

NATURE AND KINETICS OF NONSTATIONARY LIGHT ABSORPTION IN C₆₀ FILMS INDUCED BY FEMTOSECOND LASER PULSES

M.P. GORISHNYI, I.A. PAVLOV, A.V. KOVALCHUK

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Institute of Physics, Nat. Acad. of Sci. of Ukraine
(46, Prosp. Nauky, Kyiv 03028, Ukraine; e-mail: gorishny@iop.kiev.ua)

Using the “pump–probe” technique, the structure and the temporal evolution of the light absorption in C₆₀ films induced by femtosecond laser pulses in the spectral range of 2.04–2.37 eV and the pulse time interval of 0–882 ps have been studied. C₆₀ films 200 nm in thickness were obtained by thermal evaporation onto quartz substrates in a vacuum of 0.65 mPa and at room temperature.

In the probe range of 2.04–2.37 eV, the shape of the absorption spectrum induced by femtosecond laser pulses in a C₆₀ film consists of bands at 2.097, 2.164, 2.209, 2.262, 2.299, and 2.331 eV. The bands at 2.097, 2.209, and 2.262 eV are induced by electron transitions between the energy bands created by zero vibronic levels of the S₀ state and nonzero vibronic levels of S₁ state of C₆₀ molecules.

For the first time, it has been shown that the “hot” bands at 2.164, 2.299, and 2.331 eV result from the electron transitions either between the energy bands created by three nonzero vibronic levels of S₀ state, on the one hand, and the zero vibronic level of S₂ state, on the other hand, or between the energy bands created by three nonzero vibronic levels of S₁ state, on the one hand, and the zero vibronic level of S₄ state, on the other hand, of C₆₀ molecules.

The decreasing temporal kinetics of the optical density *D* under the induced absorption in C₆₀ films was approximated by a sum of three exponential terms in the pulse time interval of 0–882 ps. For probe photons with the energy *E* = 2.217 eV, the following values of relaxation times were obtained: τ_{r1} = (1.04 ± 0.13) ps, τ_{r2} = (5.81 ± 0.94) ps, and τ_{r3} = (108.0 ± 9.3) ps. The approximation of those kinetics by the Kohlrausch function (the “stretched” exponent) allowed us to evaluate the effective relaxation time τ_r as 6.0 ps, which is close to the τ_{r2}-value. The electron subsystem of C₆₀ films needs the time interval Δ*t* > 882 ps to relax into the equilibrium state.

The quantities τ_{r1} and τ_{r2} are found to depend significantly on the approximation time interval and the method used for averaging the kinetics Δ*D*_n(*t*). For τ_{r3}, this dependence is much weaker.

1. Introduction

Fullerene-containing composite materials are more and more widely applied in practice. Examples of their use in nonlinear optical limiters of light flux intensity,

solid-state photosensitizers for photodynamic therapy, devices for solar power engineering, and other domains are known well [1–3]. The results of researches concerning the electrical and optical properties of monomeric and polymerized fullerenes were summarized in review [4]. Tables in works [5, 6] with the classification of electron transitions were formed by comparing and resolving the optical spectra of C₆₀ films on quartz substrates and the transmission spectra of C₆₀ solutions in toluene, hexane, and pentane into Gaussian and Lorentzian components. Long-wave absorption in concentrated C₆₀ solutions in hexane at room temperature was explained by the formation of (C₆₀)_n-clusters [7].

In the last years, considerable attention of researchers has been focused on issues dealing with the rate of optical response by fullerene-containing composite materials, which are of substantial interest from both the scientific and practical aspects. A number of the first researches in this domain were carried out in works [8–10], where the authors used the two-beam “pump–probe” technique. The role of a “pump” beam consisted in the transfer of the electron subsystems of examined objects into an excited state, whereas the role of a “probe” beam, which was delayed with respect to the former beam by various time intervals τ_d, in reading out mesostates of the electron subsystem until it relaxed completely. The observable relaxation of the induced absorption within the time interval of 0–600 ps was described by the Kohlrausch function (the “stretched” exponent) [9, 10],

$$\Delta D_n = \alpha \exp(-(t/\tau_r)^\beta), \quad (1)$$

where *t* is the difference between a current value τ_d and a value, at which Δ*D*_n = 1; α and β are some parameters; and τ_r and Δ*D*_n are the relaxation time and the current value of normalized induced absorption, respectively.

The parameters β = 0.42 and τ_r = 43 ps did not change in the temperature range of 150–400 K [9]. When the fullerene-containing films were cooled down from 150 to 5 K, the growth of β and τ_r parameters was observed

[10]. The increase in the excitation intensity gave rise to a reduction of τ_r in undoped C_{60} films, whereas this quantity did not change in Pb-doped C_{60} films [11]. The relaxation constants were found to differ substantially in the film phase and in fullerene solutions. In particular, in C_{60} solutions, a rapid decrease of the optical response (the corresponding constant $\tau_r = 1.2$ ps) is followed by a slow growth of induced absorption [12], which, according to the authors, is associated with a reconstruction of C_{60} molecule under the action of absorbed light. The considerable deformation of a C_{60} molecule under its photoexcitation is confirmed by an observed splitting of the $H_g(1)$ mode in intramolecular vibrations [13]. The charge mobility threshold in C_{60} films equals 2.3 eV [14, 15]. The authors of work [8] supposed that, when C_{60} films are excited by 100-ps laser pulses with wavelengths of 645 and 367 (345) nm, both primary charge carriers (conduction electrons and holes) and neutral molecules in the excited state can be generated. In this case, primary charge carriers can emerge owing to one- and two-photon absorption at the excitation above (367 nm) and below (645 nm) the mobility threshold, respectively.

The analysis of literature data presented above shows that the origin of bands of the C_{60} absorption induced by a femtosecond laser has not been studied enough. In addition, the kinetics of this absorption is mainly described with the use of the Kohlrausch function, which gives an averaged (effective) magnitude for τ_r . This work aimed at establishing the nature of the induced absorption bands of C_{60} films in the probe interval of 2.04–2.37 eV. Additionally, the time dependences of the induced absorption in C_{60} films were approximated by a sum of exponential dependences with different τ_r 's, which allowed the corresponding relaxation process to be analyzed in more details.

2. Experimental Technique

Thin C_{60} films 200 nm in thickness were deposited onto quartz substrates, by using the thermal sputtering technique in a vacuum of 6.5 mPa and at room temperature. The spectra of the induced absorption ΔD in C_{60} films were studied with the use of the two-beam “pump–probe” technique [16]. The measurement routine was as follows. The first laser pulse (a pulse energy of 7.5 μ J, a pulse duration of 135–150 fs, a pulse power of 5×10^7 W, and a pulse intensity of 1.5×10^9 W/cm²) was used to excite the electron subsystem of C_{60} molecules. With the help of the probe pulse delayed in time by τ_d with respect to the pump one, the dependence $\Delta D(E, \tau_d)$, where E

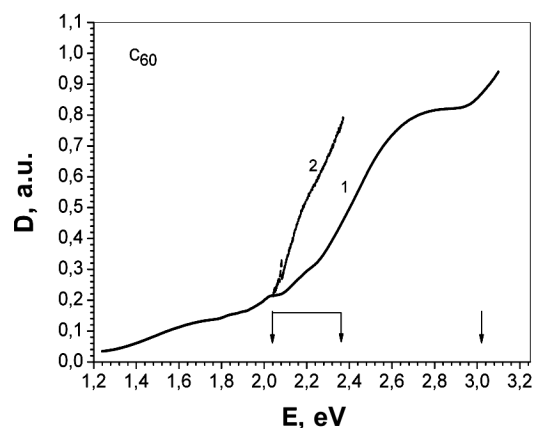


Fig. 1. Linear absorption spectra of C_{60} films 200 nm in thickness registered on a Perkin Elmer Lambda 25UV/vis spectrophotometer in the range of 1.24–3.10 eV (curve 1) with the use of the “pump–probe” technique in the range of 2.04–2.37 eV (curve 2). The energy of exciting photons equals 3.02 eV (designated by the arrow)

is the energy of photons belonging to the “white supercontinuum” of the probe pulse spectrum, was studied. The probe beam was focused on a cuvette with heavy water, which allowed us to produce the “white supercontinuum” of the radiation spectrum. The maximum intensity of the supercontinuum was observed at 1.55 eV. The photon excitation energy was $E_{ex} = 3.02$ eV.

Within the interval -2.14 ps $\leq \tau_d \leq 0.76$ ps, the time delay was varied discretely with an increment of 0.1 ps. In the range of 0.76–882 ps, the increment grew in geometric progression with a common ratio of about 1.2.

The linear absorption spectra of C_{60} films were registered on a Perkin Elmer Lambda 25UV/vis spectrophotometer. All measurements were carried out at room temperature.

3. Experimental Data

In Fig. 1, the linear absorption spectrum of a C_{60} film 200 nm in thickness registered in the photon-energy interval of 1.24–3.1 eV is depicted (curve 1). One arrow and two connected arrows mark the photon energy in the pump pulse, $E_{ex} = 3.02$ eV, and the limits of the probe interval (2.04–2.37 eV), respectively.

According to the “pump–probe” technique, the excitation and probe pulses cross the same spatial region in the C_{60} film. Temporally, they are separated by the interval τ_d (the delay time), which can be varied with the help of a delay line. In this case, the probe pulse can advance in time the pump one ($\tau_d < 0$), coincide with it ($\tau_d = 0$), or be delayed ($\tau_d > 0$). It allows us to

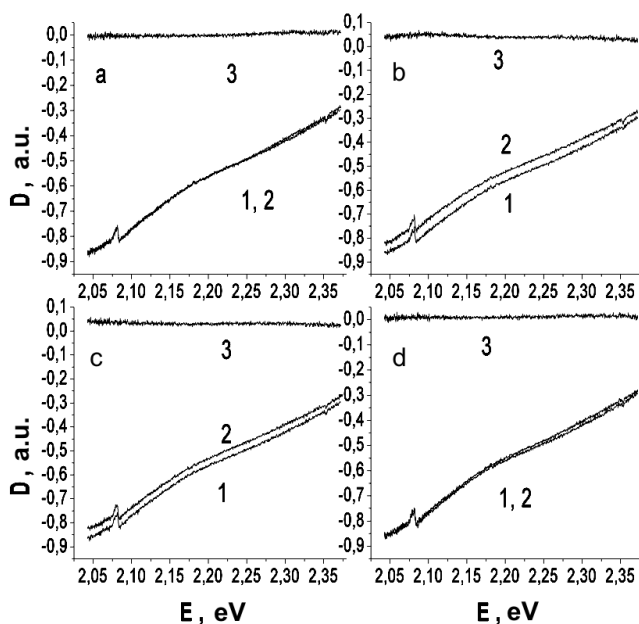


Fig. 2. Absorption spectra of C_{60} films 200 nm in thickness before (curves 1) and after (curves 2) irradiation with a laser pulse and the corresponding spectra of induced absorption (curves 3) in the range of 2.04–2.37 eV for various delay times: -0.34 (a), 0.51 (b), 0.76 (c), and 13.47 ps (d)

monitor the variations in the optical density, when C_{60} molecules transit from the excited state into the ground one.

In Fig. 2, curves 1 exhibit the spectra of the optical density, D_1 , for C_{60} films not subjected to the action of laser excitation pulses, whereas curves 2 correspond to spectra, D_2 , registered at different delay times τ_d 's. The difference $\Delta D = D_2 - D_1$ (curves 3) illustrates the variations of absorption spectra for C_{60} films in time. At negative delay times, -2.14 ps $\leq \tau_d < -0.54$ ps, the pump and probe pulses do not overlap in time, and the spectra D_1 and D_2 are identical, i.e. $\Delta D = 0$. They start to overlap each other at $\tau_d = -0.54$ ps. In this case, an insignificant induced absorption ($\Delta D > 0$) is observed in the short-wave section of the probe interval (panel a). When τ_d increases from -0.54 to 0.51 ps, the pulse overlapping degree grows, which stimulates the magnitude of ΔD to increase up to its maximum value in the whole probe region at $\tau_d = 0.51$ ps (panel b). A further growth of τ_d results in a reduction of the induced absorption to an almost zero value; for instance, at $\tau_d = 0.76$ ps (panel c) and 13.46 ps (panel d). This fact testifies that, at relatively large $\tau_d > 0$, some C_{60} molecules remain in the excited state.

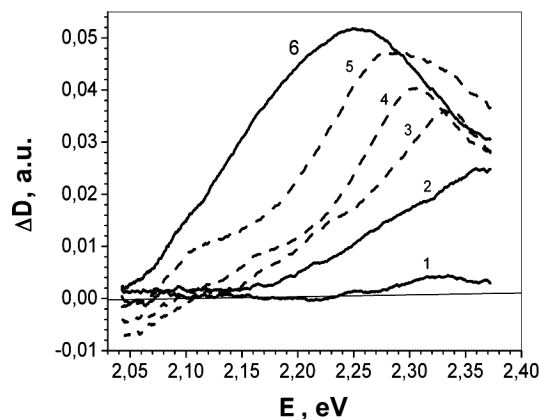


Fig. 3. Spectra of induced absorption for C_{60} films 200 nm in thickness at various delay times: -0.54 (1), -0.24 (2), -0.14 (3), -0.04 (4), 0.06 (5), and 0.26 ps (6)

The values of D_1 and D_2 were calculated by the formula

$$D = \lg \frac{I_0}{I_p}, \quad (2)$$

where I_0 and I_p are the amplitudes of signals from a photodetector (a charge-coupled device array) generated by the reference and probe pulses, respectively, decreased by the magnitudes of corresponding background components. While calculating D_1 and D_2 , the I_0 -value is the same, whereas the denominators, I_p , are different. In the first case, the I_p -value corresponds to the probe pulse that passed through the C_{60} film not irradiated with an excitation pulse. In the second case, the probe pulse passed through the same C_{60} film with the time delay τ_d after the film irradiation. Since $I_0 < I_p$ in both cases, the values of D_1 and D_2 are negative (Fig. 2). However, this fact does not affect the ΔD -value. For the sake of comparison, the D_1 -spectrum in Fig. 1 (curve 2) is matched with the linear spectrum of a C_{60} film (curve 1) at a point with the quantum energy $E = 2.04$ eV. By their structure, those spectra are similar. In the D_1 -case, the spectrum steepness is larger. This fact is associated with different characteristics of photodetectors and spectrum registration conditions.

A more detailed evolution dynamics of ΔD -spectra for τ_d 's chosen from the interval between -0.54 and $+0.26$ ps is depicted in Fig. 3. At $\tau_d = -0.54$ ps, a section with $\Delta D > 0$ (the range of C_{60} film darkening) was observed for $E = (2.27 \div 2.37)$ eV (curve 1). When negative τ_d -values approached zero (curves 2 to 4), the section of film darkening broadened and transformed into a wide structured band with two maxima, which shifted

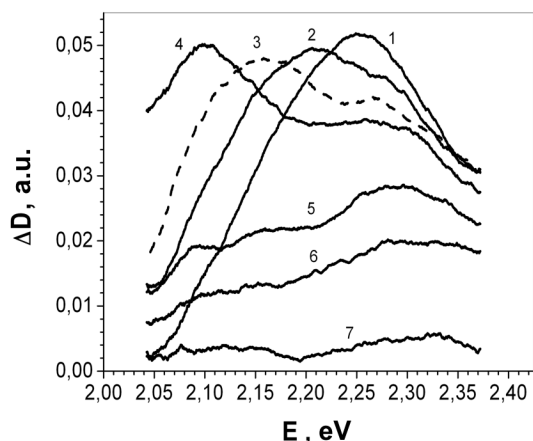


Fig. 4. Spectra of induced absorption for C_{60} films 200 nm in thickness at various delay times: 0.26 (1), 0.36 (2), 0.46 (3), 0.56 (4), 1.65 (5), 5.51 (6), and 882 ps (7)

toward lower E 's (the bathochromic shift). Moreover, an insignificant bleaching of C_{60} films was observed in the long-wave spectral section, $E = (2.04 \div 2.12)$ eV. The interval of film bleaching disappears, and the integrated intensity in the darkening range increases for delay times of 0.06 and 0.26 ps (curves 5 and 6, respectively).

In Fig. 4, the ΔD -spectra are shown for some delay times chosen from the interval of 0.26–882 ps. At $\tau_d = 0.26$ ps, the maximum of the structured darkening band is located at about 2.25 eV. In its long-wave side, a weak band at 2.09 eV is observed (curve 1). With the growth of τ_d , the short-wave band intensity diminishes and that of the long-wave one increases (curves 2 to 4). At $\tau_d > 0.56$ ps, the integrated intensity of the structured darkening band decreases (curves 5 to 7), with the rate of intensity fall for the short-wave band being lower than that for the long-wave one.

After a statistical treatment of experimental data reported above, the dependences of normalized ΔD_n -values on τ_d were obtained for given E -values. Figure 5 demonstrates a typical kinetics $\Delta D_n(\tau_d)$ for the probe photon energy $E = 2.213$ eV and in the delay time intervals from -2.14 to $+882$ ps (panel a) and from -2.14 to -7.0 ps (panel b). At the zero delay time, $\Delta D_n = 0.5$.

In this work, we also obtained the averaged relaxation kinetics $\Delta D_n(t)$ for various E 's from the probe interval of 2.04–2.37 eV. The averaging over E included 70 points in the spectrum of induced absorption for C_{60} films.

In Fig. 6, the averaged relaxation kinetics $\Delta D_n(t)$ is shown for the photon energy $E = 2.213$ eV (curve 1). The kinetic curves calculated according to the Kohlrausch formula with $\alpha = 0.72$ and various β - and τ_r -values are also depicted. Curve 3 ($\beta = 0.41$ and

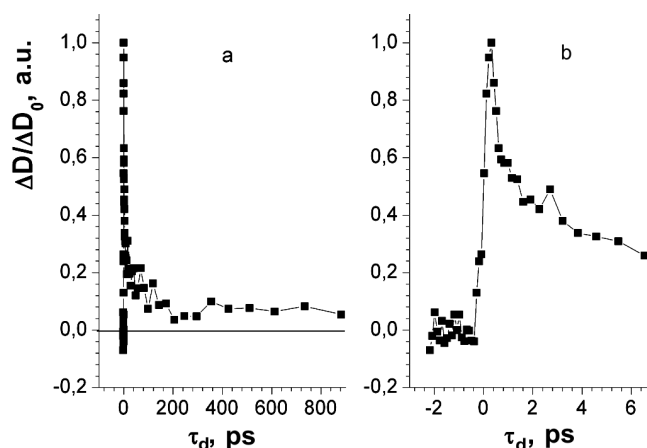


Fig. 5. Dependences of the induced absorption in C_{60} films 200 nm in thickness on the delay time τ_d for probe photons with the energy $E = 2.213$ eV in the intervals from -2.14 to 882 ps (a) and from -2.14 to 7.0 ps (b). The magnitude of induced absorption ΔD is normalized to the value $\Delta D_0 = 0.04983$

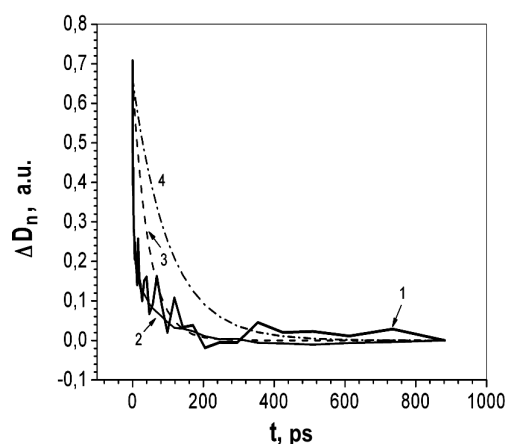


Fig. 6. Kinetics of the normalized induced absorption $\Delta D_n(t)$ in a C_{60} film 200 nm in thickness for probe photons with the energy $E = 2.213$ eV (1) and its approximation by the Kohlrausch function with the following parameters β and τ_r : 0.41 and 6.0 ps (2), 0.41 and 18.6 ps (3), and 0.43 and 43.0 ps (4), respectively

$\tau_r = 18.6$ ps [10]) was found to pass closer to curve 1 than curve 4 ($\beta = 0.42$ and $\tau_r = 43.0$ ps [9]). Curve 2 corresponds to $\beta = 0.41$ and $\tau_r = 6.0$ ps. It agrees better with real curve 1. Hence, the time evolution of the induced absorption in C_{60} films has a non-exponential character, which is confirmed by literature data [5, 9–11].

More information was obtained when the kinetics $\Delta D_n(t)$ was approximated by a sum of three simple components with different relaxation times according to the

Table 1. Coefficients and relaxation times for the induced absorption in C₆₀ films 200 nm in thickness for various photon energies in the probe interval of 2.04–2.37 eV

N	E , eV	ΔD_{n0} , a.u.	A_1 , a.u.	τ_{r1} , ps	A_2 , a.u.	τ_{r2} , ps	A_3 , a.u.	τ_{r3} , a.u.
1	2.359	0.12555	0.17442	0.796	0.21082	4.194	0.35773	102.76
2	2.334	0.12396	0.19824	0.732	0.25721	4.075	0.29694	101.31
3	2.308	0.11301	0.25825	0.917	0.24778	4.983	0.26033	108.80
4	2.284	0.10593	0.33474	0.974	0.22524	5.264	0.23927	100.26
5	2.260	0.09448	0.34515	1.059	0.24673	5.573	0.20081	103.77
6	2.236	0.08154	0.42474	1.042	0.21925	6.480	0.18390	96.67
7	2.213	0.06994	0.42135	1.040	0.22008	5.699	0.17642	83.91
8	2.190	0.06977	0.51558	1.072	0.20416	6.499	0.15603	103.80
9	2.168	0.08144	0.45203	1.160	0.20379	4.634	0.15589	88.58
10	2.147	0.08849	0.53411	1.098	0.19195	5.811	0.12032	94.48
12	2.126	0.09969	0.49412	1.284	0.19180	7.170	0.09332	129.74
13	2.105	0.08728	0.54476	1.187	0.16012	7.066	0.09373	142.88
14	2.085	0.09081	0.65828	1.180	0.13305	8.120	0.09289	147.53
Av.	2.217	0.09476	0.41198	1.042	0.20861	5.813	0.18674	108.04

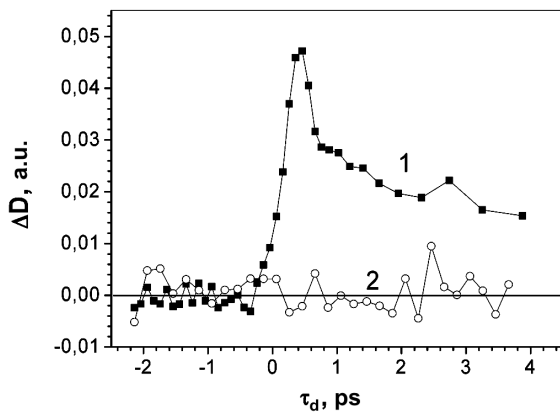


Fig. 7. Dependences of the induced absorption ΔD in C₆₀ films 200 nm in thickness (1) and a quartz substrate (2) on the delay time τ_d for the energy of probe photons $E = 2.168$ eV

equation

$$\Delta D_n = \Delta D_{n0} + \sum_{n=1}^3 A_n \exp(-t/\tau_{rn}), \quad (3)$$

where ΔD_n and ΔD_{n0} are the current and stationary, respectively, values of induced absorption in C₆₀ films; A_n is a pre-exponential factor that characterizes the contribution of the n -th process with the relaxation time τ_{rn} to the general kinetics; and t is the difference between the current τ_d -value and the τ_d -value, at which $\Delta D_n = 1$.

The values of coefficients ΔD_{n0} and A_n , and the relaxation times τ_{rn} calculated for E -values chosen from the probe region of 2.04–2.37 eV and for the time interval of 0 – 882 ps are quoted in Table 1. Those data

were obtained by averaging over every ten points in the kinetic dependence. The magnitudes of ΔD_{n0} , A_2 , and A_3 decrease and that of A_1 increases as the energy E diminishes. This means that the contribution of the first (the quickest) component, characterized by τ_{r1} , grows, as the band energy decreases. The following averaged values of relaxation times were obtained for the energy of probe photons $E = 2.217$ eV: $\tau_{r1} = (1.04 \pm 0.13)$ ps, $\tau_{r2} = (5.81 \pm 0.94)$ ps, and $\tau_{r3} = (108.0 \pm 9.3)$ ps. The values of τ_{r2} turned out close to $\tau_r = 6.0$ ps determined above from the Kohlrausch formula (Fig. 6, curve 2). The main changes in the $\Delta D_n(t)$ -kinetics are observed in the interval of 0 – 27 ps; here, it decreases by more than a factor of $e \approx 2.72$. Every five points were averaged, and the obtained dependence was approximated by two exponents—with $\tau_{r1} = (0.43 \pm 0.09)$ ps and $\tau_{r2} = (3.70 \pm 0.40)$ ps. Relatively small variations of this kinetics in the range of 27–882 ps were described by a single exponent with $\tau_{r3} = (108.7 \pm 16.5)$ ps. Hence, the magnitudes of τ_{r1} and τ_{r2} substantially depend on the selected time interval of approximation and the averaging technique. For τ_{r3} , this dependence is much weaker.

In Fig. 7, the kinetics $\Delta D(t)$ for C₆₀ films (curve 1) and a clean quartz substrate (curve 2) obtained at the energy of probe photons $E = 2.168$ eV are compared. It is evident that the substrate weakly affects the kinetics $\Delta D(t)$ for C₆₀ films. In addition, the local maximum at $\tau_d = 2.8$ ps (curve 1) is modulated by the signal from the substrate; moreover, it reveals itself in all kinetics $\Delta D(t)$ obtained for C₆₀ films with different E -values from the probe interval of 2.04–2.37 eV.

Table 2. Energies and vibronic structures of electron transitions in C₆₀ films and hexane C₆₀ solutions in the interval of 1.90–2.35 eV

N	E, eV			Transition [7]	Mode frequency $\Delta\nu$ [7]
	Band [4, 6]	Film C ₆₀ [4, 6]	Solution C ₆₀ [4, 6]		
1			1.901	$S_0 \rightarrow S_1, 0 \rightarrow 0$ band	
2	γ_0	1.918	1.999	$S_0 \rightarrow S_1 + H_u(4)$	$H_u(4) = 787 \text{ cm}^{-1}$
3	γ_1		2.036	$S_0 \rightarrow S_1 + H_u(4) + H_u(1)$	$H_u(1) = 296 \text{ cm}^{-1}$
4	γ_2	1.992	2.075	$S_0 \rightarrow S_1 + T_{1u}(4)$	$T_{1u}(4) = 1397 \text{ cm}^{-1}$
5	γ_3	2.028	2.101	$S_0 \rightarrow S_1 + T_{1u}(4) + H_g(1)$	
6	γ_5	2.097	2.179	$S_0 \rightarrow S_1 + H_u(4) + A_g(2)$	$A_g(2) = 1451 \text{ cm}^{-1}$
7			2.291		3147
8			2.344		3567

4. Discussion of Experimental Data

The energies and the vibronic structures of electron transitions in C₆₀ films and hexane C₆₀ solutions in the range of 1.90–2.35 eV are listed in Table 2. These transitions are associated with the symmetry-forbidden $h_u \rightarrow t_{1u}$ transition or the $S_0 \rightarrow S_1$ transition [4, 6]. The first excited S_1 state of C₆₀ molecule is degenerate. Therefore, the $S_0 \rightarrow S_1$ transition occurs following the Herzberg–Teller mechanism as a vibronically induced one. The band contour of this transition is mainly formed by the active asymmetric Jahn–Teller modes $H_u(4) = 787 \text{ cm}^{-1}$ and $T_{1u}(4) = 1397 \text{ cm}^{-1}$, and the totally symmetric Franck–Condon modes $H_g(1) = 296 \text{ cm}^{-1}$ and $A_g(2) = 1451 \text{ cm}^{-1}$ of non-associated C₆₀ molecules [7].

In the hexane solution of C₆₀, the $0 \rightarrow 0$ band of the $S_0 \rightarrow S_1$ transition is observed at 1.902 eV (Table 2, row 1). It is absent from the absorption spectrum of a C₆₀ film. The vibronic mode $H_u(4)$ manifests itself in the film γ_0 -band at 1.918 eV and the C₆₀ molecular transition at 1.999 eV (row 2). The modes $H_u(4)$ and $H_g(1)$ compose a molecular band at 2.036 eV, but do not manifest themselves in the absorption spectrum of a C₆₀ film (row 3). The mode $T_{1u}(4)$ is responsible for the molecular transition bands at 2.075 eV and the γ_2 -band of a C₆₀ film at 1.992 eV (row 4). The bands γ_3 and γ_5 are connected with the mode combinations $T_{1u}(4) + H_g(1)$ and $H_u(4) + A_g(2)$, respectively (rows 5 and 6). The origin of the C₆₀ molecular transitions at 2.291 and 2.344 eV has not been explained yet. We may suppose that the former is formed by the combination of two $A_g(2)$ -modes and one $H_g(1)$ modes, whereas the latter by the combination of two either $A_g(2)$ or $T_{1u}(4)$ modes and one $H_u(4)$ mode.

In a C₆₀ molecule, the highest filled level, S_0 , has the h_u symmetry; and the lowest unoccupied one, S_1 , has the t_{1u} symmetry [4, 6]. At the excitation $h_u t_{1u}^*$, one

electron remains at the level S_0 , and one electron appears at the level S_1 [11, 17]. As a result, the symmetry-allowed degenerate transitions $h_g \rightarrow h_u$ and $g_g \rightarrow h_u$ from the lower located filled levels h_g and g_g , respectively, and the transition $t_{1u} \rightarrow h_{2g}$, where h_{2g} are the higher located non-occupied levels of the split S_4 state, become possible. When the solid-state phase is formed, the molecular electron levels of C₆₀ molecules transform into bands owing to the intermolecular interaction. In the C₆₀ films, the excitations $h_g h_u^*$, $g_g h_u^*$, and $t_{1u} h_{2g}^*$ are connected with transitions from the occupied lower bands into the zero band (S_0 band) with an energy of 1.714 eV and from the first band (S_1 band) into two split S_4 bands (E and F bands with energies of 2.442 and 2.628 eV, respectively [4]). The latter two transitions can be imposed on the transition from the S_0 band into the split S_2 band (A and B bands with energies of 2.41 and 2.70 eV, respectively [4]).

The average bathochromic shift of bands γ_0 , γ_2 , γ_3 , and γ_5 for C₆₀ films with respect to those for the C₆₀ solution amounts to 0.082 eV (Table 2). If we suppose that this shift is characteristic of all other bands of the $S_0 \rightarrow S_1$ transition, then the bands of corresponding band-to-band transitions can be observed in a C₆₀ film at 1.819, 2.209, and 2.262 eV. The probe interval includes only transitions with energies of 2.097 (γ_5 band), 2.209, and 2.262 eV.

The contours of absorption bands are governed by the vibronic structure and the population of electron energy levels that combine in corresponding transitions. Electron transitions take place mainly from the zero vibronic level of the lower (ground) state onto various vibronic levels of the upper (excited) states. In addition, “hot” absorption bands can be observed, when electrons are excited from higher (nonzero) vibronic levels of the ground state.

In our work, the energy of a C₆₀ molecule increases by 3.02 eV if one photon of a pump laser pulse is absorbed.

This energy is enough for electrons to transit to vibronic levels of the S_1 and S_2 states. In this case, the electron subsystem of a C_{60} film is in a nonequilibrium state. Therefore, after the action of the excitation pulse has terminated, the relaxation processes that bring the system back to the initial state or a transition into a new equilibrium state takes place. These processes are the thermalization of electrons and the luminescence, which give rise to the occupation of vibronic levels of the S_0 and S_1 states. The fact that the vibrational modes $H_u(4)$ and $T_{1u}(4)$ are observed in the luminescence spectra of concentrated C_{60} solutions in hexane [7] testifies in favor of the latter process. Excitation of electrons from nonzero vibronic levels by a probe pulse is responsible for the appearance of “hot” absorption bands.

In the spectra of induced absorption by C_{60} films in the probe interval of 2.04–2.37 eV, the bands at 2.097, 2.209, and 2.262 eV were observed, which are typical of the linear spectra for these films considered above, as well as the additional bands at 2.164, 2.299, and 2.331 eV (Figs. 3 and 4). In the ascending order of their energies, the additional bands were identified as interband transitions associated with the molecular transitions $S_0 + H_u(4) + A_g(2) \rightarrow S_2$, $S_0 + H_u(4) + H_g(1) \rightarrow S_2$, and $S_0 + H_u(4) \rightarrow S_2$, where S_2 is the zero vibronic level of the second excited state (band A). Hence, those bands can be classified as “hot”. If we suppose that the systems of vibronic levels for the S_0 and S_1 states of a C_{60} molecule coincide, the “hot” bands obtained for the C_{60} film can be identified as the interband transitions between nonzero vibronic levels of the S_0 state and zero vibronic levels of the split S_1 state.

The contour shape $\Delta D(E)$ of the structured band that arises owing to the absorption in C_{60} films induced by a femtosecond laser is determined by the intensity ratio for separate bands considered above and changes in time. When the probe and pump pulses start to overlap in time ($\tau_d = -0.54$ ps), the high-energy bands at 2.262, 2.299, and 2.331 eV emerge in the $\Delta D(E)$ spectra (Fig. 3, curve 1). When τ_d varies from -0.54 to 0.06 ps, the low-energy bands at 2.097, 2.164, and 2.209 eV also make their contribution to the structured band $\Delta D(E)$ (Fig. 3, curves 2 to 5). The integrated intensity of the structured band is maximal at $\tau_d = 0.26$ ps, and its maximum coincides with a band at 2.262 eV (Fig. 3, curve 6). If τ_d increases from 0.26 to 882 ps, the integrated intensity of the structured band $\Delta D(E)$ decreases, which is associated with a decrease of the overlapping of pump and probe pulses and a reduction in the population of the bands formed by nonzero vibronic levels of the S_0 and S_1 states (Fig. 4, curves 1 to 7). A shift of the

position of the structured band maximum from 2.262 to 2.097 eV is observed (Fig. 4, curves 1 and 4, respectively). According to the Franck–Condon principle, this fact testifies to a configuration modification of the potential energy surface for the S_1 state of C_{60} molecules at their excitation from the ground state. The electron subsystem of C_{60} films relaxes into the equilibrium state after the time interval $\Delta t > 882$ ps.

The energies of those bands that form the contour of the induced absorption band for C_{60} films are designated in Table 2 by the bold font. For the “hot” band at 2.334 eV, the τ_{r1} - and τ_{r2} -values are smaller than their counterparts for the band at 2.260 eV. The presence of the induced absorption $\Delta D > 0$ for the bands at 2.097, 2.209, and 2.262 eV may testify to an increase in the population of the S_0 band formed by zero vibronic levels of the S_0 state of C_{60} molecules, as a result of electron transitions either from the lower filled degenerate band formed by the levels h_g and g_g or from the upper bands in the course of the electron thermalization and luminescence processes.

Laser pump pulses generate the nonequilibrium population of the bands formed by vibronic levels of the S_0 and S_1 states of a C_{60} molecule. Therefore, changes in the intensities of separate bands (Figs. 3 and 4) mainly result from a reduction in the population of those bands in time, which can be described by a sum of three exponents with different τ_r 's. To elucidate the origin of each component, the luminescence and photoconductivity spectra have to be registered, which will be a purpose of our further research.

5. Conclusions

In the probing range of 2.04–2.37 eV, the shape of the absorption spectrum induced by femtosecond laser pulses in a C_{60} film consists of the bands at 2.097, 2.164, 2.209, 2.262, 2.299, and 2.331 eV. The bands at 2.097, 2.209, and 2.262 eV are induced by electron transitions between the energy bands created by zero vibronic levels of the S_0 state and nonzero vibronic levels of the S_1 state of C_{60} molecules. For the first time, it has been shown that the “hot” bands at 2.164, 2.299, and 2.331 eV result from electron transitions either between the energy bands created by three nonzero vibronic levels of the S_0 state and the zero vibronic level of the S_2 state or between the energy bands created by three nonzero vibronic levels of S_1 and the zero vibronic level of the S_4 state of C_{60} molecules.

The decreasing temporal kinetics of the optical density D for the induced absorption in C_{60} films was

approximated by a sum of three exponential terms in the time interval 0–882 ps. For probing photons with the energy $E = 2.217$ eV, the following values of relaxation times were obtained: $\tau_{r1} = (1.04 \pm 0.13)$ ps, $\tau_{r2} = (5.81 \pm 0.94)$ ps, and $\tau_{r3} = (108.0 \pm 9.3)$ ps. The approximation of those kinetics by the Kohlrausch function (the “stretched” exponent) allowed us to evaluate the effective relaxation time τ_r as 6.0 ps, which is close to the τ_{r2} -value. The electron subsystem of C60 films needs the time interval $\Delta t > 882$ ps to relax into the equilibrium state. The quantities τ_{r1} and τ_{r2} were found to depend significantly on the approximation time interval and the method used for averaging the kinetics $\Delta D_n(t)$. For τ_{r3} , this dependence is much weaker.

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1. I.M. Belousova, O.B. Danilov, and A.I. Sidorov, *Opt. Zh.* **76**, No. 4, 71 (2009).
2. A.A. Mak, I.M. Belousova, V.M. Kiselev, A.S. Grenishin, O.B. Danilov, and E.N. Sosnov, *Opt. Zh.* **76**, No. 4, 4 (2009).
3. I.M. Belousova, O.B. Danilov, T.D. Muravyova, I.M. Kislyakov, V.V. Ryl'kov, T.K. Kris'ko, O.I. Kiseiyov, V.V. Zarubaev, A.K. Sirotkin, and L.B. Piotrovskii, *Opt. Zh.* **76**, No. 4, 97 (2009).
4. T.L. Makarova, *Fiz. Tekh. Poluprovodn.* **35**, 257 (2001).
5. S. Leach, M. Vervloet, A. Despres, E. Breheret, J.P. Hare, T.S. Dennis, H.W. Kroto, R. Taylor, and D.R.M. Walton, *Chem. Phys.* **160**, 451 (1992).
6. J. Hora, P. Panek, K. Navratil, H. Handlirova, J. Humlicek, H. Sitter, and D. Stifter, *Phys. Rev. B* **54**, 5106 (1996).
7. V.S. Pavlovich and E.M. Shpilevskii, *Zh. Prikl. Spektrosk.* **77**, 362 (2010).
8. S.V. Tchekalin, A.P. Yartsev, and V. Sundstrem, *Zh. Eksp. Teor. Fiz.* **120**, 810 (2001).
9. R.A. Cherville and N.J. Halas, *Phys. Rev. B* **45**, 4548 (1992).
10. T. Juhasz, X.H. Hu, C. Suarez, W.E. Bron, E. Maiken, and P. Taborek, *Phys. Rev. B* **48**, 4929 (1993).

11. S.D. Brorson, M.K. Kelly, U. Wenschuh, R. Buhleier, and J. Kuhl, *Phys. Rev. B* **46**, 7329 (1992).
12. S.V. Tchekalin, E. Okesson, V. Sandstrem, and V.M. Faretidinov, *Pis'ma Zh. Eksp. Teor. Fiz.* **58**, 286 (1993).
13. A.L. Dobryakov, S.A. Kovalenko, V.S. Letokhov, Yu.V. Lozovik, G. Marovskii, Yu.A. Matveets, V.M. Faretidinov, and N.R. Ernsting, *Pis'ma Zh. Eksp. Teor. Fiz.* **61**, 957 (1995).
14. C.H. Lee, G. Yu, D. Moses *et al.*, *Phys. Rev. B* **48**, 8506 (1993).
15. D. Moses, C.H. Lee, B. Kraabel *et al.*, *Synth. Metals* **70**, 1419 (1993).
16. I.V. Blonskyi, M.S. Brodyn, and A.P. Shpak, *Ukr. Fiz. Zh. Oglyady* **3**, 93 (2006).
17. S.B. Fleischer, E.P. Ippen, G. Dresselhaus, M.S. Dresselhaus, A.M. Rao, P. Zhou, and P.C. Eklund, *Appl. Phys. Lett.* **62**, 3241 (1993).

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ПРИРОДА І КІНЕТИКА НЕСТАЦІОНАРНОГО ПОГЛИНАННЯ СВІТЛА ПЛІВКАМИ C₆₀, НАВЕДЕНОГО ФЕМТОСЕКУНДНИМИ ЛАЗЕРНИМИ ІМПУЛЬСАМИ

М.П. Горішній, І.А. Павлов, О.В. Ковальчук

Резюме

Використовуючи методику “збудження–зондування”, досліджено структуру і часову еволюцію наведеного фемтосекундними лазерними імпульсами поглинання плівок C₆₀ у спектральній області 2,04–2,37 еВ та часовому діапазоні 0–882 пс. Плівки C₆₀ товщиною 200 нм отримані на кварцових підкладках термічним напиленням у вакуумі 6,5 мПа при кімнатній температурі.

Контури спектра поглинання плівок C₆₀, наведеного фемтосекундними імпульсами, в області зондування 2,04–2,37 еВ формують смуги при 2,097; 2,164; 2,209; 2,262; 2,299 і 2,331 еВ. Смуги при 2,097; 2,209 і 2,262 еВ зумовлені електронними переходами між зонами, утвореними нульовими вібронними рівнями S₀-стану і ненульовими вібронними рівнями S₁-стану молекули C₆₀ відповідно.

Вперше встановлено, що “гарячі” смуги при 2,164; 2,299 і 2,331 еВ зумовлені електронними переходами між зонами, утвореними ненульовими вібронними рівнями S₀- або S₁-станів і нульовими вібронними рівнями S₂- або S₄-станів молекули C₆₀ відповідно.

Часові кінетики спадання оптичної густини ΔD наведеного поглинання плівок C₆₀ в діапазоні 0–882 пс апроксимовано трьома експонентами. Для зондуючих фотонів з енергією $E = 2,217$ еВ одержано такі значення часів релаксації: $\tau_{r1} = (1,04 \pm 0,13)$ пс; $\tau_{r2} = (5,81 \pm 0,94)$ пс і $\tau_{r3} = (108,0 \pm 9,3)$ пс. При апроксимації цих кінетик функцією Кольрауша (“розтягнута” експонента) уточнено величину ефективного часу рела-

ксації τ_p . Вона становить 6,0 пс і є близькою до величини τ_{p2} . В рівноважний стан електронна система плівок C_{60} релаксує через проміжок часу $\Delta t > 882$ пс.

Встановлено, що величини τ_{p1} і τ_{p2} суттєво залежать від вибраного часового діапазону апроксимації і способу усереднення точок кінетики $\Delta D_n(t)$. Для τ_{p3} ця залежність значно менша.