}^{-}) and cation of PVCz (PVCz^{+}).

peak around 970 nm observed for C_{60}–doped PIPMA films is safely assigned to $^1C_{60}{}^*$ on the basis of the coincidence of the spectral band shape and its maximum with those previously reported.[2,6] For C_{60}–doped PVCz films, the absorption band in the wavelength range above 850 nm (a peak around 930 nm and a peak estimated to be between 1050 and 1080 nm) is ascribed to C_{60}^-, and the absorption band at 770 nm to $PVCz^+$,[7] indicating that the charge-separated state ($PVCz^+$–C_{60}^-) between PVCz and C_{60} is produced immediately after excitation with a picosecond 532 nm laser pulse. One notices the following two points in Fig. 2: (1) the absorption spectra observed immediately after excitation depend on the solvents and (2) although the spectrum for the C_{60}–1,4-dimethylnaphthalene solution is markedly different from that for C_{60}–PIPMA films, it is not assigned to that of $C_{60}{}^-$.

Since the transient absorption spectra of the C_{60}–*trans*-decalin, –*o*-dichlorobenzene, and –chlorobenzene solutions are very similar to those of $^1C_{60}{}^*$ in PIPMA films as well as in benzene and toluene solutions reported previously,[2—6,8] the spectra of these solutions are safely assigned to the $S_n \leftarrow S_1$ transition of C_{60}. This assignment is supported by the spectral evolution of the time-resolved absorption spectra of these solutions. As a typical example, the spectral evolution for the C_{60}–*trans*-decalin solution is shown in Fig. 3. With an increase in the delay time after excitation, the absorption with a peak around 740 nm appears and increases. This absorption is safely assigned to the triplet state of C_{60} ($^3C_{60}{}^*$) on the basis of an agreement of the spectral band shape and its maximum with those previously reported.[1b,1d,1e] During the temporal evolution of the spectra, isosbestic points are detected at ca. 595 and 792 nm. As shown in Fig. 3b, the decay profile of the absorbance at 960 nm corresponds with the growth profile of $^3C_{60}{}^*$ monitored at 740 nm, and the time constant of the spectral change was found to be 1.2 ns. This time constant is equal to the lifetime (1.2 ns) reported for $^1C_{60}{}^*$ in toluene and benzene solutions and in PSt, PMMA, and PIPMA films.[2—5,8] Strictly viewing the spectra of $^1C_{60}{}^*$ of these five solutions ((1)—(5) in Fig. 2), we notice that the spectra slightly depend on the solvents.

Figure 4 shows the time-resolved absorption spectra of a C_{60}– 1,4-dimethylnaphthalene solution excited with a 532 nm picosecond laser pulse and the time dependence of the absorbances monitored at 745 and 937 nm, respectively. This solution shows the most different transient absorption spectrum from those of $^1C_{60}{}^*$ of the above five solutions among the C_{60}-solutions measured (Fig. 2); its ground-state absorption spectrum is also the most different because of the appearance of the CT transition (Fig. 1). With the delay time after excitation, an absorption with a peak around 750 nm appears and increases. Although this absorption spectrum is similar to the $^3C_{60}{}^*$-absorption spectra reported previously as well as that of the above C_{60}–*trans*-decalin solution (Fig. 3a), it may not be simply ascribed to $^3C_{60}{}^*$, because its bandwidth is slightly broad and its peak shifts slightly to longer wavelengths compared to the latter spectra (vide infra). During

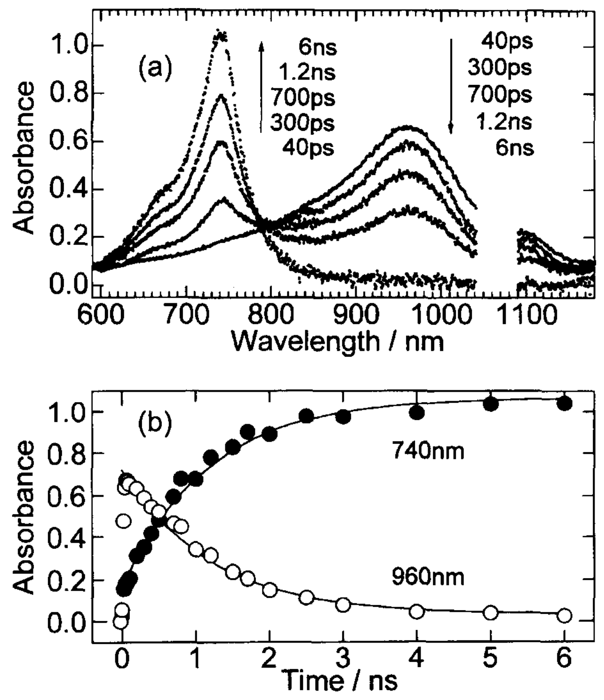

Fig. 3. (a) Time-resolved absorption spectra of C_{60} in the *trans*-decalin solution (concentration: slightly less than saturated solution), excited with a 532 nm picosecond laser pulse. (b) Time profiles of transient absorbance at 960 and 740 nm of the same sample solution. The solid lines represent the time constant of 1.2 ns.

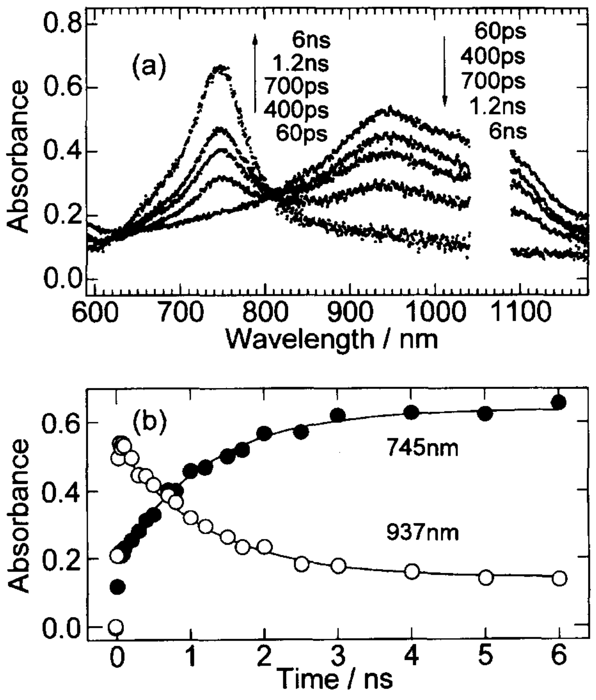

Fig. 4. (a) Time-resolved absorption spectra of C_{60} in the 1, 4-dimethynaphthalene solution(9.0×10^{-4} mol dm^{-3}), excited with a 532 nm picosecond laser pulse. (b) Time profiles of transient absorbance at 937 and 745 nm of the same sample solution. The solid lines represent the time constant of 1.2 ns.

spectral evolution, isosbestic points are observed at ca. 630 and 810 nm. The decay time (1.2 ns) of the absorbance monitored at 937 nm is in agreement with the growth time of the absorbance monitored at 745 nm. That is, the transient absorption spectrum observed immediately after excitation for the C_{60}–1,4-dimethylnaphthalene solution has the same decay-time constant as the lifetime of $^1C_{60}{}^*$ in the above five solutions as well as in PSt, PMMA, and PIPMA films,[2—5] although its spectral shape is considerably different from those (the spectrum of $^1C_{60}{}^*$) of the five C_{60} solutions. In addition, the early-gated absorption changes to absorption similar to that of $^3C_{60}{}^*$, both with the decay-time constant of 1.2 ns and with keeping isosbestic points.

Also, for all of the other C_{60}-solutions examined in the present work, we observed time evolutions of the time-resolved absorption spectra similar to those shown in Figs. 3a and 4a, where the spectra at the early gated window depend on the solvent as aforementioned (Fig. 2), and those in the late time region are also slightly dependent on the solvent (vide infra). On the contrary, the decay profiles of the absorbance monitored around 935—970 nm corresponded to the growth ones of the absorbance around 745—740 nm, the same as those in Figs. 3b and 4b. In addition, the time constants were found to be 1.2±0.05 ns for all solutions. Thus, for all C_{60}-solutions which contain solutions showing clear ground-state CT absorption spectra, the transient absorption spectra observed immediately after excitation change to absorption spectra similar to those of $^3C_{60}{}^*$ both with the same time constant (1.2 ns) as the lifetime of $^1C_{60}{}^*$ and with the isosbestic points, whereas their spectral shapes depend on the solvents. Such a solvent-dependence of the spectral shape of the C_{60}-transient absorption has never, to the best of our knowledge, been reported before.

Here, we discuss the transient absorption observed immediately after excitation (the early-gated absorption). In terms of the ground-state absorption spectra of C_{60} in solution, Gallagher et al. suggested the presence of an axial quadrupole in $^1C_{60}{}^*$, which is preferentially stabilized by polar solvents or by solvents with a tendency to interact through π-stacking. The interaction through π-stacking was deduced from the observation that the shift of the absorption increases from benzene-derivatives substituted with electron-withdrawing groups, though benzene, to benzene substituted with electron-donating groups.[21] Although chlorobenzene has an electron-withdrawing group and both its dielectric constant and refractive index are large compared with those of the other solvents (Table 1), the early-gated transient absorption spectrum of C_{60} in chlorobenzene shows a spectral shape intermediate between the C_{60}–benzene and –toluene solutions. In addition, although the dielectric constant of *o*-dichlorobenzene is very large, the spectral shape of the C_{60}–*o*-dichlorobenzene solution is intermediate between the C_{60}–*trans*-decalin and –benzene solutions. Furthermore, although veratrole is a benzene derivative substituted with two methoxy groups, the spectral shape of the transient absorption of C_{60} in veratrole is similar to that of the C_{60}–1,4-dimethylnaphthalene solution; these two solvents with small I_p form ground-state CT complexes with C_{60}. These results indicate that the early gated absorption spectra of C_{60} in solution do not correlate with the number of π-electrons of the solvent molecules, the properties of their substituents, their refractive indexes, or their dielectric constants, but to the I_p of the solvent molecules.

As shown in Fig. 2, the spectral deviation from the absorption spectrum of $^1C_{60}{}^*$ of the *trans*-decalin or *o*-dichlorobenzene solution increases as the I_p of solvent molecules decreases. The absorption band for solvents with small I_p is extraordinarily broad, which may indicate that it is composed of more than one broad transition. That is, one may see that in addition to the absorption band of $^1C_{60}{}^*$ observed for the C_{60}–*trans*-decalin or –benzene solution, a new absorption band appears and its intensity increases with a decrease in the I_p of the solvent molecules, although the mesitylene and 1,2,3,5-tetramethylbenzene solutions ((7) and (9) in Fig. 2) are exceptional for the increase in the intensity. This suggests a possibility that the spectral change depending on the I_p of solvent molecules can be ascribed to the appearance of a transition with the CT character. However, as we can see from Fig. 2, even if I_p of the solvent molecules of the donors varies from 8.82 eV for toluene to 7.82 eV for 1,4-dimethylnaphthalene, the estimated spectral shift is remarkably small (ca. 470 cm^{-1}, i.e. 0.06 eV).[24] That is, this finding is at variance with a relation for the usual CT absorption band observed for a change of the donor or acceptor in a given solvent. Hence, it is difficult to ascribe the solvent-dependent spectral shape of the early-gated absorption band to the appearance of a transition from $^1C_{60}{}^*$ to the excited CT state.

Here, in order to examine the role of the solvent molecules with a small I_p in determining the spectral shape of the early-gated absorption, we measured the time-resolved absorption spectra of a benzene solution containing C_{60} and *N*-ethylcarbazole (ECz) or PVCz, because the CT complex formation between PVCz and C_{60} is experimentally confirmed, as aforementioned. As shown in Fig. 5a, the irradiation at 532 nm corresponds to excitation of both the ground-state CT complexes and C_{60}. Since the energy level of the ion-pair states (Cz^+–C_{60}^-) produced by the direct excitation of the CT bands in a nonpolar benzene solution is higher than that of $^1C_{60}{}^*$, a rapid charge-recombination reaction in the ion-pair states takes place, thus producing $^1C_{60}{}^*$ and a neutral ground-state carbazolyl (Cz) chromophore within the laser pulse width (vide infra). Since $^1C_{60}{}^*$ produced by the recombination reaction is adjacent to the Cz chromophore with small I_p, its absorption spectral shape is expected to be affected by the neighboring Cz chromophore. In fact, the early-gated absorption spectra of the ECz– and PVCz–C_{60} benzene solutions are not due to ionic species (Cz^+ and $C_{60}{}^-$); further, they are different from that of $^1C_{60}{}^*$ in a benzene solution (Fig. 5b), whereas the time evolutions of their spectra (the presence of isosbestic points, an appearance of $^3C_{60}{}^*$ and its increase with a decrease in $^1C_{60}{}^*$) were the same as those observed for the above-mentioned other solutions. In addition, using mixed solvents of veratrole–*trans*-decalin or 1, 2-dimethylnaphthalene–*trans*-decalin, we found that the de-

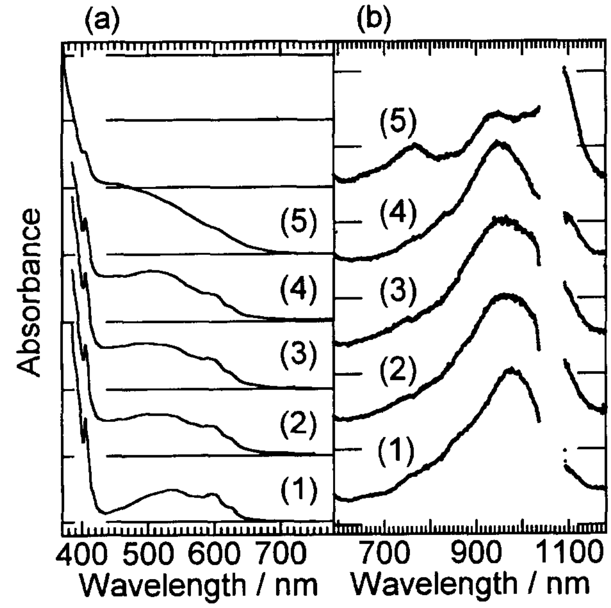

Fig. 5. (a) Ground-state absorption spectra of benzene solutions containing C_{60} and carbazolyl chromophores of various concentration. (b) Time-resolved absorption spectra observed at 40 ps after excitation. The concentration of C_{60} is 7.8×10^{-3} mol dm^{-3}.The concentration of carbazolyl units: (2) 0.51 mol dm^{-3} of PVCz, (3) 0.78 mol dm^{-3} of PVCz, (4) saturated concentration of ECz. As references: (1) C_{60}–benzene solution and (5) C_{60}–PVCz films.

viation of the early-gated absorption spectra of C_{60} in these mixed solvents from the ${}^1C_{60}{}^*$-absorption spectrum of the *trans*-decalin solution increased with the content of veratrole or 1,2-dimethylnaphthalene, whereas the temporal evolutions of their absorption spectra were the same as those for all other solutions. These results indicate that when one electron-donating molecule capable of forming CT complexes with C_{60} is adjacent to ${}^1C_{60}{}^*$, the spectral shape of the early-gated absorption differs from that of the normal ${}^1C_{60}{}^*$ in a solvent such as *trans*-decalin and benzene.

Because there exists a correlation between the spectral shape of the excited states of C_{60} and the I_p of solvent molecules, a candidate for the interpretation of the solvent-dependent spectral shape may be an excited-state complex (exciplex) formation between ${}^1C_{60}{}^*$ and solvent molecules. Here, the exciplex means excited-state complexes with a large contribution of the full CT-state (${}^1(C_{60}^-$–Solvent molecule$^+)^*$) configuration compared to that of the locally excited-state one. However, it is difficult to accept this candidate for the interpretation because of the following reasons: (1) As aforementioned, even the spectrum of the C_{60}–1,4-dimethylnaphthalene solution is not assigned to that of $C_{60}{}^-$. (2) Both the presence of the isosbestic points observed during the spectral evolution and the constant decay time of 1.2 ns, irrespective of solvents, require the establishment of rapid equilibrium between ${}^1C_{60}{}^*$ and the excited-state complexes. However, since the energy level of the excited-state complexes depends on the solvents of donors, it is impossible to establish such rapid equilibrium for all of the C_{60}-solution systems examined; in fact, the energy levels of the full CT state in these solvents are estimated to be higher than that of ${}^1C_{60}{}^*$.

Above, we described that it is difficult to accept the appearance of a transition with the CT character and the appearance of absorption due to excited-state complexes formed between ${}^1C_{60}{}^*$ and solvent molecules to interpret the solvent-dependent early-gated absorption spectra of C_{60}. However, since C_{60} is a spherical large molecule having a three-dimensional-like π-electronic system, the behavior of CT interaction concerning C_{60} molecules may be different from those of normal compounds having planar π-electronic systems. Hence, the above two interpretations referring CT character might not be completely denied.

On the basis of detailed studies of resonance Raman spectra of C_{60} in solution, the following items have been reported: numerous observed features are due to relaxation of the Raman selection rules caused by a reduction of the high symmetry of C_{60} in the solvent environment; a solvent-induced distortion of C_{60} which removes the degeneracy of its LUMO probably occurs through a donation of solvent-electron density to C_{60} via an enlarged external pπ lobe at each carbon; and the distortion is pronounced for aromatic solvents where the interaction is expected to occur through a π-stacking arrangement.[26] Integrating these reports, the correlation between the spectral shape of the C_{60}-excited states and the I_p of the solvent molecules, and the constant decay time of 1.2 ns irrespective of solvents, we can ascribe the solvent-dependent early-gated absorption spectra of C_{60} to ${}^1C_{60}{}^*$ with a distortion induced by specific interactions with solvents molecules through the donation of their π-electron density without forming obviously excited-state complexes. Since such an electron-donating interaction increases with decreasing I_p of the solvent molecules, a decrease in the I_p of the solvent molecules should result in an increase in the deviation of the ${}^1C_{60}{}^*$-absorption spectra from those in a solvent with a large I_p.

The specific interactions that induce a distortion of ${}^1C_{60}{}^*$ may, in a sense, imply ${}^1C_{60}{}^*$-solvent complex formation, although evidence of C_{60}-solvent complex formation in the ground state is not found appreciably for the ground-state absorption spectra of C_{60}-solutions, as aforementioned, but is suggested by their resonance Raman spectra.[26] In other words, this suggests that the locally excited state of C_{60} (${}^1C_{60}{}^*$–Solvent-molecule) with an extremely small contribution of the full CT-state configuration is likely to be responsible for the solvent-dependent early-gated absorption spectra of C_{60}. Although the contribution of the full CT-state configuration to the locally excited-state one is extremely small, a slight increase in the contribution induces an increase in the distortion of ${}^1C_{60}^*$ because of the high symmetrical structure of C_{60}, which situation results in an increase in the deviation of the ${}^1C_{60}{}^*$-absorption spectra from those in a solvent with a large I_p.

The excited state of C_{60} affected by such specific interactions is expected to result not only in a spectral change in the ${}^1C_{60}^*$-absorption band, but also in a change in its decay time.

As aforementioned, however, the decay times of 1.2±0.05 ns are independent of the solvents. Ma and Sun reported that the fluorescence spectrum of C_{60} in a 1-methylnaphthalene solution is slightly red-shifted and that its fluorescence yield is slightly large compared to those in the other solvents.[9] This suggests that a specific interaction induced by the donation of solvent-electron density to C_{60} is so weak that probably no change in the decay time of $^1C_{60}{}^*$ is found. Since the $S_n \leftarrow S_1$ absorption spectra of C_{60} are observed in the low-energy range (long wavelength range), a change in the spectral shape is most likely observed with an enhancement, even if such specific interactions are small.

As for methyl-substituted benzenes, in particular for mesitylene and 1,2,3,5-tetramethylbenzene, the change in the absorption spectral shape shows a slightly different tendency compared with those for the other solvents, as shown in Fig. 2. This suggests the presence of a steric effect on the solvent-induced distortion of C_{60}.

Transient Absorption Spectra upon Excitation of the Ground-State CT Absorption Band around 450 nm. We reported that the ionic species of C_{60}^- and $PVCz^+$ were detected for time-resolved absorption spectra monitored immediately after direct excitation of the CT absorption band of C_{60}–doped PVCz films.[8] Here, we measured the transient absorption spectra upon excitation of the ground-state CT absorption band around 450 nm of C_{60}-solutions. Figure 6a shows time-resolved absorption spectra of the C_{60}–2-ethylnaphthalene solution excited with a picosecond 450 nm laser pulse. Even in the spectra observed immediately after excitation, no absorption spectra of the ionic species of 2-ethylnaphthalene cation (with peaks at 630 and 690 nm)[27] and $C_{60}{}^-$ were found, but the same spectra as that observed upon direct excitation of C_{60} ((10) in Fig. 2) were observed. As shown in Fig. 6b, the temporal evolution of the absorption spectra is also the same as that of the time-resolved absorption spectra upon excitation of a 532 nm picosecond laser pulse, where the decay and growth of the spectra around 938 and 744 nm, respectively, are demonstrated both with a time constant of 1.2 ns and with isosbestic points. In addition, when the C_{60}–veratrole solution was excited with a 450 nm picosecond laser pulse, neither veratrole cation[27] nor $C_{60}{}^-$ were detected for the early-gated spectra, but both the spectra and their temporal evolution were the same as those observed on direct excitation of C_{60}. Thus, even if the absorption band of CT complexes formed between C_{60} and solvent molecules with a small I_p is excited, the same transient absorption spectra and their time evolution as those upon direct excitation of C_{60} are observed. Since the direct excitation of CT bands creates charge-separated (CS) states ($^1(C_{60}^-$–Solvent-molecule$^+)^*$), very rapid charge-recombination reaction most probably takes place to result in $^1C_{60}{}^*$. In fact, its reaction rate was estimated to be 4×10^{12} s^{-1} [29] on the basis of the energy gap (0.81 and 0.72 eV for 2-ethylnaphthalene and veratrole systems, respectively)[28] between the CS state and $^1C_{60}{}^*$ (2.0 eV). That is, the rapid charge-recombination process in the CS state is expected to be completed within the excitation-laser pulse width of the present measurement system.

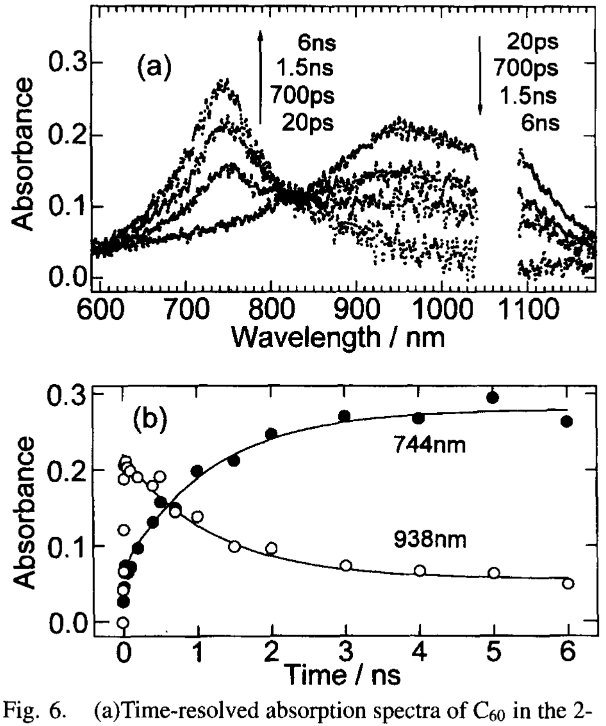

Fig. 6. (a)Time-resolved absorption spectra of C_{60} in the 2-ethylnaphthalene solution (6.5×10^{-4} mol dm^{-3}), excited with a 450 nm picosecond laser pulse. (b) Time profiles of transient absorbance at 938 and 744 nm of the sam sample solution. The solid lines represent the time constant of 1.2 ns.

Scurlock and Ogilby have reported that the excitation on ground-state contact CT complexes between C_{60} and substituted naphthalenes results in the normal fluorescence of C_{60}, which is the same as that observed for the C_{60}–toluene solution without naphthalenes, and that an excited-state complex with the CT character decays to yield a locally excited fluorescent state of C_{60}.[10] As aforementioned, Ma and Sun have reported that the fluorescence spectral shape of the C_{60}– 1-methylnaphthalene solution is similar to those in the other solvents used, although its spectral peak is slightly red-shifted and its fluorescence yield is slightly large compared with those in the other solvents.[9] Thus, the present results concerning the transient absorption measurement are consistent with those of these fluorescence measurements.

The fact that the same absorption spectral shapes of C_{60}-excited states are observed irrespective of the excitation of C_{60} or CT complexes is consistent with the above interpretation—the solvent-dependent transient absorption spectra of C_{60} are responsible for the distortion of $^1C_{60}{}^*$ which is specifically induced by solvent molecules through the donation of their π-electron density without forming obviously excited-state complexes.

Absorption Spectra of C_{60}-Excited State Observed in Late-Time Regions. Figure 7 shows the absorption spectra of the excited state of C_{60}-solutions observed in the late-time region. As aforementioned, all of the spectra rose both with a time constant of 1.2±0.05 ns and with keeping the isosbestic

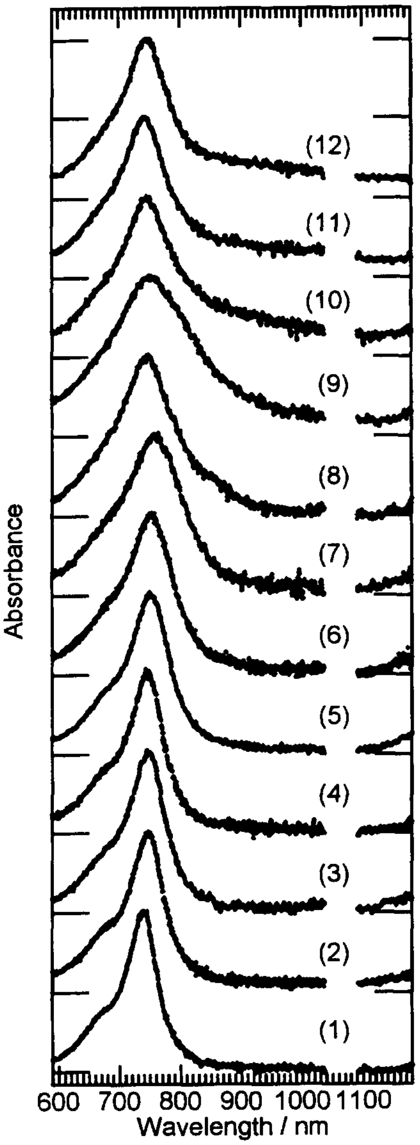

Fig. 7. Absorption spectra of C_{60}-excited state observed in the late-time region: (1) *trans*-decalin, (2) *o*-dichlorobenzene, (3) benzene, (4) chlorobenzene, (5) toluene, (6) *o*-xylene, (7) mesitylene, (8) anisole, (9) 1,2,3,5-tetramethylbenzene, (10) 2-ethylnaphthalene, (11) veratrole, and (12) 1,4-dimethylnaphthalene. Concentrations are the same as those in Fig. 2. The spectra are presented in order of I_p of solvents. These spectra were observed at 6 ns after excitation.

points. One notices that the spectra become broader along with decreasing I_p of the solvent molecules and, in particular, that the spectra for the methyl-substituted benzenes become broader along with an increase in the number of methyl substitutions. However, the deviation of the spectra from that of the C_{60}–*trans*-decalin solution (the absorption spectrum of $^3C_{60}{}^*$) is considerably small compared with those of $^1C_{60}{}^*$, which is consistent with the fact that the previously reported $^3C_{60}^*$-absorption spectra have not shown any large variation from experiment to experiment. The specific behavior of the absorption spectra for the methyl-substituted benzene solution system is similar to that observed for the $^1C_{60}{}^*$-absorption spectra.

As aforementioned, the absorption spectra of the C_{60}–solutions in the late time region slightly depend on I_p of the solvent molecules. Assuming that the deviation in the spectral shape from that of $^3C_{60}{}^*$ in *trans*-decalin is also ascribable to the same reason as that for $^1C_{60}^*$, these spectra are assigned to the $T_n \leftarrow T_1$ absorption of C_{60}. That is, the spectra of $^3C_{60}{}^*$ are also responsible for the distortion of C_{60} induced by solvents molecules through the donation of their π-electron density without forming obviously excited-state complexes.

Conclusion

The absorption spectra of C_{60}-excited states in twelve solvents did not depend on the dielectric constant of the solvents or their refractive index, but on their ionization potential. The dependence was large for the spectra of $^1C_{60}{}^*$ observed immediately after excitation, while they were considerably small for those of $^3C_{60}{}^*$ in the late-time region. The spectra of $^1C_{60}{}^*$ in solvents with small I_p were rather broad compared with those in solvents with a large I_p. The broad $^1C_{60}{}^*$-spectra also changed to the spectra of $^3C_{60}{}^*$, both with isosbestic points and with a time constant of 1.2 ns. These solvent-dependent spectral shapes of the C_{60}-excited states were considered to be ascribed to C_{60}, which is specifically distorted by solvents molecules through donation of their π-electron density without forming obviously excited-state complexes.

Even if the ground-state CT absorption band around 450 nm, observed only for C_{60} in non-polar solvents with small I_p, was excited, no absorption of the ionic species was found, but the spectra were the same as those observed upon the direct excitation of C_{60}. This indicates that the photogenerated ion-pair states ($^1(C_{60}{}^-$–Solvent-molecule$^+)^*$) undergo a very rapid charge-recombination reaction resulting in $^1C_{60}{}^*$ and the ground-state solvent molecule.

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References

1 For example: a) R. J. Sension, A. Z. Szarka, G. R. Smith, and R. M. Hochstrasser, *Chem. Phys. Lett.*, **185**, 179 (1991). b) J. W. Arbogast, C. S. Foote, and M. Kao, *J. Am. Chem. Soc.*, **114**, 2277 (1992). c) L. Biczok, H. Linschitz, and R. I. Walter, *Chem. Phys. Lett.*, **195**, 339 (1992). d) A. Watanabe and O. Ito, *J. Phys. Chem.*, **98**, 7736 (1994). e) A. Watanabe and O. Ito, *J. Chem. Soc., Chem. Commun.*, **1994**, 1285. f) C. A. Steren, H. v. Willigen, L. Biczok, N. Gupta, and H. Linschitz, *J. Phys. Chem.*, **100**, 8920 (1996).

2 G. Sauve, N. M. Dimitrijevic, and P. V. Kamat, *J. Phys. Chem.*, **99**, 1199 (1995).

3 W. Ebbesen, K. Tanigaki, and S. Kuroshima, *Chem. Phys. Lett.*, **181**, 501 (1991).

4 M. Lee, O-K. Song, J-C. Seo, D. Kim, Y. D. Suh, S. M. Jin, and S. K. Kim, *Chem. Phys. Lett.*, **196**, 325 (1992).

5 M. Gevaert and P. V. Kamat, *J. Phys. Chem.*, **96**, 9883 (1992).

6 A. Watanabe, O. Ito, M. Watanabe, H. Saito, and M. Koishi, *J. Chem. Soc., Chem. Commun.*, **1996**, 117.

7 S. Nath, H. Pal, D. K. Palit, A. V. Sapre, and J. P. Mittal, *J. Phys. Chem. B.*, **102**, 10158 (1998).

8 A. Itaya, I. Suzuki, Y. Tsuboi, and H. Miyasaka, *J. Phys. Chem. B.*, **101**, 5118 (1997).

9 B. Ma and Y-P. Sun, *J. Chem. Soc., Perkin. Trans. 2*, **1996**, 2157.

10 R. D. Scurlock and P. R. Ogilby, *J. Photochem. Photobiol. A. Chem.*, **91**, 21 (1995).

11 V. V. Golovlev, W. R. Garrett, and C. H. Chen, *J. Opt. Soc. Am. B*, **13**, 2801 (1996), and cited therein.

12 J. Barroso, A. Costela, I. Garcia-Moreno, and J. L. Saiz, *J. Phys. Chem. A*, **102**, 2527 (1998).

13 H. Miyasaka, T. Moriyama, S. Kotani, R. Muneyasu, and A. Itaya, *Chem. Phys. Lett.*, **225**, 315 (1994).

14 Y. Wang, *Nature*, **356**, 585 (1992).

15 Y. Wang and A. Suna, *J. Phys. Chem. B.*, **101**, 5627 (1997).

16 R. V. Bensasson, E. Bienvenue, M. Dellinger, S. Leach, and P. Seta, *J. Phys. Chem.*, **98**, 3492 (1994).

17 O. Ermer, *Helv. Chim. Acta*, **74**, 1339 (1991).

18 W. A. Scrivens and J. M. Tour, *J. Chem. Soc., Chem. Commun.*, **1993**, 1207.

19 J. Catalan, J. L. Saiz, J. L. Laynez, N. Jagerovic, and J. Elguero, *Angew. Chem., Int. Ed. Engl.*, **34**, 105 (1995).

20 J. Catalan, *New J. Chem.*, **19**, 1233 (1995).

21 S. H. Gallagher, R. S. Armstrong, P. A. Lay, and C. A. Reed, *J. Phys. Chem.*, **99**, 5817 (1995).

22 For example: a) Y. Wang, *J. Phys. Chem.*, **96**, 764 (1992); Y.-P. Sun, C. E. Bunker, and B. Ma, *J. Am. Chem. Soc.*, **116**, 9696 (1994). b) S. P. Sibley, R. L. Campbell, and H. B. Silber, *J. Phys. Chem.*, **99**, 5274 (1995).

23 S. P. Sibley, Y. T. Nguyen, R. L. Campbell, and H. B. Silber, *Spectrochim. Acta, Part A*, **A53**, 679 (1997).

24 We decomposed the spectra into two components, extrapolating the absorption spectra in the 1040—1090 nm wavelength range and assuming both that the spectral shape of one component is similar to that of the $S_n \leftarrow S_1$ absorption of the C_{60}-*trans*-decalin solution and that the spectral shape of the other band is Gausian functional form. It was difficult to decompose the early-gated spectra of (2)—(4) in Fig. 2, and the decomposition to two bands with the above two assumptions was not able to be perfectly fitted to all the spectra of (5)—(12) in Fig. 2. However, a new absorption was found, and its relative peak intensities to the other absorption band in the decomposed spectra increased with decreasing I_p of solvent molecules, except for mesitylene and 1,2,3,5-tetramethylbenzene. In addition, their peaks showed very slight shift to long wavelengths (to low wavenumbers).

25 W. A. Scrivens and J. M. Tour, *J. Chem. Soc., Chem. Commun.*, **1993**, 1207. They reported that formation of precipitates between C_{60} and mesitylene is unusual rapid. Although we also observed the formation of precipitates for the C_{60}-mesitylene solution during measuring transient absorption spectra, the spectra shown in the Figures were measured before the formation of the precipitates.

26 a) S. H. Gallagher, R. S. Armstrong, R. A. Lay, and C. A. Reed, *Chem. Phys. Lett.*, **248**, 353 (1996). b) S. H. Gallagher, R. S. Armstrong, W. A. Clucas, R. A. Lay, and C. A. Reed, *J. Phys. Chem. A*, **101**, 2960 (1997).

27 T. Shida, "Electronic Absorption Spectra of Radical Ions," Elsevier, Amsterdam (1988).

28 These values were estimated as follows: the energy of the charge-separated state (C_{60}^{-}–Cz^{+}) E_{IP} with respect to the ground state can be expressed as

$$E_{IP} = I_p - E_a + P_+ + P_- + C,$$

where I_p is the ionization potential of the carbazolyl chromophore in the gas phase, E_a is the electron affinity of C_{60} (2.65 eV), P_+ and P_- are the polarization energies of Cz^+ and C_{60}^{-}, respectively, and C is the Coulomb energy. On the assumption that the Born equation is applicable to non-polar benzene solution, the polarization energy P was estimated by the equation; $P_\pm = -(e^2/8\pi\varepsilon_0 r_\pm)\ [1-(1/\varepsilon)]$, where e is the elementary charge, ε_0 is permitivity of the vacuum, and $r_\pm$ is the effective radius of the cation or anion. Here, we used 5 and 3.5 Å for r of C_{60}^{-} and Cz^+ (r_- and r_+), respectively. The magnitude of C was estimated as $C = -e^2/(4\pi\varepsilon\varepsilon_0 R_{IP})$, where R_{IP} is the center-to-center distance between Cz^+ and $C_{60}{}^-$ in the ion-pair state. We used 8.5 Å as R_{IP}.

29 H. Miyasaka, S. Kotani, A. Itaya, G. Schweitzer, F. C. De Schryver, and N. Mataga, *J. Phys. Chem. B*, **101**, 7978 (1997).