

# Ultrafast relaxation of photoinduced darkening in a fullerite

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(Submitted 23 June 1993)

*Pis'ma Zh. Eksp. Teor. Fiz.* **58**, No. 2, 134–138 (25 July 1993)

The mechanisms for excitation and energy relaxation of charge carriers over times  $\sim 100$  fs in a  $C_{60}$  film have been studied by femtosecond laser spectroscopy. The absorption was studied as a function of the laser beam intensity. An increase in the absorption, with a peak at vanishingly small delay times, gives way to an electronic-vibrational relaxation with time scales  $\tau_1 \sim 1$  ps and  $\tau_2 \sim 30$  ps.

Femtosecond laser spectroscopy is making it possible to study the evolution of various processes in solids in real time, thereby presenting a unique opportunity to directly determine interaction constants, changes in the electron spectrum during the appearance of a new phase, etc. (Refs. 1 and 2, for example).

In this letter we are reporting the use of femtosecond laser spectroscopy to study excited states in  $C_{60}$  and the mechanisms for the relaxation of these states at times in the femtosecond range.

The test sample was a  $C_{60}$  film on a quartz substrate. It was excited by light pulses with a length  $\sim 100$  fs and a frequency  $\hbar\omega_p = 2.02$  eV; the latter was much larger than the band gap,  $E_g \approx 1.6$  eV. The excitation intensity could be varied over the range  $\sim 10^{10}$ – $10^{12}$  W/cm<sup>2</sup> with the help of neutral filters and changes in focusing. The diameter of the excitation spot was about 100  $\mu\text{m}$ . The sample was probed in the spectral region 1.8–2.3 eV by a  $\approx 100$ -fs pulse with a broad spectrum, which was focused to a spot  $\approx 50$   $\mu\text{m}$  in diameter inside the excitation spot. The repetition frequency of the exciting and probe pulses was  $\approx 1$  Hz. The apparatus is described in Ref. 3. The smallest step in the variation of the delay time was 50 fs. The maximum delay time was  $\approx 10$  ps.

The results showed that the sample is darkened in the spectral region 1.8–2.3 eV by the exciting pulse. The extent of the darkening at a fixed delay of the probe pulse with respect to the exciting pulse depends on the probe energy, reaching a maximum at  $\hbar\omega \approx 2.3$  eV.

Figure 1 shows some typical curves of the time dependence of the change in optical density,  $\Delta D$ . While studying  $\Delta D$  as a function of the intensity of the exciting light pulse, we found that an increase in this intensity leads to a proportionate increase in the height of the peak at vanishingly short delay times (Fig. 2). We also found that

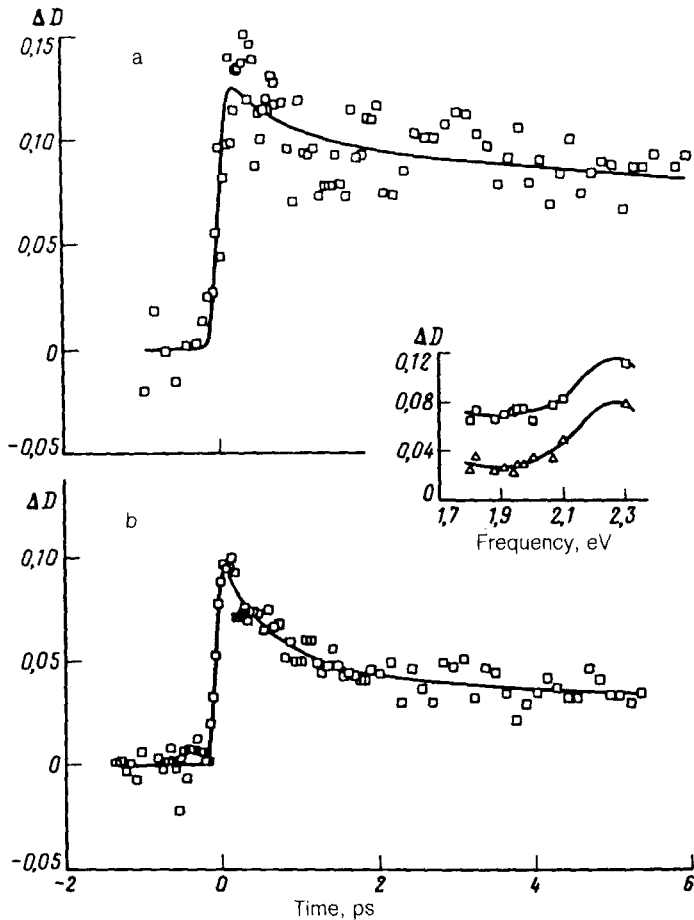


FIG. 1. Time evolution of the change in optical density,  $\Delta D(t)$ . a—At the frequency  $\hbar\omega_p=2.3$  eV; b—1.82 eV. The inset shows spectra of the change in optical density for delay times of 0.5 (squares) and 4 ps (triangles).

at high intensities the shape of the peak is described quite well by the autocorrelation function of the exciting pulse. This behavior of the peak at extremely short delay times suggests that the peak stems from a two-photon absorption (one photon from the exciting pulse and the other from the probe pulse) from the ground state and an excited state.

Approximating the experimental kinetic curves  $\Delta D_{\text{exp}}(t)$  by theoretical curves  $\Delta D_{\text{theor}}(t)$ , and allowing for the contribution of two-photon transitions to the absorption, we found the following values for the relaxation rate of the optical density:  $\gamma_1 \approx 1.3 \pm 0.3 \text{ ps}^{-1}$  ( $\tau_1 \approx 800 \pm 200 \text{ fs}$ ) and  $\gamma_2 \sim 0.03 \text{ ps}^{-1}$  ( $\tau_2 \sim 30 \text{ ps}$ ). Assuming that the peak at extremely short delay times is due to two-photon absorption, we find an estimate  $\beta \sim 2 \times 10^{-8} \text{ cm/W}$  for the coefficient of two-photon absorption.

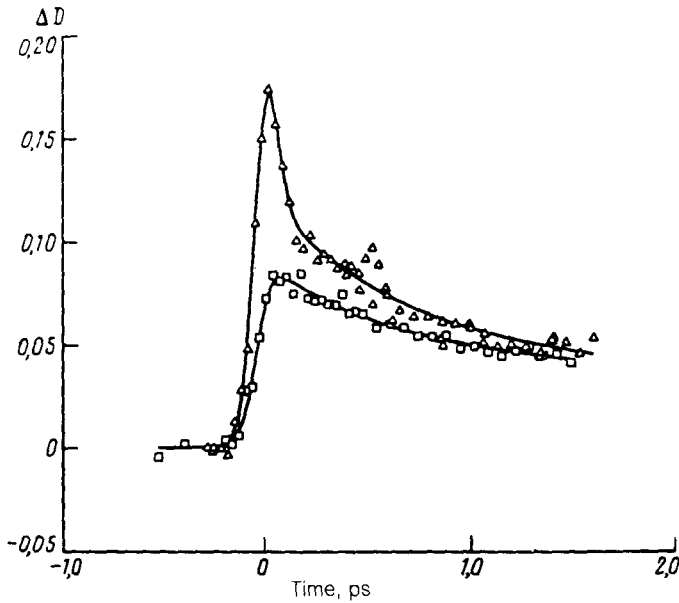


FIG. 2. Time evolution of the change in optical density,  $\Delta D(t)$ , at the frequency  $\hbar\omega_p = 1.88$  eV at two intensities. Squares)  $I \approx 10^{11}$ ; triangles)  $\approx 2 \times 10^{11}$  W/cm<sup>2</sup>.

What physical factors would lead to an increase in absorption in fullerites? In its crystalline state, C<sub>60</sub> is a semiconductor with a band gap  $E_g \approx 1.6$  eV. The spectral region studied here corresponds to transitions from an upper group of valence bands to a lower group of conduction bands, i.e., to  $h_u \rightarrow t_{1u}$  transitions in Fig. 3. These transitions are dipole-forbidden in C<sub>60</sub> molecules. The weak absorption in this region results from a vibron mixing of states. In the solid phase, the mixing of states is even greater, because of the crystal field.

The filling of states in the group of bands  $t_{1u}$  (by the exciting pulse) makes possible dipole-allowed transitions from the lower group of conduction bands into higher-lying bands: the  $t_{1u} \rightarrow h_g$  transitions in Fig. 3. The absorption for these transitions<sup>4-8</sup> falls in the region  $\hbar\omega \approx 2.2 \pm 0.45$  eV, i.e., in the part of the spectrum which we studied. An emptying of states in the  $h_u$  group of bands should lead to a similar increase in absorption, since dipole-allowed transitions from the group of valence bands  $h_g + g_g$  to vacant states of valence-band group  $h_u$  become possible (Fig. 3). The absorption for these transitions is in the region<sup>4-8</sup>  $\hbar\omega \approx 1.4 \pm 0.5$  eV; i.e., it overlaps the spectral region studied.

Another possible cause of an increase in absorption would be an increase in the matrix element of the dipole-moment operator for  $h_u \rightarrow t_{1u}$  transitions. Such an increase might result from an increase in the vibron mixing of the  $t_{1u}$  and  $t_{1g}$  states ( $h_u$  and  $h_g$ ) caused by a pumping of intramolecular  $a_u$ ,  $t_{1u}$ , and  $h_u$  vibrations (and several other

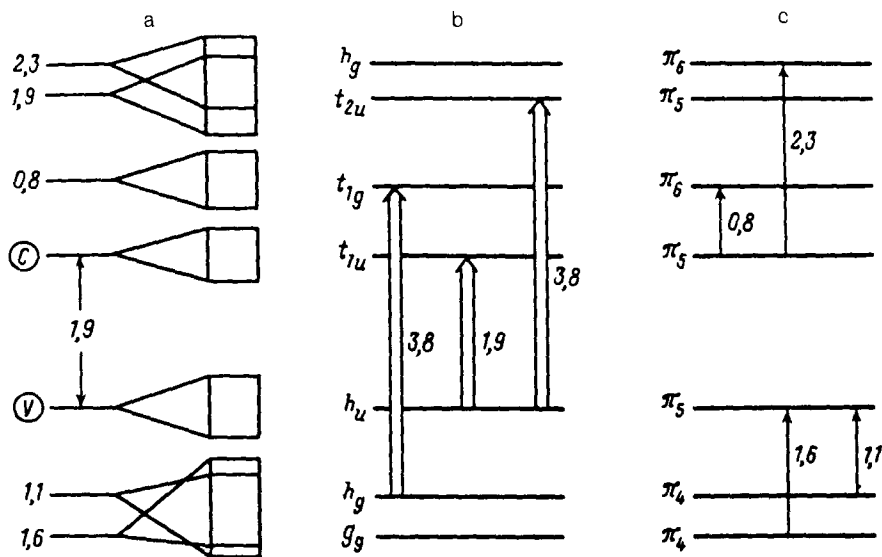


FIG. 3. Energy levels and optical transitions in this fullerite. a: Splitting of molecular levels in a crystal. The lines show that the centers of groups of bands. The number to the left of a line is the distance (in eV) from the corresponding group of bands to the lower group of conduction bands (for the conduction bands) or to the upper group of valence bands (for the lower bands). b: One- and two-photon transitions during absorption of the exciting pulse. The designations of the groups of bands are given to the left of the lines. c: One-photon transitions in the excited state. The numbers beside the arrows are the distances (in eV) between the corresponding groups of bands.

odd vibrations) during absorption of the exciting pulse. As a result, the absorption coefficient should increase in the spectral region  $\hbar\omega \sim 1.9 \pm 0.45$  eV.

An increase in absorption due to transitions from an excited state might differ in time dependence from an increase due to a strengthening of the vibron mixing of states. In the former case, for the spectral region of interest here, the rapid increase in absorption during the filling of states in the bands by hot carriers would be followed by some decrease in absorption, with the time scale of an electronic-vibrational interaction. The reason is that, as they cool down, the hot carriers leave states corresponding to large absorption coefficients and go to states with a smaller absorption coefficients (for the wavelength region of interest here). In the latter case, there would be an increase in absorption due to a pumping of intramolecular  $a_u$ ,  $t_{1u}$ , and  $h_u$  vibrations (and several other odd vibrations) during absorption of the exciting pulse. There would then be a slow increase in absorption due to an anharmonic decay of some vibrations created in the course of the energy relaxation of the charge carriers: the intramolecular  $a_g$  and  $h_g$  vibrations, which would relax to  $t_{1u}$ ,  $t_{2u}$ ,  $g_u$ , and  $h_u$  vibrations with the time scale of a phonon-phonon interaction. The  $h_g$  vibrations, which are not completely symmetric, might also lead to a broadening (or splitting) of the  $t_{1u}$  bands as the result of a Jahn-Teller effect.

The spectral and temporal behavior of the optical density indicates that the

change in absorption results primarily from a filling of electron states and an emptying of hole states in the  $t_{1u}$  and  $h_u$  bands, respectively. The time evolution would result from the relaxation of free carriers involving intramolecular and intermolecular vibrations (phonons). In a first step, both high-frequency  $a_g$  and  $h_g$  intramolecular vibrations and low-frequency intermolecular vibrations (lattice phonons) would be emitted. As a result of the carrier cooling, states near the bottom of the conduction band would be filled by electrons, and states near the top of the valence band by holes. When the energies of the charge carriers are insufficient for the emission of intramolecular vibrations, the emission of lattice optical phonons would become the primary relaxation mechanism. Correspondingly, the relaxation time would change; specifically, it would increase significantly, as it is seen to do experimentally.

The transition of electrons from the  $t_{1u}$  band into a higher-lying band due to  $t_{1u} \rightarrow h_g$  transitions, as well as the transition of holes from the  $h_u$  band to a lower-lying band due to  $h_g + g_g \rightarrow h_u$  transitions, which occur in a two-step absorption of photons of the exciting pulse, would lead to a restoration of the original absorption level. Accordingly, after the passage of an intense exciting pulse, one would observe a weak dependence of the change in optical density on the intensity of this pulse.

According to the band arrangement (Fig. 3) in crystalline  $C_{60}$  at energies  $\hbar\omega \sim 2$  eV, two-photon  $h_g \rightarrow t_{1g}$  and  $h_u \rightarrow t_{2u}$  transitions are possible. We believe that  $h_g \rightarrow t_{1g}$  transitions would be predominant. The electrons and holes resulting from this transition would not participate in single-photon transitions with an energy  $\hbar\omega \sim 2$  eV, and they would not affect the value of  $\Delta D$  in the region of a slow variation. In the excited state (when states in the  $h_u$  band group are freed), new channels open up for two-photon transitions:  $h_g + g_g \rightarrow t_{1g}$  through an intermediate  $h_u$ . Two-photon transitions (both photons coming from the exciting pulse), like two-step transitions, should have the result that the change in the optical density with increasing intensity of the exciting pulse reaches saturation at delay times corresponding to the onset of a "steady-state" value (at high excitation intensities). This behavior agrees with the  $\Delta D(t)$  curves found experimentally.

We wish to thank V. V. Golovlev for assistance in the experiments. This study was supported financially in part by the Russian Fundamental Research Foundation.

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Translated by D. Parsons