

# Generation of charge carriers in C60 films by 100-fs laser pulses with photon energies above and below the mobility edge

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**Abstract.** Primary stages of photoinduced processes are studied in C60 films excited by 100-fs laser pulses at wavelengths of 645 and 367 nm, the fraction of excited molecules being no more than several percent. Probing in the broad spectral range from 400 to 1100 nm showed that both charged (cations and electrons) and neutral (excited molecules) components were produced upon irradiation by the laser pulse. For both excitation wavelengths, charge carriers were produced due to direct optical excitation rather than due to singlet–singlet annihilation. Anions were produced with a delay of  $10^{-13}$ – $10^{-11}$  s through electron trapping by C60 molecules.

**Keywords:** femtosecond spectroscopy, fullerenes, charge carriers.

## 1. Introduction

The dynamics of inducing photoconduction in C60 films has attracted the attention of scientists over nearly ten recent years. In some studies (see, e.g., Ref. [1]), the conclusion was made that charge carriers are produced through direct optical excitation by photons with energy above 2.3 eV (the mobility edge) and through singlet–singlet annihilation at lower photon energies. However, these experiments were made with picosecond time resolution, which is insufficient for revealing primary photoprocesses in solids.

The relaxation of photoexcited molecules in C60 films was also studied with femtosecond resolution [2–8] (see review [2]). In all these papers, the experimental results were interpreted assuming that the excitation produces only one component, which can transform during its relaxation into other intermediate components and photoproducts. The nature of the primary component was treated differently (Frenkel exciton [3], charge transfer exciton [4], molecule in an excited state [5], charge carriers [6], etc.) and, therefore, different relaxation mechanisms were proposed.

The one-component treatment is explained by the fact that probing in most studies was performed at the same wavelength as excitation. Under these conditions, it is impossible, in principle, to reveal the multicomponent nature of the system under study. In the experiments with broadband probing, the excitation intensity in most cases (if not in any case) was such that more than 10% of molecules were excited. For this proportion of excited molecules, the dominant relaxation channel represents singlet–singlet relaxation of neighbouring molecules [2, 5, 7], which substantially hampers the study of other rapid decay channels.

In the experiments with broadband probing reported here, the fraction of excited molecules was not higher than several percent so that the role of annihilation processes was substantially lowered, which allowed us to observe the dynamics of production and decay of primary photoproducts, both neutral and charged, at different excitation intensities.

## 2. Experimental

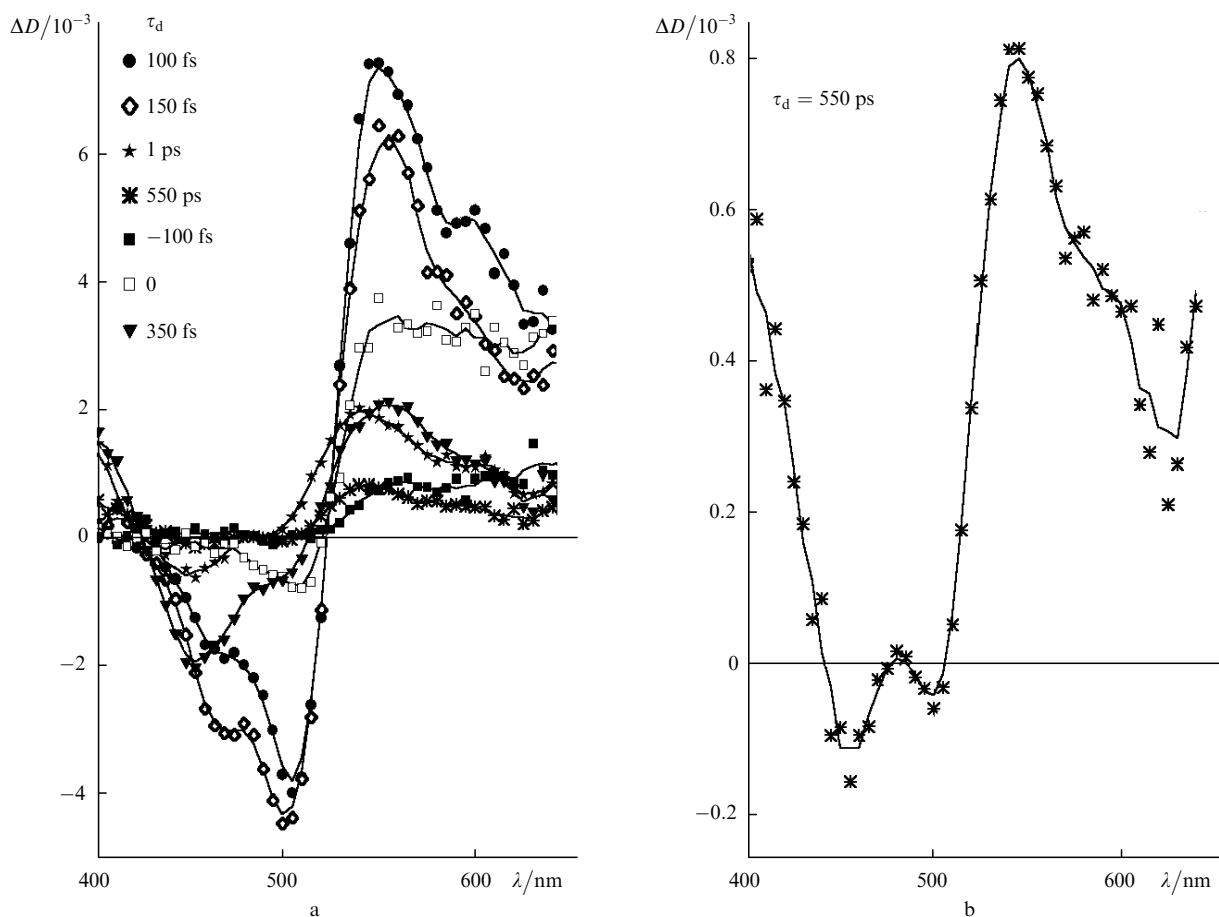
We used the femtosecond pump–probe technique for studying the dynamics of difference absorption spectra of C60 films 140–190 nm thick, which were deposited on quartz substrates. The films were excited by 100-fs pulses at 645 nm ( $10^{10}$ – $10^{11}$  W cm<sup>-2</sup>) and 367 nm ( $10^9$  W cm<sup>-2</sup>) and probed by weak pulses of femtosecond supercontinuum in a spectral range of 400–1100 nm in the range of delay times from –1 to 550 ps. The pulse repetition rate was 5 kHz.

A sample was continuously moved in the direction perpendicular to the laser beam. The displacement velocity was chosen so that the form of kinetics and difference spectra was unchanged with increasing exposure for the same time delay (in order to avoid a noticeable accumulation of photoproducts upon irradiation of the films). All the experiments were performed at room temperature. Samples were kept in the air. Because of this, to eliminate the effect of oxygen, the films were illuminated from the side of the substrate. We also measured the energy absorbed by a sample.

## 3. Experimental results and discussion

We found that the main bands observed in the difference spectrum were the same independently of the excitation wavelength. One of the most substantial characteristics of the spectrum is the appearance of specific features in the spectral region 400–530 nm, which are typical of the electroabsorption spectrum of C60 films [9] (Fig. 1, a decrease in absorption at 465 and 500 nm), during the action of the

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**Figure 1.** Difference spectra  $\Delta D$  of the C 60 film 190-nm thick, measured for different delay times  $t_d$  and a 367-nm excitation pulse ( $\Delta D$  is the optical density of the film).

excitation pulse. This is certainly explained by the appearance of local electric fields in a sample, which do not vanish even for the maximum time delays (the electroabsorption features are clearly seen even for  $t_d = 550$  ps, Fig. 1b). This shape of the difference spectrum shows that the optical excitation at 367 and 645 nm results in the generation of charge carriers.

Analysis of the dynamics of the difference spectrum showed that the spectral range under study contains several regions which strongly differ in relaxation (Fig. 2). The difference in the relaxation kinetics observed in different spectral probing ranges (400–530 nm, 450–700 nm, 700–1100 nm) suggests that these characteristic bands have different nature (for simplicity, they will be referred to as 500-, 600-, and 900-nm bands). This means that at least three different components simultaneously exist in the system, each of them having its own relaxation kinetics. The characteristic bands of these components are strongly overlapped in the difference spectrum. In addition, the character of relaxation in different bands differently depends on the excitation intensity and the presence of oxygen.

It is well known that the latter factor strongly affects photoconduction because oxygen produces in C 60 very efficient deep traps for charge carriers [10]. Because oxygen is accumulated under ordinary conditions in C 60 films at a depth of about 20 nm from the film–air interface [11], its effect can be observed in experiments with short-wavelength excitation, for which the absorption depth is considerably smaller than the film thickness (for  $\lambda = 367$  nm, this depth is

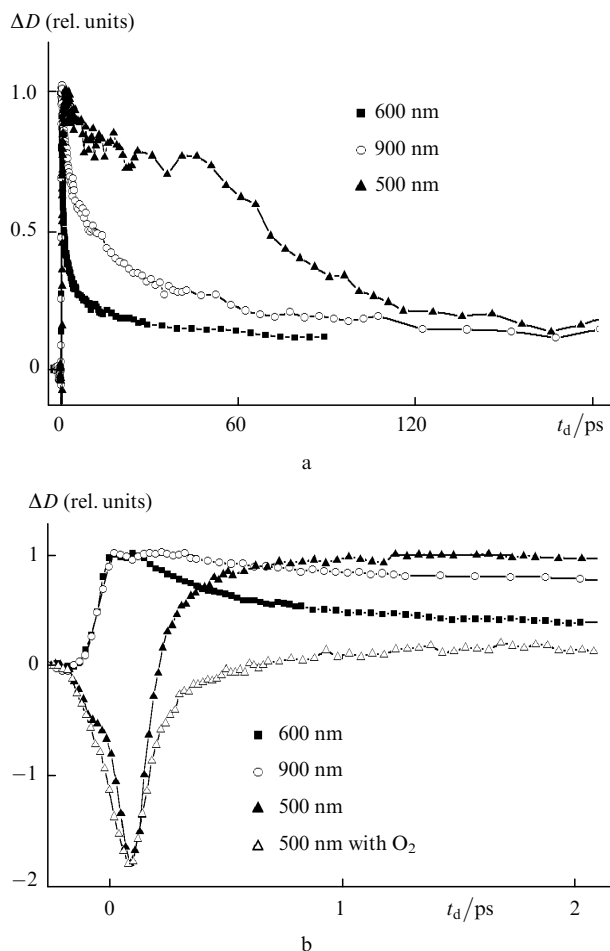
about 40 nm). Thus, comparing the data on 367-nm excitation of a film from the side of air and from the side of the substrate, one can make inferences about the effect of oxygen on the dynamics of processes under study.

These studies revealed the effect of oxygen on the kinetics of the 500-nm band (Fig. 2b), a weaker effect on the kinetics of the 900-nm band, and the absence of effect on the kinetics of the 600-nm band. The conclusion was made that the first two kinetics characterised the relaxation of charged components, whereas the latter characterised the relaxation of a neutral component. The 600-nm absorption band was assigned to excited C 60\* molecules, the 900-nm band was assigned to C 60+ cations, and the 500-nm band was assigned to C 60- anions.

The comparison of the dynamics of difference spectra at different wavelengths suggests the following sequence of processes proceeding in the system:

(1) Excitation of C 60 molecules results in the production of C 60+ (900-nm band), C 60\* (600-nm band), and e<sup>-</sup> (conduction electrons, which are the majority charge carriers in C 60 films [10]). The electric field of the charges produced in a film causes electroabsorption changes in the spectrum of unexcited molecules (Fig. 1) because of the changes in their polarisability and the dipole moment [12]. The rise-times of the kinetics of formation of 600- and 900-nm bands and electroabsorption changes in the spectrum are determined by the pulse duration (Fig. 2).

(2) Because the mobility of conduction electrons is several orders of magnitude higher than that of C 60+ [10], it is



**Figure 2.** Kinetics of changes in absorption  $\Delta D$  (on different time scales) in characteristic bands of the difference spectrum for a 367-nm excitation pulse. The spectra were measured upon excitation and probing from the side of the air ("with  $O_2$ ") ( $\Delta$ ) and from the side of the substrate (the remaining points).

reasonable to attribute rapid changes in the kinetics immediately after an excitation pulse to conduction electrons. Therefore, the increase in absorption in the kinetics of the 500-nm band observed in the range of time delays from 0.1 to 10 ps (Fig. 2b) is caused by an electron ( $e^-$ ) trapping by unexcited molecules accompanied by the formation of the  $C_{60}^-$  anion, which has a rather strong absorption in this band. The efficiency of this process is provided by a high electron affinity of  $C_{60}$  (2.65 eV [10]). In the presence of oxygen, the electron  $e^-$  is efficiently captured by deep traps and, therefore, the rate of anion formation and the anion yield decrease. The anion production due to electron trapping is accompanied by a more slow anion-cation recombination, which leads to a decrease in absorption in the kinetics of the 500-nm band.

(3) Electrons also recombine with cations, which is responsible for a rapid part of the decrease in cation absorption in the 900-nm band (Fig. 2). The slow part of the decrease is associated with the cation-anion recombination.

(4) The relaxation of neutral excited molecules (600-nm band) may be associated with exciton quenching by charge carriers [13].

## 4. Conclusions

It follows from the results of our study that the production of primary charge carriers in  $C_{60}$  films is caused by direct optical excitation when the photon energy exceeds 2.3 eV and, at lower photon energies, by two-photon absorption [8], provided the intensity is insufficient for a substantial manifestation of singlet-singlet annihilation. It is evident that the two-photon absorption increases with increasing intensity and, therefore, the annihilation processes are insignificant in the generation of charge carriers.

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