INFLUENCE OF STATIC AND MICROWAVE MAGNETIC FIELDS ON PHOTOGENERATION OF FREE CHARGE CARRIERS IN DONOR-ACCEPTOR COMPLEX TBPDA·$(C_{60})_2$

D.V. Lopatin[1], V.V. Rodaev[1], A.V. Umrikhin[1], D.V. Konarev[2], A.L. Litvinov[2], R.N. Lyubovskaya[2]

1. Tambov State University, Tambov, 392622 Russia

2. Institute of Problems of Chemical Physics RAS, Chernogolovka, 142432 Russia

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Abstract: The effect of a weak magnetic field with B_0<1 T on photoconductivity of the donor-acceptor complex TBPDA·$(C_{60})_2$ has been found. The RYDMR spectrum is evidence of a spin nature of the mechanism of free charge carrier generation in magnetic fields. A model of triplet-triplet annihilation of charge transfer excitons has been suggested. The model interprets the effect of a weak magnetic field on photoconductivity in TBPDA·$(C_{60})_2$.

Fullerene C_{60} is a new π–acceptor, which essentially differs from other planar π-acceptors by large size, spherical shape, high symmetry and polarizability [1]. These features provide the design of materials possessing unusual magnetic and conductive properties [2]. Fullerenes also have unique photoacceptor properties. Different fullerene based composites, dyads and triads show efficient electron transfer from chromophores to fullerenes and the formation of charge separated states with lifetimes up to tens ms [3]. This makes fullerene compounds promising materials for photovoltaic devices. Thus, it seems interesting to study electron-optical properties of C_{60} compounds, particularly, donor-acceptor complexes with amines.

The goal of this work was to find and study the effect of weak static and microwave magnetic fields on electron-optical properties, particularly, photoconductivity of C_{60} complex with N,N,N',N'–tetrabenzyl-*p*-phenylenediamine: TBPDA·$(C_{60})_2$ [4].

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Synthesis of single crystals of TBPDA·$(C_{60})_2$ was described elsewhere [4]. Photoconductivity was excited by white light of a 150 W halogen tube. Photoconductivity was characterized by current "I" running through indium contacts attached to one of the faces of the samples with silver paste. The contacts were under direct voltage of 10-50 V. Current values were measured with a charge amplifier connected with PC. The cell filled with the sample was put in a resonator of a standard Radiopan SE/X 2547 spectrometer.

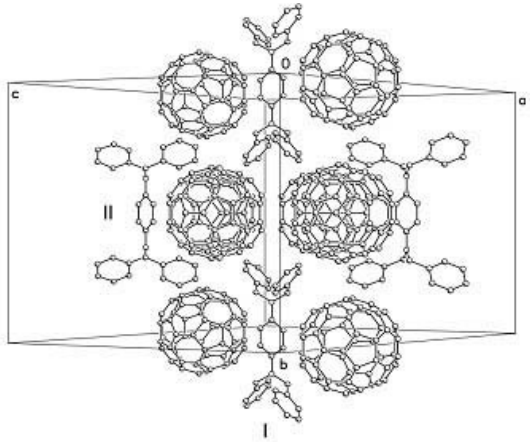

Figure -1. The projection of crystal structure of TMPDA·$(C_{60})_2$ along the c-axis.

TBPDA·$(C_{60})_2$ has a layered structure [4]. Fullerenes form distorted puckered layers arranged along a diagonal to the *ac* plane (Fig. 1). Each C_{60} molecule has 5 neighboring C_{60} ones in the layer with center-to-center distances of 9.77-10.67 Å, several of them being shorter than the van der Waals diameter of the C_{60} molecule (10.18 Å). Due to strong puckering of the C_{60} layers, each C_{60} molecule also has two neighboring C_{60} ones from the adjacent layer with a center-to-center distance of 10.25 Å. TBPDA molecules occupy cavities between the C_{60} layers (Fig. 1) and form van der Waals contacts with the C_{60} molecules by phenyl substituents (molecule ***I***, the C…C distances in the 3.42 – 3.55 Å range) and the central phenylene groups (molecule ***II***, the C…C distances in the 3.33 – 3.52 Å range).

The UV-vis-NIR spectrum of TBPDA·$(C_{60})_2$ is a superposition of the spectra of TBPDA and C_{60}. A broad band in the 700-1100 nm range and the maximum at 896 mn can be attributed to charge transfer (CT) from TBPDA to C_{60} at the absorption of light quantum. However, the IR and EPR spectra of TBPDA·$(C_{60})_2$ indicate the absence of any charge transfer from TBPDA to C_{60} in the ground state. Thus, TBPDA·$(C_{60})_2$ is a neutral CT complex.

Different mechanisms of photoinduced electron transfer are possible under excitation of C_{60} complexes with amines by white light (Fig. 2) [4].

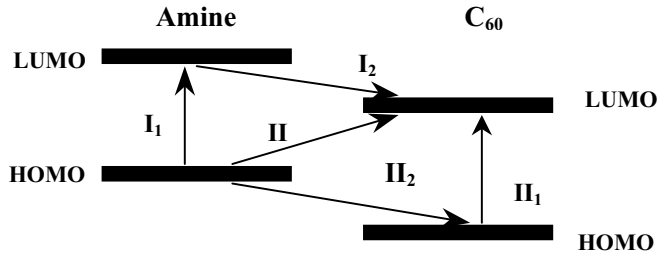

Figure -2. The diagram of possible mechanisms of photoinduced electron transfer in the C_{60} complexes with amines.

Photoexcitation of the donor component (Fig. 2, I_1) is followed by electron transfer to the C_{60} molecule (Fig. 2, I_2). However, photoexcitation of amines is possible only in the UV-range.

Since the C_{60} molecule is a stronger acceptor in the excited than in the ground state, photoexcitation of C_{60} (Fig. 2, II_1) can also result in electron transfer from the donor to the excited C_{60} molecule (Fig. 2, II_2). Due to that the direct HOMO-LUMO transitions are symmetry forbidden in the C_{60}, photoexcitation is realized mainly at energies higher than 2 eV.

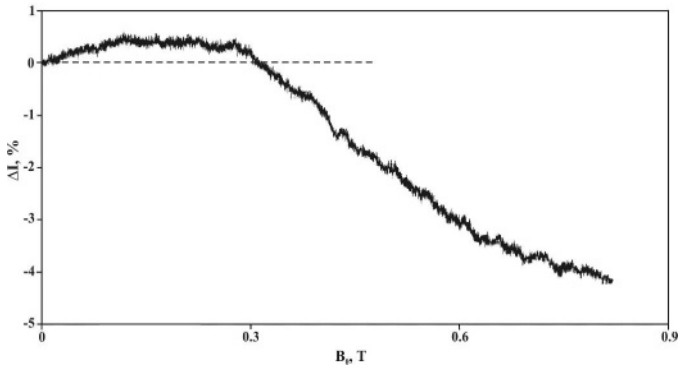

Figure -3. The dependency of relative changes of photocurrent ΔI in TBPDA·$(C_{60})_2$ on magnetic field induction B_0.

Direct intermolecular charge transfer from the donor to the C_{60} molecule (Fig. 2, III) is also possible at the excitation by white light. As it was mentioned above, the CT band in the TBPDA·$(C_{60})_2$ is observed at 1-2 eV.

It was found that in the TBPDA·$(C_{60})_2$ single crystals in neutral ground state show low conductivity, $\sigma \sim 10^{-12}$ $(\Omega^*cm)^{-1}$. Upon illuminating the sample with white light one observes the 10^3 increase of photocurrent, which remains unchanged for 10^4 s. It was found that photoconductivity of TBPDA·$(C_{60})_2$ is sensitive to magnetic field (MF) with $B_0 < 1$ T. The dependency of photocurrent on B_0 is characterized by sign inversion at 0.3 T (Fig. 3) and conceivably attains saturation at 1 T. The sign inversion field dependency is characteristic of processes associated with the effect of MF on concentration of triplet charge transfer excitons in molecular crystals [5].

Photoexcitation of the complex is accompanied by charge transfer from the donor TBPDA molecule to the acceptor C_{60} one and CT-exciton is formed. Depending on mutual orientation of spins of components (electrons and holes), CT-exciton can be either a singlet or a triplet one. Free charge carriers are formed in molecular crystals mainly due to thermal or impurity dissociation of triplet CT-excitons [6].

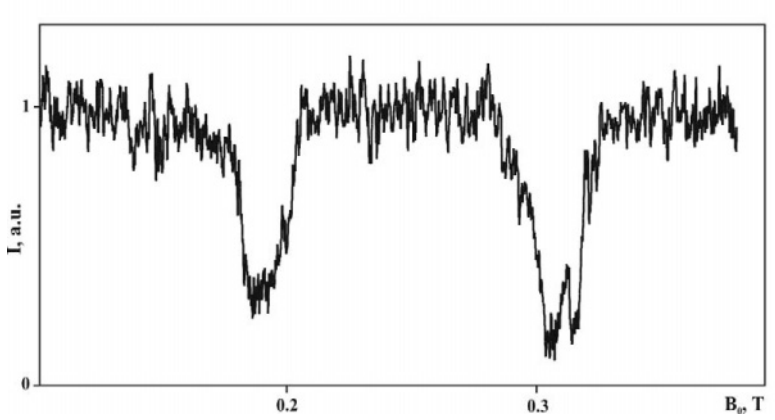

Figure -4. The RYDMR spectrum for TBPDA·$(C_{60})_2$. Microwave magnetic field frequency ν=8.96 GHz.

A spin nature of the effect of MF on photogeneration of free charge carriers was verified under experimental conditions of the registration of an EPR spectrum detected by photoconductivity measurements (RYDMR-Reaction Yield Detected Magnetic Resonance) of TBPDA·$(C_{60})_2$. The spectrum (Fig. 4) contains two resonance peaks of negative polarity at 0.189 and 0.312 T, the peak halfwidth is 0.009 T. The second peak has a fine structure.

The effect of magnetic field on a spin - dependent reactions in solids is valid, provided that [7]: the time τ_{pair} of particles staying in the paired state must be longer than the time needed for mixing the spin states τ_{ev}, but shorter than the relaxation time τ_{rel} with the value typical for molecular crystals $10^{-6} - 10^{-8}$ s: $\tau_{ev} < \tau_{pair} < \tau_{rel}$.

The time τ_{ev} depends on the mechanism of spin evolution. For the dipole-dipole mechanism $\tau_{ev} = \hbar / g\mu D$, where D is the dipole-dipole energy of interaction, μ is the Bohr magneton. The values $\tau_{ev}=2.7\cdot10^{-11}$ s, and $\tau_{pair}=3.1\cdot10^{-9}$ s were calculated for TBPDA·$(C_{60})_2$.

The RYDMR spectrum of the TBPDA·$(C_{60})_2$ crystals is interpreted by a model, which considers external-field modulation of a triplet-triplet exciton annihilation rate constant [6]. The kinetic model of triplet-triplet exciton annihilation can be presented as follows:

$$T + T \underset{K_{-1}}{\overset{\frac{1}{9}K_1}{\rightleftarrows}} {}^{1,3,5}(T...T)_i \xrightarrow{K_S|S_i|^2} S_1 + S_0, \qquad (1)$$

where $(T\ldots T)_i$ - intermediate pair state formed in one of nine possible, *i*th, a spin state; K_1, K_{-1} - rate constants of collision and back scattering; $K_S \left| S_i \right|^2$ - the rate constant of annihilation for the *i*th spin state, S_i-amplitude of singlet components in this state.

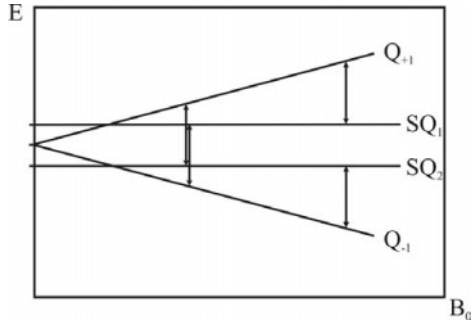

Figure -5. The scheme of resonance transitions in the (T…T) complex.

In magnetic fields with B_0>0.1 T only two levels, SQ_1 and SQ_2 generally contain a singlet component S, which defines the transition of a pair to a final singlet state. These transitions cause partial emptying of the SQ_1 and SQ_2 levels. Microwave magnetic field stimulates mainly transitions from the quintiplet levels Q_{+1} and Q_{-1} to the SQ_1 and SQ_2 ones (Fig. 5), whose occupancy increases. Since the total rate constant (1) defined as

$$\gamma = \frac{1}{9} K_1 \sum_i^9 \frac{K_S |S_i|^2}{K_{-1} + K_S |S_i|^2},$$

is a function of stationary occupancies of the levels of the (T…T) complex, the above mentioned resonance transitions result in the increase of γ.

The increased yield of the reaction products of (1) results in lower concentration of triplet excitons and, consequently, a lower number of free charge carriers formed in molecular crystals that is justified by two resonance peaks of negative polarity in the RYDMR spectrum of TBPDA·$(C_{60})_2$.

The effect of weak magnetic field with B_0 <1 T on photoconductivity of the donor-acceptor layered complex TBPDA · $(C_{60})_2$ has been found. The RYDMR spectrum is evidence of a spin nature of the mechanism of free charge carrier generation in magnetic fields. The information on structure, energy and time performances of short-lived intermediate charge transfer states can be obtained from the analysis of the RYDMR spectrum. A model of triplet-triplet annihilation of charge transfer excitons has been suggested. The model interprets the effect of weak magnetic field on photoconductivity in TBPDA·$(C_{60})_2$.

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REFERENCES

1. Dresselhaus M. S., Dresselhaus G., Eklund P.C. Science of Fullerenes and Carbon Nanotubes, Academic Press, San Diego, 1996.
2. Konarev D.V., Lyubovskaya R.N., *Russ. Chem. Reviews,* 1999, **68** (1), 19-38.
3. Sariciftci N.S., Heeger A.J. Handbook of organic conductive molecules and polymers», ed. H.S. Nalwa, John Wiley and Sons, 1997, **1**, p. 414.
4. Konarev D.V., Kovalevsky A.Yu., Litvinov A.L., Drichko N.V., Tarasov B.P., Coppens P., Lyubovskaya R.N., *J. Solid State Chem.*, 2002, **168** (2), 474-485.
5. Johnson R.C., Merrifield R.E., Avakian P., Flippen R.B., *Phys. Rev. Lett.* 1967. **19** (6), 285-287.
6. Pope M., Swenberg C. Electronic processes in organic crystals, Clarendon Press, Oxford, 1982.
7. Buchachenko A.L., Frankevich E.L., Chemical generation and reception of radio and microwaves, VCH Publishers, New York, 1994.