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Photophysical properties of (η^2-C_{60})Pd(PPh_3)$_2$ complex in benzene. Picosecond and nanosecond laser photolysis

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Absorption spectra of the photoexcited (η^2-C_{60})Pd(PPh_3)$_2$ complex in benzene were obtained by picosecond and nanosecond laser photolysis. The spectra are compared with those observed for photoexcited states of fullerene C_{60} and charge-transfer states of C_{60} complexes with ternary amines. The relaxation kinetics of excited (η^2-C_{60})Pd(PPh_3)$_2$ complex has three components with characteristic lifetimes τ_1 = 43 ps, τ_2 = 1500 ps, and τ_3 = 1.17 μs. The results are discussed in terms of the four-level scheme of the excited complex.

Key words: fullerene C_{60}, palladium complexes; photophysical properties, laser photolysis.

The main photochemical and photophysical properties of fullerenes in solutions have by now been studied in detail.[1–14] Absorption spectra for singlet and triplet excited states of C_{60} and C_{70} were obtained,[4,8–10] and times of intersystem crossing of $S_1 \rightarrow T_1$ and $T_1 \rightarrow S_0$ transitions in various solvents, including those containing a heavy atom, were determined.[11,12] It is shown that photoexcited fullerenes C_{60} and C_{70} react actively with both electron donors and acceptors in electron transfer processes[7,9,10] and enter cycloaddition reactions.[13] The published data on photophysical and photochemical properties of C_{60} derivatives coordinated with transition metals are presented to a considerably lesser extent.[6] The purpose of this work is to study the spectra of the photoexcited complex (η^2-C_{60})Pd(PPh_3)$_2$ (**1**) by picosecond and nanosecond laser photolysis and to measure lifetimes of excited states of this complex in benzene.

Experimental

Complex **1** was synthesized by the reaction of C_{60} with Pd(PPh_3)$_4$ in toluene followed by crystallization from the solution.[15] The studied solutions of crystalline complex **1** in benzene purified by the standard procedure were prepared under anaerobic conditions, and the concentration of the complex was $6 \cdot 10^{-4}$ mol L^{-1}. Absorption spectra of solutions in C_6H_6 were recorded on a Specord M40 spectrophotometer.

Experiments on picosecond laser photolysis were carried out using an Nd^{3+}-aluminate laser in the active-passive mode locked regime. The duration of the generation pulse was ~20 ps. Samples were excited by the second harmonic of the laser (the wavelength of the excitation pulse λ_{exc} = 540 nm, density of the excitation energy was lower than 5 mJ cm^{-2}). The picosecond continuum from the first harmonic pulse of the laser, which excited an H_2O—D_2O (1 : 1) mixture, was used as the probe pulse. The value of the induced absorption was measured by two silicon photodiodes mounted at the outlet gap of an MDR-2 monochromator. Experiments were performed by the standard pumping-probing procedure.

Experiments on nanosecond laser photolysis were performed using an Nd^{3+}—YAG laser in the Q-switched mode. The duration of the generation pulse was 12 ps. Samples were excited by the second harmonic of the laser (the wavelength of the excited pulse λ_{exc} = 532 nm, the density of the excitation energy was lower than 5 mJ cm^{-2}). The light of a fluorescent xenon lamp was used as the probing radiation. The induced absorption was registered by a monochromator, a photoelectron amplifier, and an analog-digital converter with a buffer storage attached to a computer. All measurements were performed at 23 °C.

Results and Discussion

Complex **1** forms dark-green benzene and toluene solutions sufficiently stable in air, while its irreversible dissociation to yield free C_{60} occurs rapidly in benzonitrile. The characteristic spectral property of the formation of complex **1** is the appearance of an intense absorption band at 436 nm and bands at 613 and 658 nm. The absorption spectrum of the benzene solution of **1** [λ/nm (ε/L mol^{-1} cm^{-1}): 334 (37500), 436 (9800), 613 (5100), and 658 (4000)] substantially differs from that of the initial fullerene C_{60} in benzene [λ/nm (ε/L mol^{-1} cm^{-1}): 336 (54000), 407 (3300), 540 (907), and 598 (803)]. It is assumed[16] that the absorption bands at 436, 613, and 658 nm in the spectrum of **1** are the charge-transfer bands, because they undergo a bathochromic shift, when the nonpolar solvent (benzene) is changed for the more polar one (a toluene—acetonitrile mixture).

The photoexcitation of complex **1** with visible light results in the appearance of an intense absorption spectrum typical of the excited states of the complex. The differential absorption spectra of photoexcited complex **1**

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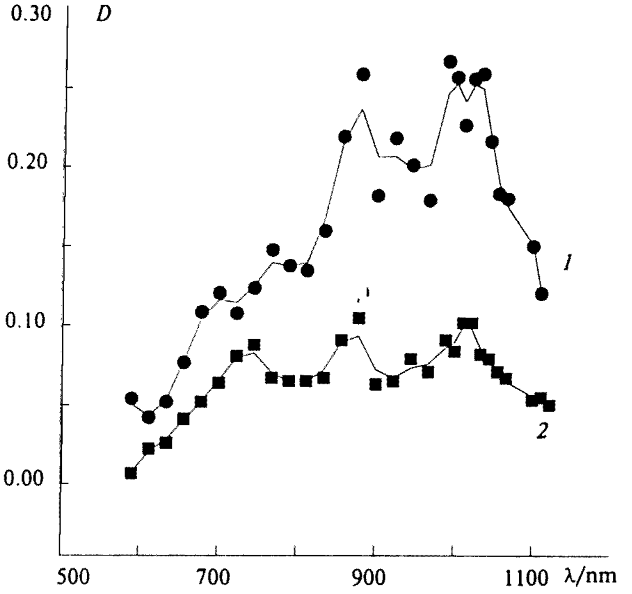
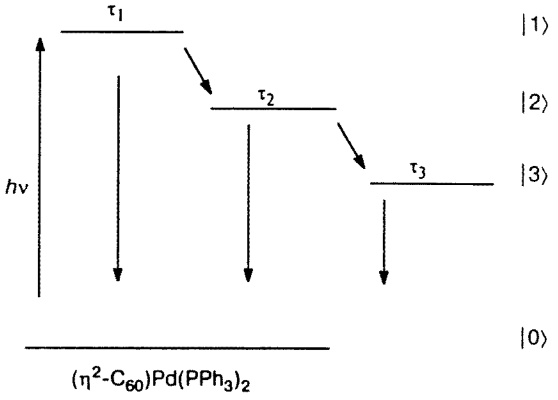


Fig. 1. Spectra of the photoexcited complex $(\eta^2\text{-}C_{60})Pd(PPh_3)_2$ in the picosecond time scale (λ_{exc} = 540 nm); here and in Figs. 2—4 $[(\eta^2\text{-}C_{60})Pd(PPh_3)_2] = 6 \cdot 10^{-4}$ mol L^{-1}. Time delay is 10 ps (*1*) and 1200 ps (*2*) (experimental points).

in the range from 580 to 1150 nm with time delays (t) equal to 10 and 1200 ps are presented in Fig. 1. Two absorption bands at approximately 870 and 1010 nm are distinctly observed in the spectrum with short time delays. When the time delay is close to 1 ns, the intensity of these bands decreases, and an additional absorption band appears at 750 nm. Its appearance is associated with the transitions between the excited states of complex **1**. The characteristic times of the transitions can be determined from the kinetic curves of the optical density decay at λ = 750 and 1060 nm (Fig. 2). These curves somewhat differ: an optical density decay is observed at λ = 1060 nm in the time scale shorter than 1200 ps, while the optical density remains almost unchanged at λ = 750 nm in the time range from 300 to 1200 ps. This plateau is explained by the appearance of a new state of the complex due to the relaxation of the preceding excited state. In the spectrum of the C_{60} molecule, the absorption band at 750 nm is characteristic for the lowest triplet excited state.[8] Therefore, it can be supposed that the appearance of the band in the region of 750 nm is caused predominantly by the formation of the relatively long-lived triplet excited C_{60} in complex **1**. This supposition is confirmed by the differential absorption spectra of excited complex **1** in submicrosecond and microsecond time scales (Fig. 3), which present a distinct absorption band at 750 nm, whose form is similar to that of the characteristic band of the $T_1 \rightarrow T_x$ transition of free C_{60} (*cf.* Ref. 8). It is also noteworthy that both kinetic curves presented in Fig. 2 contain a fast component with the characteristic time decay close to 40—50 ps. All these experimental data can be explained on the basis of the simplest four-level scheme with nonradiative transitions (Scheme 1).

Scheme 1



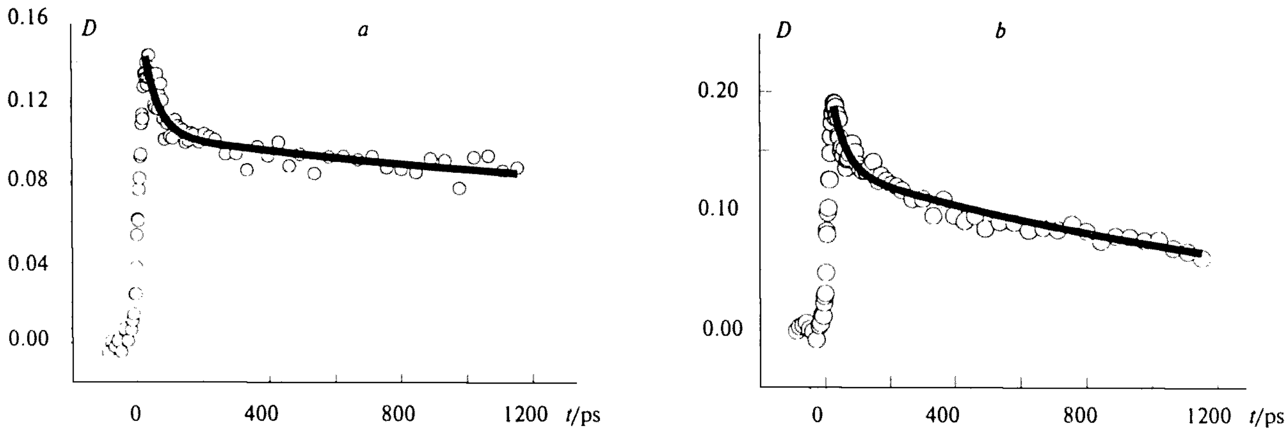


Fig. 2. Kinetic curve of the relaxation of the photoexcited state of the complex $(\eta^2\text{-}C_{60})Pd(PPh_3)_2$ in the picosecond time scale (λ_{exc} = 540 nm): *a*, λ = 750 nm, the circles indicate experimental points, the line shows the calculation by Eq. (2); *b*, λ = 1060 nm, the circles indicate experimental points and the line shows the calculation by Eq. (1).

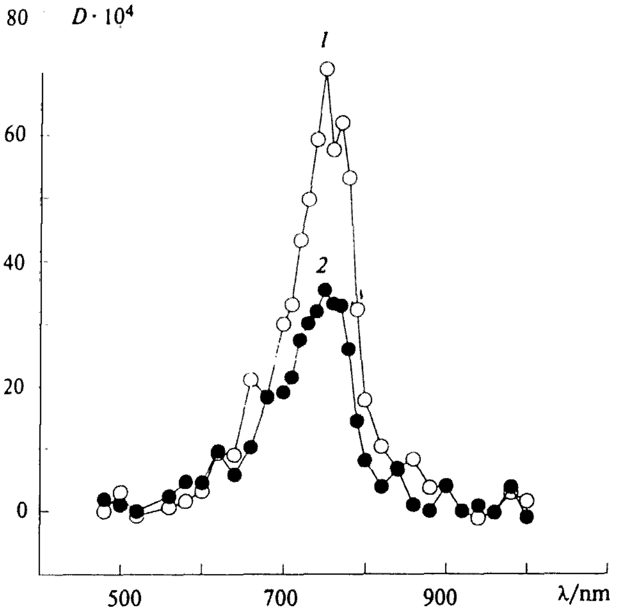


Fig. 3. Spectra of the photoexcited complex $(\eta^2\text{-}C_{60})Pd(PPh_3)_2$ in the microsecond time scale (λ_{exc} = 532 nm). Time delay is 0.1 μs (*1*) and 0.8 μs (*2*) (experimental points).

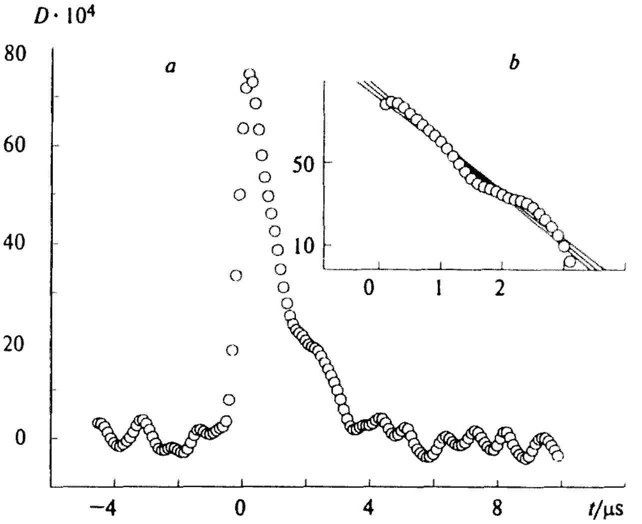


Fig. 4. Kinetic curve of the relaxation of the photoexcited state of the complex $(\eta^2\text{-}C_{60})Pd(PPh_3)_2$ in the microsecond time scale (λ_{exc} = 532 nm) at λ = 750 nm (*a*) and its semilogarithmic anamorphosis (*b*).

According to this scheme, the kinetic curve of the optical density decay at λ = 1060 nm is approximated by the biexponential dependence

$$A\exp(-t/\tau_1) + B\exp(-t/\tau_2), \tag{1}$$

where τ_1 = 43±10 ps, τ_2 = 1530±150 ps, A = 0.104±0.014, and B = 0.135±0.004.

The corresponding curve at λ = 750 nm is approximated by the dependence

$$A_1\exp(-t/\tau_1) + B_1\exp(-t/\tau_2) - C(\tau_1/\tau_2)[1 - \exp(-t/\tau_1)] + C[1 - \exp(-t/\tau_2)], \tag{2}$$

where τ_1 = 43±10 ps, τ_2 = 1530±150 ps, A_1 = 0.073±0.006, B_1 = 0.106±0.002, and C = 0.069±0.005 (see Fig. 2).

The decrease in the optical density in the microsecond time scale is determined by the exponential law with the lifetime of the excited state τ_3 = 1.17±0.03 μs (Fig. 4).

The existence of the fast component in the picosecond kinetics of the complex relaxation can be explained in different ways. The transition $|1\rangle \rightarrow |2\rangle$ can be associated with the deactivation of the excessive vibrational energy upon the formation of the equilibrium conformation of the photoexcited complex. States $|1\rangle$ and $|2\rangle$ can be different electronic states of the complex, and then $|1\rangle \rightarrow |2\rangle$ means the interelectronic transition. It should be noted that the four-level scheme considered above can be complicated by additional transitions, for example, those of the type $|1\rangle \rightleftharpoons |2\rangle$, $|2\rangle \rightleftharpoons |3\rangle$. The simplest three-level scheme of transitions of S_0, S_1, and T_1 is insufficient for the description of the observed kinetics of relaxation of complex **1**, because three substantially different values of relaxation time are revealed.

In the picosecond time scale, the positions of maxima and the forms of bands in the spectrum of photoexcited complex **1** differ from those of both the absorption of the $S_1 \rightarrow S_x$ transition of free C_{60} in toluene[8] and the bands of the $C_{60}^{\cdot-}$ radical anion in the absorption spectra of the photoexcited charge-transfer complexes formed by C_{60} with ternary amines in chlorobenzene.[14] For example, the absorption maximum of the $S_1 \rightarrow S_x$ transition of free C_{60} in toluene[8] lies in the range from 940 to 960 nm. In the spectra of the photoexcited charge-transfer complexes with amines, the C_{60}^{-} anion corresponds to the band with a maximum at ~1070 nm, whose form and position almost coincide with those of the band of the free radical anion $C_{60}^{\cdot-}$ (see Ref. 14). If the bands at 870 and 1010 nm in the spectrum of photoexcited complex **1** are considered as the band of the locally excited S_1 state of C_{60} shifted to the short-wave range and the band corresponding to the C_{60}^{-} anion in the $(\eta^2\text{-}C_{60})Pd(PPh_3)_2$ molecule, respectively, the photoexcited state of complex **1** can likely be interpreted as the superposition of the S_1 state of C_{60} and the charge-transfer state (C_{60}^{-}). In terms of this assumption, the bathochromic shift in the absorption spectra of the ground state of the complex observed[16] upon an increase in the polarity of the solvent can be qualitatively explained as the manifestation of the charge-transfer state. In addition, the authors of Ref. 6, devoted to the study of photophysical properties of the complex $(\eta^2\text{-}C_9H_7)Ir(CO)(\eta^2\text{-}C_{60})$ (**2**), observed the insensibility of the allowed absorption band at 436 nm toward the polarity of the solvent and supposed that this band was caused by the π—π*-transition of C_{60} in the complex. The transitions in excited complex **2** are interpreted in terms of the three-level scheme of S_0, S_1, and T_1. The characteristic time in complex **2** for the $S_1 \rightarrow T_1$ transition is not longer than 18 ps, and it is 100 ns for the $T_1 \rightarrow S_0$ transition. Since the times of the transitions in complex **2** are substantially shorter than those in free C_{60}, it is assumed[6] that the increase in the rate of the interelectronic transitions is caused by the effect of the heavy atom Ir on the intersystem crossing in C_{60}. Our previous study of the external heavy atom effect on such processes for solutions of C_{60} in MeI, $CHBr_3$, CCl_4, and toluene[12] shows that the time of the $S_1 \rightarrow T_1$ transition changes in this series as follows: 30 (MeI), 170 ($CHBr_3$), 1040 (CCl_4), and 1130 (toluene) ps, while the times of the $T_1 \rightarrow S_0$ transition are 5.8 (MeI), 47 ($CHBr_3$), 140 (CCl_4), and 116 (toluene) μs. It is quite probable that the heavy Pd atom affects the rate of intersystem crossing in C_{60}. This is indicated by the close values of the characteristic time of two of three transitions (τ_1 = 43 ps and τ_3 = 1.17 μs) in complex **1** and free C_{60} in the solvents containing a heavy atom (MeI) and by the fact that these characteristic times are comparable by an order of magnitude for Pd and Ir complexes. A more exact assignment of the photoexcited states of **1**, the study of the contribution of the charge-transfer state to the spectra of C_{60} complexes with metals, and the analysis of possible transitions between them require a detailed quantum-chemical modeling of the system, which was not the task of this work.

Thus, the spectra of photoexcited complex **1** in benzene were obtained by picosecond and nanosecond laser photolysis. The comparison of these spectra with those characteristic of the excited states of free C_{60} and the charge-transfer states in the C_{60} complexes with ternary amines made it possible to interpret hypothetically the photoexcited state of complex **1** as the superposition of the S_1 state of C_{60} and the charge-transfer state followed by the formation of the C_{60}^- anion. The study of the kinetics of the relaxation of photoexcited **1** revealed three components with the characteristic times τ_1 = 43 ps, τ_2 = 1500 ps, and τ_3 = 1.17 μs. The comparison of these values with the times of the transitions in photoexcited complex **2** [6] and with the times of intersystem crossing in C_{60} makes it possible to hypothesize the effect of the heavy Pd atom on the rate of intersystem crossing in C_{60}. The results obtained can be explained in terms of the four-level scheme with nonradiative transitions.

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