Charge recombination in photoexcited charge transfer complexes between fullerenes and triphenylamine. Effect of the solvent polarity

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The relaxation of photoexcited charge transfer complexes between C_{60} and C_{70} fullerene molecules and triphenylamine was studied by the picosecond laser photolysis technique in solvents of various polarities. A scheme of transitions from the radical-ion pair state to the ground and local-excited states of the complex was proposed. The rate constants of the transition between the radical-ion and local excited states were calculated in terms of the one-mode electron transfer model. The suggested scheme of transitions in excited complexes is sufficient for the description of the main kinetic regularities in this system and the dependence of the yield of triplet fullerene on the polarity of the medium upon the relaxation of the complex.

Key words: fullerenes, charge transfer complexes, electron transfer; picosecond laser photolysis.

The photoinduced transfer of charges followed by their recombination in the radical-ion pair formed in solutions, solid matrices, and biological systems is an important fundamental problem of photophysics and photochemistry. It is known that electron transfer rate constants are controlled by the following factors:

— the value of the electron-electron interaction (V) determining the transfer of an electron between an electron donor and acceptor;

— the Franck—Condon factor (FC) related to the value of the energy gap ΔG between the redox states;

— the electron-vibrational interaction (S), which is directly expressed by the intramolecular reorganization energy (λ_{in}) and the frequency of intramolecular vibrations (ω_{in}) related to the electron transfer $S = \lambda_{in}/h\omega_{in}$, as well as by the external reorganization energy of a polar solvent (λ_0) and characteristic times of dielectric relaxation of dipoles of the solvent τ_L.[1—21]

The photoinduced electron transfer followed by the charge recombination in charge transfer complexes is a convenient experimental system for checking and developing the present theoretical concepts on the electron transfer, because in this system, as far as is possible, processes of diffusion collisions between a donor and acceptor are ruled out, and reagents are remote at a distance close to a sum of the molecular radii.[9—21] Previously, we have studied the processes of charge recombination in several complexes with transfer of charges between C_{60} or C_{70} and tertiary aromatic amines.[12a—14] The inverse dependence of the rate constant of charge recombination on ΔG was established.

This work used the picosecond laser photolysis technique to study the effect of the medium polarity on the charge recombination for complexes with the transfer of a charge between C_{60} or C_{70} and triphenylamine (TPA). These complexes are of special interest, because in low-polar solvents, for example, in chlorobenzene ($\varepsilon = 5.62$), the energy level of the radical-ion pair is close in value to the local-excited first singlet state of a fullerene molecule in the complex. Therefore, the radical-ion pair can relax to both the ground state and local-excited singlet and triplet states of fullerenes. The polarity of a medium ε affects the position of the level of the radical-ion state ΔG and the value of the external reorganization energy of the medium λ_0. As a result, the rate of transitions from the charge-transfer state to the local-excited and ground states of the complex changes.

We studied the kinetics of transition in the photoexcited complexes of C_{60} and C_{70} with TPA at different polarities of the solvent ε. The experimental dependences of the kinetics of relaxation of these complexes and the quantum yield of the triplet fullerene on ε were compared with the simulations. The development of the model was based on the concepts on the transition between the charge-transfer state and local-excited states as the transfer of an electron between the radical anion C_{60}^{-} and radical cation TPA^{+}. Some data on the parameters, which are necessary for this calculation, were obtained previously[13—15] in independent experiments when the dependence of the charge recombination rate constant on ΔG was analyzed in a series of complexes between fullerenes and tertiary aromatic amines.

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For photoexcited complexes between fullerenes and amines (see Refs. 22—29), it is typical that the complex excited to the charge-transfer state is a contact radical-ion pair. The relaxation rate of this state has been analysed in terms of the electron transfer theory only in three works.[12a—14]

Experimental

C_{60} and C_{70} fullerenes obtained by the previously described method[30] were used. They were purified by column chromatography on Al_2O_3. The purity of the fullerenes was higher than 98%. Solvents (chlorobenzene and benzonitrile) were purified from admixtures according to standard procedures by multiple distillation. Triphenylamine was recrystallized from chlorobenzene.

Picosecond experiments were carried out on a laser kinetic spectrometer equipped with a personal computer. A picosecond laser with an Nd^{3+} : YAP-active element, three amplification cascades, and an active-passive mode synchronization was used (wavelength of generation at the main harmonic was 1080 nm, pulse duration at the half-height was 18 ps). The second harmonic of the laser generation of 540 nm was used for the excitation of a sample, and the density of the excitation energy of a sample was varied from 0.1 to 5 mJ cm^{-2}. In this interval of excitation energies, the energy of the laser had no effect on the kinetics of the observed signal. A picosecond laser continuum excited by a pulse of the main harmonic of the laser in an equimolar mixture of H_2O and D_2O was used for recording absorption spectra and kinetic curves of a change in the optical density of a sample after excitation.

Kinetic curves of a change in the optical density in the photoexcited system were recorded by two silicon photodiodes mounted behind an MDR-2 aperture monochromator. Differential spectra of the photoexcited sample were determined using the same procedure. In addition, an optical multichannel detection system based on two devices with charge connection (PZS-detectors) mounted behind a monochromator was used for recording differential excitation spectra. In this case, unlike the system with two photodiodes, an absorption spectrum can be simultaneously recorded by 512 channels and an optical spectrum can be recorded in more detail. However, the multichannel system has considerable restrictions in sensitivity in the near IR region, and measurements with two diodes substantially supplement the data obtained.

Experiments were carried out in air in a 2-mm quartz cell at room temperature. Reagents were stirred to prevent the decomposition of a sample. The concentration of fullerene was ~$5 \cdot 10^{-4}$ mol L^{-1}, and the concentration of TPA was ~1.2 mol L^{-1}. Experimental conditions were chosen in such a way that the concentration of the fullerene that was unbound in the complex was minimum.

Results and Discussion

C_{60} and C_{70} fullerenes with TPA in solutions form charge transfer complexes.[12—14] The X-ray analysis of single crystals of a complex between C_{60} and TPA showed a 1 : 1 composition. The main spectral parameters of the complex were presented in Refs. 13 and 14. As shown below, the relaxation of the excited complex depends on the polarity of the solvent ε.

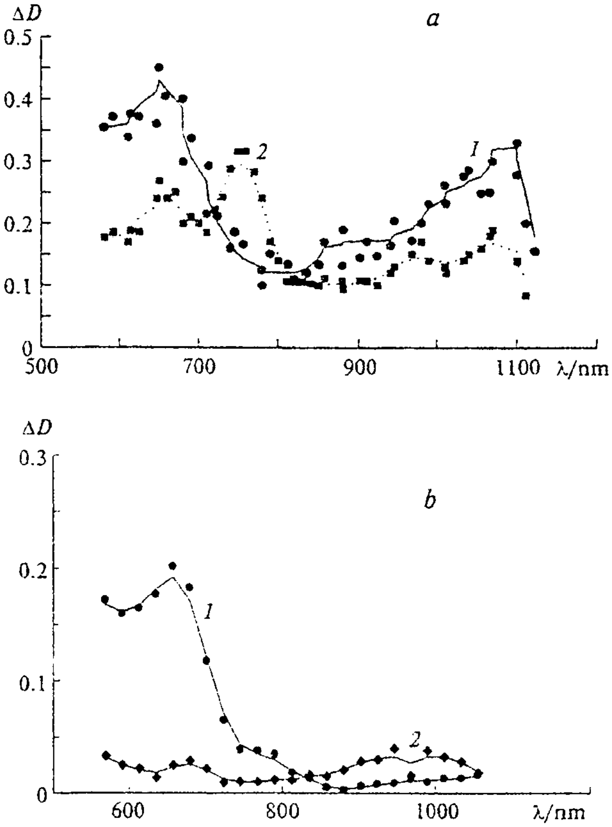

Fig. 1. Differential absorption spectra upon excitation of C_{60}—TPA and C_{70}—TPA in chlorobenzene. The spectra were obtained using two photodiodes; the delay time was 5 ps (*1*) and 1200 ps (*2*).
a, C_{60}—TPA ($[C_{60}] = 5 \cdot 10^{-4}$ mol L^{-1}; [TPA] = 1.15 mol L^{-1}); *b*, C_{70}—TPA ($[C_{70}] = 4 \cdot 10^{-4}$ mol L^{-1}, [TPA] = 1.2 mol L^{-1}).

The differential absorption spectra upon excitation of C_{60}—TPA and C_{70}—TPA in chlorobenzene (Fig. 1) are a superposition of the absorption spectrum of the fullerene radical anion and the TPA^+ radical cation. An absorption band of the C_{60}^- radical anion at ~1070 nm and that of the TPA^+ radical cation at ~650 nm are observed in the spectrum in Fig. 1, *a*. The spectrum of the system with C_{70} contains a band of TPA^+ and a broad band of C_{70}^- at the same times (see Fig. 1, *b*). The formation of the radical-ion pair occurs over a time shorter than the duration of the exciting pulse, *i.e.*, more rapidly than 18 ps. As TPA^+ and the fullerene radical anion decay in chlorobenzene, characteristic absorption bands of the triplet-excited fullerene appear in the spectra: λ = 750 nm for C_{60} and $\lambda \approx$ 980 nm for C_{70}. At the initial times, the differential absorption spectra of solutions of C_{60} and C_{70} without amine (S_1—S_x-transitions of the excited fullerene molecule) differ substantially from the spectra of the systems with the added amine.[12b,32,35]

Figure 2, *a*, *b* shows that the T_1—T_x-absorption (λ = 750 nm) for the C_{60}—TPA system is observed in

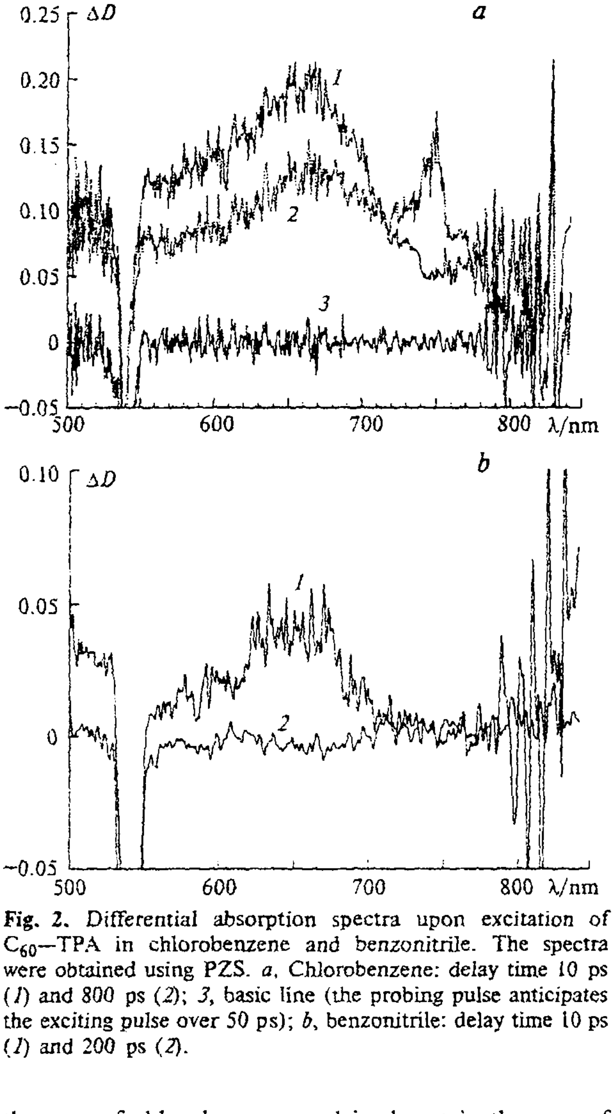

Fig. 2. Differential absorption spectra upon excitation of C_{60}—TPA in chlorobenzene and benzonitrile. The spectra were obtained using PZS. *a*, Chlorobenzene: delay time 10 ps (*1*) and 800 ps (*2*); *3*, basic line (the probing pulse anticipates the exciting pulse over 50 ps); *b*, benzonitrile: delay time 10 ps (*1*) and 200 ps (*2*).

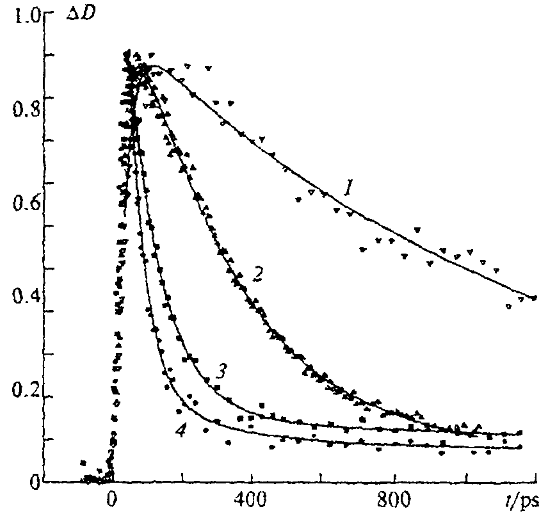

Fig. 3. Change in the optical density (λ = 1040 nm) with time for C_{60}—TPA; $[C_{60}] = 5 \cdot 10^{-4}$ mol L^{-1}, $[TPA] = 1.15$ mol L^{-1}. *1*, Chlorobenzene 100%; *2*, chlorobenzene 80% + benzonitrile 20%; *3*, chlorobenzene 30% + benzonitrile 70%; *4*, benzonitrile 100%. The approximation of experimental points by the biexponential function is shown by solid lines.

the case of chlorobenzene and is absent in the case of benzonitrile. In addition, it also can be seen from Fig. 2 that the excited state decays in benzonitrile much faster than in chlorobenzene.

For the C_{60}—TPA system, the rate of a decrease in the absorption at 1040 nm increases as the molar fraction of benzonitrile increases (Fig. 3). In the case of low-polar chlorobenzene, the kinetics at short times (shorter than 100—200 ps) are somewhat "pulled" (see Fig. 3, curve *1*). The kinetics curves of absorption of TPA^+ (λ = 650 nm) are similar to the curves for λ = 1040 nm. These relaxation curves are mainly caused by the recombination of charges in the pair of C_{60}^- and TPA^+. The kinetics curves of the decay of the fullerene radical anion (λ = 1040 nm) and TPA^+ radical cation (λ = 650 nm) are similar but do not coincide. This is associated with the fact that the absorption bands of the radical ions of the singlet- and triplet-excited states are partially overlapped. For example, the wavelength of 1040 nm is close to the wavelength of the absorption maximum of the C^-_{60} radical anion (λ = 1070 nm), but the S_1—S_x-absorption is possible at 1040 nm, because the maximum of the S_1—S_x-absorption band of the excited C_{60} is located at λ = 980 nm.[32]

The change in the optical density at 750 nm (maximum of the absorption band of the T_1-state of C_{60}) with time in the C_{60}—TPA system with different molar fractions of benzonitrile is shown in Fig. 4. As can be seen,

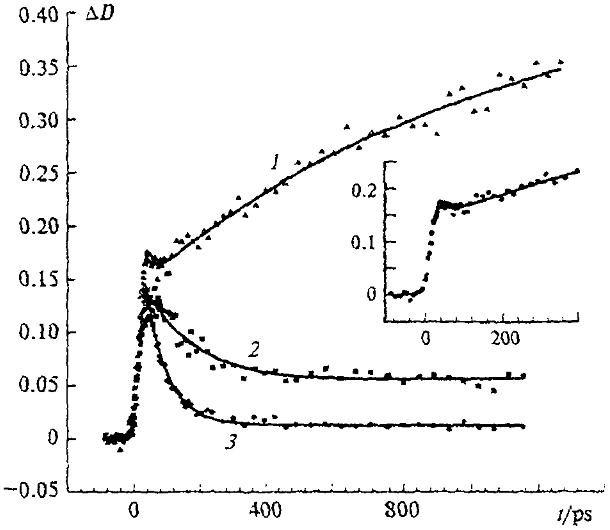

Fig. 4. Change in the optical density (λ = 750 nm) with time for C_{60}—TPA; $[C_{60}] = 5 \cdot 10^{-4}$ mol L^{-1}, $[TPA] = 1.15$ mol L^{-1}. *1*, Chlorobenzene 100%; *2*, chlorobenzene 80% + benzonitrile 20%; *3*, benzonitrile 100%. The approximation of experimental points by the biexponential function is shown by solid lines. The initial stage of the kinetic curve is shown in insertion.

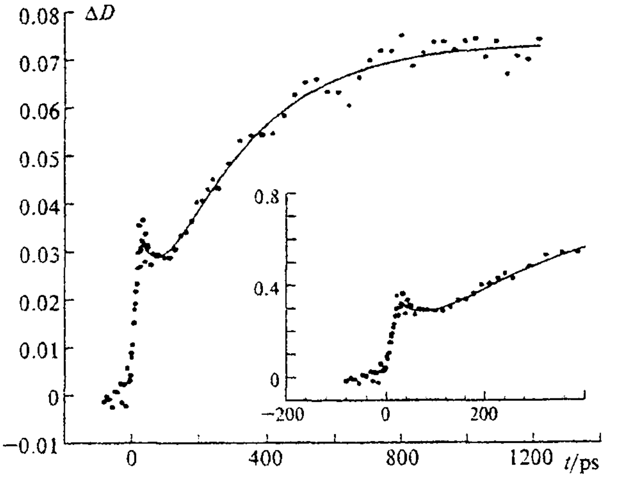

Fig. 5. Change in the optical density (λ = 945 nm) with time for C_{70}—TPA in chlorobenzene; $[C_{70}]$ = $4 \cdot 10^{-4}$ mol L^{-1}, [TPA] = 1.2 mol L^{-1}. The approximation of experimental points by the biexponential function is shown by solid lines. The initial stage of the kinetic curve is shown in insertion.

the shape of the kinetic curves changes qualitatively as the molar fraction of the polar solvent increases: as ε increases, the kinetic curve of an increase in the optical density is transformed into a relaxation kinetic curve. It is noteworthy that for the times on an order of magnitude of 100 ps, the kinetic curve of the optical density has a "minimum" in the case of chlorobenzene.

The kinetic curves of a change in the optical density at 650 nm (absorption maximum for TPA^+) for the C_{70}—TPA system in chlorobenzene, a chlorobenzene—benzonitrile mixture, and benzonitrile demonstrate the same regularities as in the C_{60}—TPA system.

The kinetic curve for the C_{70}—TPA system at 980 nm (maximum of the absorption band of the excited C_{70}) is presented in Fig. 5. Figure 5 more distinctly demonstrates the change in the optical density at short times (~100 ps) in the case of chlorobenzene: in this case, the "minimum" of the optical density is observed as for C_{60}.

Generalizing the obtained experimental results, we can draw the following conclusions: 1) excitation of the complexes between fullerene (F) and triphenylamine $F^{\delta+}$—$TPA^{\delta+}$ results in the formation of the charge-transfer states, which spectrally manifest themselves as a pair of radical ions F^-/TPA^+; 2) along with the relaxation to the ground state $F^{\delta-}/TPA^{\delta+}$, the decay of F^-/TPA^+ in chlorobenzene is determined by transitions to the local-excited S_1- and T_1-states of fullerene, which is indicated by a decrease followed by an increase in the optical density (see Figs. 4 and 5), as well as the "pulled" run of the curve at short times at 1040 nm (see Fig. 3); 3) as the polarity of the solvent increases, the relaxation of F^-/TPA^+ occurs mainly to the ground state of the complex, and the transitions to the local-excited S_1- and T_1-states become less important. This is indicated by the disappearance of the band of the triplet fullerene as ε increase; 4) the value of the characteristic time of an increase in the absorption at 750 nm for C_{60} and at 980 nm for C_{70} in chlorobenzene is close in value to the time of the intersystem crossing in a fullerene molecule, which is 1100±200 ps for C_{60} and 580±50 ps for C_{70}.[12b]

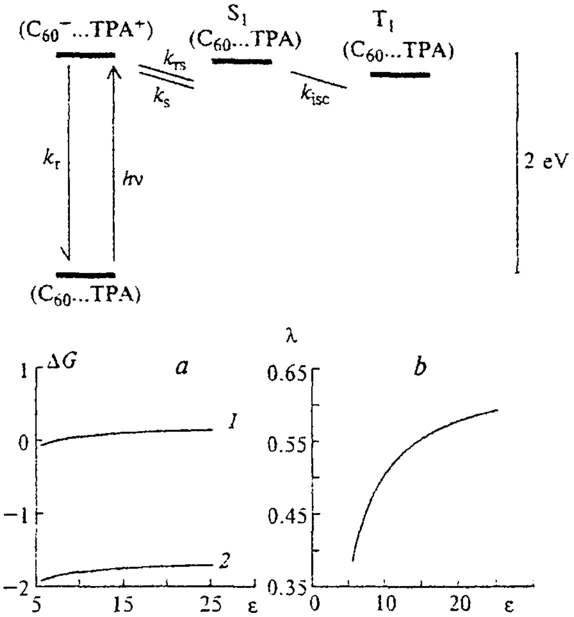

Fig. 6. Scheme of interelectronic transitions for F/TPA complexes. *a*, Dependence of the difference in energies ΔG between states on ε: *1*, $(F^*/TPA)^1$ and (F^-/TPA^+); *2*, $(F^{\delta-}/TPA^{\delta+})$ and (F^-/TPA^+); *b*, dependence of the external reorganization energy of the system λ_0 on ε.

Let us consider the obtained kinetic curves and the dependence of the yield of the triplet fullerene on the polarity of the solvent in terms of the model of transitions between individual states of the excited complex. The general scheme of possible transitions is shown in Fig. 6. The quantum yield of the triplet fullerene and the kinetics of relaxation of the excited complex are determined by the constants k_r and k_{rs}. Let us analyze the rate constants of the transitions of the radical-ion state F^-/TPA^+ to the singlet $(F^*/TPA)^1$ and ground $(F^{\delta-}/TPA^{\delta+})$ states in terms of the electron transfer theory.[1—8] The electron transfer rate constant k_{et} can be calculated from the equation:

$$k_{et} = 2\pi/\hbar \cdot V^2 \cdot \mathrm{FC}(\Delta G, \lambda_0, \lambda_{in}, \hbar\omega, kT, \tau_L), \quad (1)$$

where V is the electron-electron interaction parameter; $\hbar$ is Planck's constant; and FC is the Franck—Condon factor depending on the value of the energy gap ΔG, the values of external (λ_0) and internal (λ_{in}) reorganization energies, the frequency of vibrations ω of the electron-vibrational interaction, temperature (T), and the dynamics of relaxation of dipoles of the solvent characterized by the longitudinal time of dipole relaxation (τ_L).

The dependence of the energy of the radical-ion pair F^-/TPA^+ (ΔG_r) on the polarity ε can be determined from formula (2), as has been suggested previously.[38–40]

$$-\Delta G_r = E_{1/2}(\mathrm{TPA/TPA^+}) - E_{1/2}(\mathrm{F^-/F}) - e^2/R\varepsilon + \Delta,$$

$$\Delta = e^2/2 \cdot (1/r_{\mathrm{TPA}} + 1/r_{\mathrm{F}}) \cdot (1/\varepsilon - 1/37.5), \qquad (2)$$

where $E_{1/2}$ (C_{60}^-/C_{60}) = −0.52 eV,[32] $E_{1/2}$ (C_{70}^-/C_{70}) = −0.49 eV,[32] and $E_{1/2}$ ($\mathrm{TPA/TPA^+}$) = 1.12 eV [33] in acetonitrile relative to SCE; r_F and r_{TPA} are the radii of the fullerene and amine ions; and R = 12.5 Å is the distance between C_{60} and TPA in a single crystal of the $C_{60} \cdot$ TPA complexes.

One may believe that the position of the local-excited levels $(\mathrm{F^*/TPA})^1$ and $(\mathrm{F^*/TPA})^3$ coincides with the position of the levels of the singlet- and triplet-excited C_{60} molecules: (S_1) = 1.89, C_{70} (S_1) = 1.90, C_{60} (T_1) = 1.55, and C_{70} (T_1) = 1.60 eV,[32] and should slightly depend on the polarity of the medium. The energy gaps between the $(\mathrm{F^-/TPA^+})$ and $(\mathrm{F^*/TPA})$ levels can be calculated from the equation

$$\Delta G_s = \Delta G_r - E(S_1). \qquad (3)$$

The ΔG values for these transitions at different polarities of the medium are shown in Fig. 6, *a*. It is noteworthy that in low-polar chlorobenzene, the $(\mathrm{F^-/TPA^+})$ state is located higher than the $(\mathrm{F^*/TPA})^1$ state, while in polar benzonitrile, the $(\mathrm{F^*/TPA})^1$ level is higher than the $(\mathrm{F^-/TPA^+})$ level. The rate constants of intersystem crossing k_{isc} from the $(\mathrm{F^*/TPA})^1$ state to the $(\mathrm{F^*/TPA})^3$ state are likely close in value to the constants in isolated fullerene molecules, and for C_{60}, $k_{\mathrm{isc}} = 0.769 \cdot 10^9$ s^{-1} [12b,31,5,36] and for C_{70}, $k_{\mathrm{isc}} = 1.86 \cdot 10^9$ s^{-1}.[12b,35,36] Since the quantum yield of the triplet fullerene is close to unity, the intersystem crossing is the main channel of relaxation of the S_1-state for C_{60} and C_{70}.[12b,36]

The following substantial simplifications will be made further in the discussion: 1) The formation of the solvate-separated radical-ion pair $\mathrm{F^-/TPA^+}$ due to the diffusion motion and dissociation of $\mathrm{F^-/TPA^+}$ will not be taken into account. The decomposition of the tight radical-ion pair to form a solvate-separated pair should be accelerated as ε of the medium increases,[22] which should result in a decrease in the yield of the singlet- and triplet-excited fullerene. 2) Electron transfer rate constants will be considered in the one-mode approximation.[2] 3) Values of the electron-electron interaction parameters V, internal reorganization energy λ_{in}, and frequency of vibrations ω for the $(\mathrm{F^-/TPA^+})^1$—$(\mathrm{F^{\delta-}/TPA^{\delta+}})$ and $(\mathrm{F^-/TPA^+})^1$—$(\mathrm{F^*/TPA})^1$ transitions can differ. Nevertheless, for estimation, all these parameters are accepted to be equal for both transitions. Previously, based on the analysis of the extinction coefficient of the charge-transfer band in the complexes of C_{60} with TPA, the V value was obtained to be equal to 565 cm^{-1}.[12a,13] This value corresponds to the transition $(\mathrm{F^-/TPA^+})^1 \rightarrow (\mathrm{F^{\delta-}/TPA^{\delta+}})$. The high value of V is caused by a strong electron-electron interaction in the charge transfer complexes.[12a–14] Taking into account the analysis of the dependence of k_{et} on the value of the energy gap ΔG in several complexes with the transfer of a charge between C_{60} or C_{70} [12a–14] and various aromatic tertiary amines, it was shown that the internal reorganization energy λ_{in} is close to 0.32 eV. This value corresponds to the λ_{in} values for the charge transfer complexes of planar aromatic molecules with tertiary aromatic amines.[21]

The value of the reorganization energy of the medium λ_0 can be determined from the expression

$$\lambda_0 = e^2 \cdot [1/(2r_{\mathrm{F}}) + 1/(2r_{\mathrm{TPA}}) - 1/R] \cdot (1/\varepsilon_0 - 1/\varepsilon), \qquad (4)$$

where ε_∞ is the dielectric permeability at optical frequencies. The dependence of λ_0 on ε is shown in Fig. 6, *b*. The condition of applicability of Eq. (4) is the inequality $\lambda_0 \gg kT$.[1]

The value of the FC factor can be calculated according to the equation[2]

$$\mathrm{FC} = \sqrt{\frac{1}{\lambda_0 kT \cdot 4\pi}} \cdot \sum_{n=0} \frac{S^n}{n!} \cdot \exp(-S) \times$$

$$\times \frac{\exp[-(\lambda_0 + n \cdot \hbar\omega + \Delta G)^2 / (4\lambda_0 kT)]}{1 + H_n},$$

$$H_n = \frac{4\pi V^2 \tau_{\mathrm{L}}}{\lambda_0 \hbar} \cdot \frac{S^n}{n!} \cdot \exp(-S), \qquad (5)$$

similarly to that obtained previously[12a–14] by the analysis of the dependence of k_r on the value of the energy gap ΔG. Here H_n is the nonadiabaticity parameter; $S = \lambda_{\mathrm{in}}/\hbar\omega$; and τ_{L} = 5.67 ps for chlorobenzene[12a–14] and 5.03 ps for benzonitrile.[37]

According to Eqs. (1)—(5), we calculated the rate constants k_r and k_{rs} for various ε values from 5.62 for chlorobenzene to 25.2 for benzonitrile.

Let us consider the kinetics of the population of individual states to compare the experimental kinetic curves and the experimental dependence of the quantum yield of the triplet fullerene on the polarity of the medium. According to the scheme of transitions (see Fig. 6), the population of the states is described by the following system of equations:

$$\left.\begin{aligned} &d[\mathrm{CT}^1]/dt = -(k_r + k_{rs}) \cdot [\mathrm{CT}^1] + k_s \cdot [\mathrm{S}] \\ &d[\mathrm{S}]/dt = -(k_s + k_{\mathrm{isc}}) \cdot [\mathrm{S}] + k_{rs} \cdot [\mathrm{CT}^1] \\ &d[\mathrm{T}]/dt = k_{\mathrm{isc}} \cdot [\mathrm{S}] \\ &[\mathrm{CT}^1]_{t=0} = 1;\ [\mathrm{S}]_{t=0} = 0;\ [\mathrm{T}]_{t=0} = 0 \end{aligned}\right\}, \qquad (6)$$

where the following designations were accepted for brevity: $\mathrm{CT}^1 = (\mathrm{F^-/TPA^+})^1$; $\mathrm{S} = (\mathrm{F^*/TPA})^1$; $\mathrm{T} = (\mathrm{F^*/TPA})^3$; and $k_s = k_{rs} \cdot \exp[-\Delta G_s/(kT)]$.

The observed kinetic curves are the sum of the optical densities of the CT-, S-, and T-states

$$D(\lambda) = \varepsilon_{\mathrm{CT}}[\mathrm{CT}] + \varepsilon_{\mathrm{S}}[\mathrm{S}] + \varepsilon_{\mathrm{T}}[\mathrm{T}]. \qquad (7)$$

The analytical solution of the system of equations (6) has the following form:

$$\left\|\begin{matrix}[\mathrm{CT}]\\ [\mathrm{S}]\end{matrix}\right\| = \left\|\begin{matrix}c_{11}\\ c_{21}\end{matrix}\right\| \cdot \exp(\lambda_1 t) + \left\|\begin{matrix}c_{12}\\ c_{22}\end{matrix}\right\| \cdot \exp(\lambda_2 t), \qquad (8)$$

where λ_1 and λ_2 and coefficients c_{11}, c_{21}, c_{12}, and c_{22} can be expressed by the rate constants of the transitions:

$$\lambda_{1,2} = \frac{(a+d) \pm \sqrt{(a+d)^2 - 4(ad-bc)}}{2};$$

$$a = -(k_\mathrm{r} + r_\mathrm{rs});\ b = k_\mathrm{s};\ c = k_\mathrm{rs};\ d = -(k_\mathrm{s} + k_\mathrm{isc});$$

$$c_{11} = (\lambda_1 - a)/(\lambda_1 - \lambda_2);\ c_{12} = (\lambda_2 - a)/(\lambda_1 - \lambda_2);$$

$$c_{21} = (\lambda_2 - a) \cdot (\lambda_1 - a)/b \cdot (\lambda_2 - \lambda_1);\ c_{22} = -c_{21}. \qquad (9)$$

In the limit of $t \to \infty$, the quantum yield of the triplet fullerene is determined by the equation

$$[\mathrm{T}] = k_\mathrm{isc} \cdot c_{21} \cdot \left[\frac{\exp(\lambda_1 t) - 1}{\lambda_1} - \frac{\exp(\lambda_2 t) - 1}{\lambda_2}\right]. \qquad (10)$$

The experimental kinetic curves recorded at the wavelengths of 1040 and 650 nm for the C_{60} system at different polarities of the medium were approximated by the biexponent. The obtained experimental values of λ_1 and λ_2, as well as the calculated dependences of the λ_1 and λ_2 coefficients on ε, are presented in Fig. 7. As can be seen, the simulation corresponds to the dependence of the λ coefficients on the polarity of the solution.

The results of the calculations of the populations of the $(F^-/TPA^+)^1$, $(F^*/TPA)^1$, and $(F^*/TPA)^3$ states and the kinetic curves are shown in Fig. 8. It follows from Fig. 8 that the model curves reflect the main specific features of the experimental kinetic curves presented in Figs. 3—5 for the value of the frequency of intramolecular vibrations $\hbar\omega$ = 500 cm^{-1}:

1) an increase in the optical density of the solution for λ = 750 nm (C_{60}—TPA), λ = 980 nm (C_{70}—TPA) in chlorobenzene with the characteristic time close to the time of the S—T-transition in C_{60} and C_{70} molecules;

2) the kinetic curves demonstrate the existence of a "minimum" of the optical density at 100—200 ps;

3) acceleration of a decrease in the optical density as the polarity of the medium increases with a change in the characteristic time from 1000 ps in chlorobenzene to 50 ps in benzonitrile, as well as "pulling" of the kinetics of a change in the optical density at λ = 1040 nm in chlorobenzene.

The comparison of the experimental and theoretical dependences of the quantum yield of the triplet fullerene on the polarity of the medium can serve as an additional and independent check of the suggested model of relaxation of the complex. The dependence of the quantum yield of $(F^*/TPA)^3$ on the polarity of the medium for C_{60}—TPA, which was experimentally measured in this work and by other authors,[22] and the calculated dependence are presented in Fig. 7, *c*. Despite substantial simplifications accepted in the model, it can be seen that the semiquantitative agreement between the calculation and experiment is achieved under the assumption of a low frequency of intramolecular vibrations ω ($\hbar\omega$ = 500 cm^{-1}).

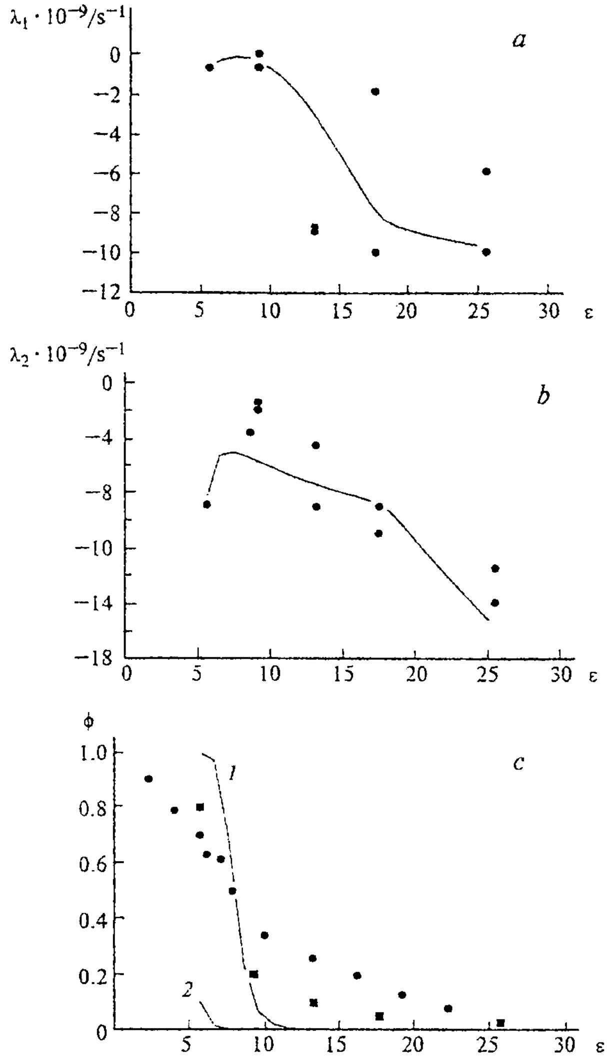

Fig. 7. Dependences of relaxation constants of the optical density λ_1 (*a*) and λ_2 (*b*) obtained by the biexponential approximation of the kinetic curves in the C_{60}—TPA system on the polarity of the solvent ε for wavelengths of 1040 and 650 nm. Experimental values are shown by points, and the calculated dependence obtained from Eqs. (1)—(9) under the assumption of the frequency $\hbar\omega$ = 500 cm^{-1} is shown by solid lines. *c*. Experimental dependence of the quantum yield of triplet $C_{60}{}^T$ on the polarity of the solvent. Points, the data of Ref. 23; squares, the data of the present work: *1*, calculation under the assumption that $\hbar\omega$ = 500 cm^{-1}; *2*, $\hbar\omega$ = 1500 cm^{-1}.

The ω frequency is a significant parameter in the calculation of the FC factor and, hence, rate constants. The value $\hbar\omega$ = 1500 cm^{-1} corresponding to the C=C vibrations in a molecule is usually accepted in the

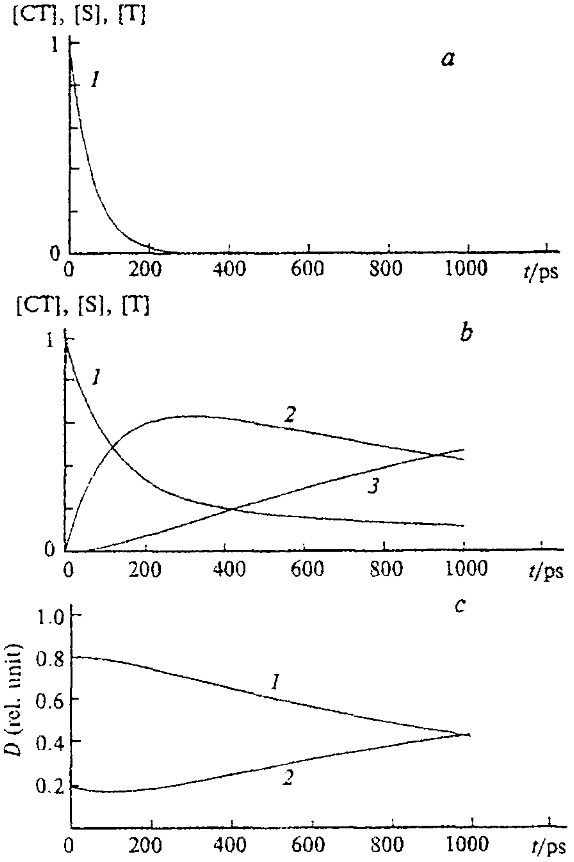

Fig. 8. Calculated kinetics of the population of the (F^-/TPA^+), $(F^*/TPA)^1$, and $(F^*/TPA)^3$ states in chlorobenzene and acetonitrile. Electron transfer rate constants were calculated under the assumption that $\hbar\omega$ = 500 cm^{-1}.
a, Benzonitrile: *1*, kinetics of the population of the ST-state (F^-/TPA^+), the population of the singlet and triplet states is negligible; *b*, chlorobenzene: *1*, kinetics of the population of the (F^-/TPA^+) state; *2*, S-states = $(F^*/TPA)^1$; *3*, T-states = $(F^*/TPA)^3$; *c*, model kinetics of the optical density at λ = 1040 (*1*) and 750 nm (*2*) for the C_{60}—TPA system.

analysis of this factor in charge transfer reactions of planar aromatic hydrocarbons.[15—18,20,21] However, the use of this value results in a qualitative discrepancy between the considered model and experiment. It has been previously shown[12a—14] that in a series of tertiary aromatic amines, the dependence of k_T on the value of the energy gap ΔG is described under the assumption of a low value of $\hbar\omega$ (~1500 cm^{-1}) and is mentioned as the main specific feature in a series of fullerene complexes with tertiary aromatic amines.[12a—14] The dependence of the kinetics of relaxation of the fullerene complex with one amine (triphenylamine) on the polarity of the medium, which was studied in this work, independently confirms the conclusion about a low value of the ω frequency. This frequency corresponds to vibrations of the whole carcass of a fullerene molecule. Thus, using the main parameters necessary for the calculation of the FC factor and description of the dependence of k_{ct} on the value of the energy gap ΔG in the series of the complexes with the transfer of a charge between C_{60} or C_{70} and several tertiary aromatic amines,[13—15] one can determine the main regularities in the kinetics of relaxation of excited states of the photoexcited complexes of C_{60} or C_{70} with TPA at different polarities of the solvent.

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