Spin Properties of Paramagnetic Centers Photogenerated in Crystals of Complexes between C60 and TPA.

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Paramagnetic centers photogenerated in crystals of C_{60}:TPA complexes were studied by 3-cm and 2-mm EPR. Two types of centers with different relaxation and dynamic behavior were found. The temperature dependence of the rotation frequency demonstrates the phase transition.

The electronic properties are studied by various methods: scanning calometry, electronic microscopy and IR spectroscopy, *etc.* [1,2]. One of the most efficient method is ^{13}C NMR spectroscopy. However, this method can not detect the fast molecular rotation [3,4].

Some fullerene systems have an unpaired electron. Therefore these systems can be studied by EPR. Typically such investigations are carried out at 3-cm wave band EPR [1,2]. The single line with linewidth of 0.1-1.3 mT and $g \cong 2$ of C_{60}^{-} radicals was attributed to spin $S=1/2$. In some fullerene systems the radical pairs with $g \cong 2$ were detected (see *e.g.* Ref.[5]). The line splitting of a triplet pair allows one to determine a distance between the paramagnetic centers and a rate of molecular motion. The latter value was determined by *Closs et al.* [5] to be 10^{12} – 10^{13} Hz at room temperature.

Previously we have shown [6] that the 2-mm relative to the 3-cm waveband EPR gives the increase of both the accuracy and sensitivity of the method in the investigation of structural, dynamics and other properties of different condensed systems. The present work first demonstrates the advantages of 2-mm waveband

EPR spectroscopy in more complete study of fullerenes systems. Here we present the results of the spin dynamics study in the photoilluminated C_{60}/TPA (triphenylamine) crystals. Crystals of C_{60}/TPA were grown from solution of the mixture of C_{60} with TPA in chlorobenzen. The concentration ratio between C60 and TPA was about 0.001:1 M in the solution. About one half of C_{60} molecules are in the binding form of charge transfer complexes in chlorobenzene [11]. Black crystals of a suitable size for single X-ray crystallography are obtained within one week. The crystals C_{60}/TPA were washed with acetone from the TPA. For the control experiments the crystals of C_{60} from chlorobenzene without TPA addition have been obtained. IR analysis of C_{60}/TPA intercalate revealed the expected signals for C_{60} and TPA with small addition of chlorobenzene absorption whereas in C_{60} crystals from clear chlorobenzene the absorption bands of solvents are more pronounced. In the C_{60}/TPA crystals the significant absorption band perturbation was observed. The detailed study of this perturbation which should be attributed to the charge transfer complexes formation. X-ray analysis showed the crystal composition 1:1 for C_{60}:TPA. These crystals were illuminated by the light $l > 400$ nm, the light flux was about 30 W/cm^2. The formation of long lived paramagnetic centers (PC) were observed after the illumination. The formation of the C_{60}^{-}:TPA^{+} pairs could be suggested.

At 3-cm waveband the paramagnetic centers (PC) in the sample demonstrates single *Lorentzian* line with g=2.0023 and peak-to-peak linewidth ΔB_{PP}=0.15 mT (Fig.1,a). PC was detected in the crystal to be dissociated at the sample dissolvation in the oxygen free chlorbenzene. The solution of the dissolved crystals is diamagnetic. The second moment M_2 of crystalline complex was calculated to be $8.96 \cdot 10^{-2}$ mT^2. The linewidth of a separate spin-packet was determined from the second moment value as $\Delta B_{SP}=(M_2/3)^{1/2}$ to be 0.17 mT at 300 K. This value is higher than the ΔB_{PP} value. It is probably due to the spin dynamics in the complex.

The central region of second derivative of the absorption signal is presented in Fig.2. Evidently in the sample there is small part of hyperfine interacting with nuclear spins. The hyperfine structure presented in Fig.2 should be attributed to spin interaction with five non-equivalent protons with I=1/2 and nitrogen with I=1 in the complex cation. The splitting between lines of 5.4 mT allows to evaluate the spin density on cation protons, $\rho(0)=2.4\cdot10^{-3}$.

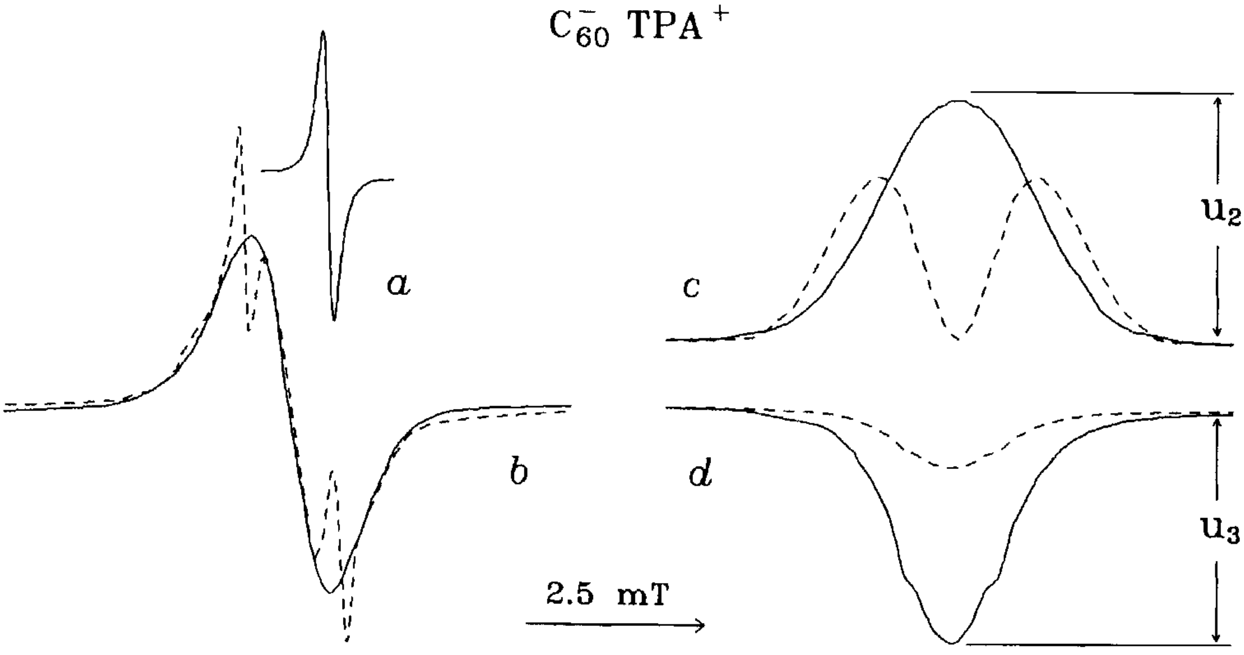

Fig.1. In phase (*a-c*) and π/2-out-of-phase (*d*) components of first derivative of the absorption (*a*,*b*) and dispersion (*c*,*d*) signals of $C_{60}^{-}TPA^{+}$ complex detected at 3-cm (*a*) and 2-mm (*b-d*) wavebands EPR. The first derivative of π/2-out-of-phase component of dispersion signal shown by solid line (insert *d*) is shown by dotted line (insert *b*). u_2 and u_3 components of the dispersion signal detected at B_1=0.02 mT and $B_1=B_{1o}$ are also shown by solid and dotted lines in (*c*) and (*d*) inserts respectively.

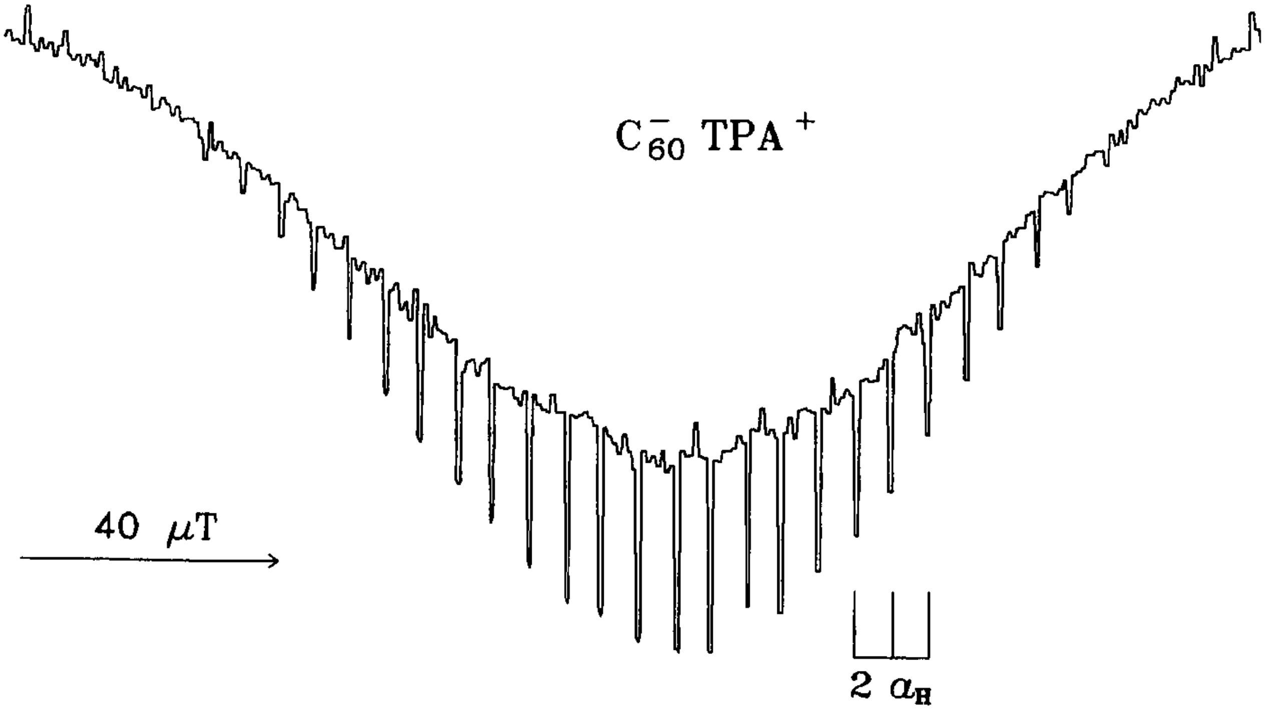

Fig.2. The central region of the second harmonic of X-band absorption signal of $C_{60}^{-}TPA^{+}$ complex registered at room temperature.

At 2-mm waveband the complex is characterized by *Gaussian* symmetrical single line with g=2.00231 (Fig.1,b). The ΔB_{PP} value increases from 1.08 up to 1.17 mT at the temperature increase in 100-300 K range. The spin susceptibility follows *Curie* law at 100-250 K and it decreases sharply at higher temperatures (Fig.3).

In both in-phase and π/2-out-of-phase terms of first harmonic dispersion signal the bell-like *Gaussian* components are detected due to an adiabatically fast passage of the inhomoneously broadened line (Fig.1,c,d). This effect does not detected earlier at lower magnetic fields. It can be explained as following: The probability P of interaction between the spins depends on the absorbed quantum energy as [7] $P \sim \exp(-h\nu_e/kT)$. It leads to the strong decrease of P at 2-mm waveband. The spin-packets become as non-interacting and their width and shapes are changed as in the case of other solid-state organic systems of the lowed dimension [6].

Both the intensity and the shape of the dispersion signals depend on amplitude and frequency ω_m of RF modulation, on polarizing magnetic field B_1, and on spin-lattice T_1 and spin-spin T_2 relaxation times of the PC. If the conditions of the adiabatic fast passage of the resonance are fulfilled, the stationary trajectory of the magnetization vector is reached. In this case the components of the dispersion signal are:

$$U=u_1\sin(\omega_m t)+u_2\sin(\omega_m t-\pi)+u_3\sin(\omega_m t-\pi/2) \qquad (1)$$

are detected in *z*, -*z*, and -*x* axes, respectively (Fig.1,c,d).

The $\omega_m T_1>1$ inequality is fulfilled for $C_{60}^{-}TPA^{+}$ complex. Therefore its dispersion signal is determined mainly by two later terms of Eq.(1). In this case the relaxation times can be calculated from amplitudes of u_2 and u_3 dispersion components (Fig.1,c,d) as

$$T_1 = 3\omega_m (1+6\Omega) / \left[\gamma_e^2 B_{1_0}^2 \Omega (1+\Omega)\right] \qquad (2,a)$$

$$T_2 = \Omega/\omega_m \qquad (2,b)$$

where $\Omega=u_3/u_2$ and B_{1_0} is the value of B_1 when $u_1=-u_2$ (Fig.1,c).

The temperature dependencies of the effective relaxation times of PC in $C_{60}^{-}TPA^{+}$ are present in Fig.3. The Figure 3 shows that T_1 (T) and T_2 (T) functions differ on those of some metals and compounds of lowed dimension. The break in the curves could be attributed to the structural conformation transition in the system at $T_c \cong 250$ K. The T_c value is near to that of phase transition in C_{60} single crystal [1,2]. It is accompanied with the ibrative reorientation of preferable

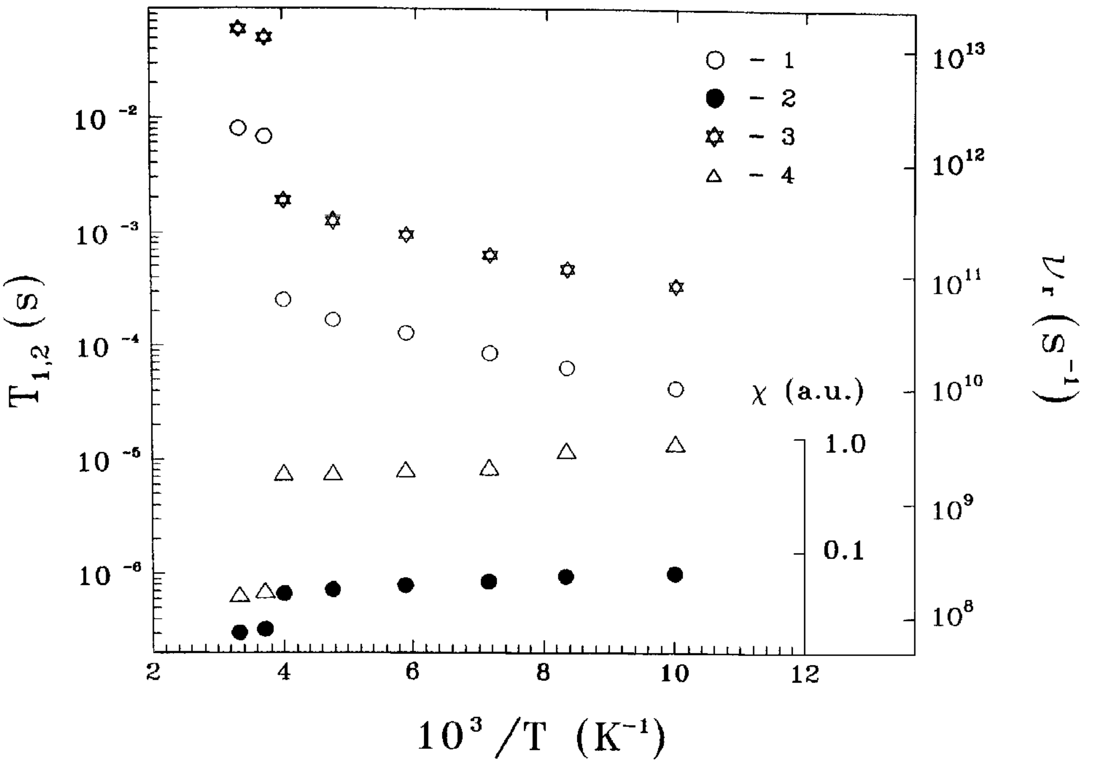

Fig.3. The *Arrhenius* temperature dependencies of the effective spin-lattice T_1 (*1*) and spin-spin T_2 (*2*) relaxation times, the frequency of rotation mobility ν_r (*3*), and relative susceptibility χ (*4*) of paramagnetic centers in $C_{60}^{-}TPA^{+}$ complex.

axis of some C_{60} molecules by 22° and the change of the crystal unit volume.

The mutual rotational motion of spin and C_{60} molecule with characteristic time $\tau_r = \nu_r^{-1}$ induces a magnetic field $B_{loc}(t)$ in the place of localization of other electron and nuclear spins, so influencing their magnetic relaxation rates. The anisotropic dipole interactions are stronger than hyperfine interactions in $C_{60}^{-}TPA^{+}$ complex. Therefore the equation for spin-lattice relaxation rate of PC in polycrystalline sample can be written as [8]:

$$T_1^{-1} = \frac{1}{3}\gamma_e^2 M_2 P\left[J(\omega_e) + 4J(2\omega_e)\right] \quad (3)$$

where P is the probability of the spin situation on each crystal unit and $J\left(\omega_e\right) = 2\nu_r / \left(\nu_r^2 + \omega_e^2\right)$ [3].

The temperature dependence of the rotational spin diffusion rate ν_r calculated for $C_{60}^{-}TPA^{+}$ from Eq.(3) at $\omega_e\tau_r \ll 1$ is also presented in Fig.3. The Figure 3 shows that the spin rotation frequency increases monotonicaly with the temperature increase from 100 up to $T_c \cong 250$ K and then increases sharply up to $1.5 \cdot 10^{13}$ s^{-1} at 300 K. As in the case of single crystal C_{60}, such a drop is probably caused by the phase transition accompanied by the change of the unit size. This process decreases the energy barrier of the molecular rotation that leads to an the increase of the motion rate in the complex. The frequency of molecular rotation was determined to be $\nu_r = 1.2 \cdot 10^{12} \exp(-0.024/kT)$ at $T \leq T_c$. The preexponent corresponds to an upper frequency limit for optical phonons in solids. The activation energy E is near to the phonon energy of C_{60} single crystal, 0.025 eV [9], however, it is less then that of C_{60} rotation, 0.052 eV determined by X-ray structure analysis [10]. Such a discrepancy can be explained by the larger size of elemental unit of $C_{60}^{-}TPA^{+}$ complex that should lead to the decrease of rotational barrier for PC.

The first derivative of $\pi/2$-out-of-phase component of the dispersion signal shown in Fig.1,d is presented by dotted line in Fig.1,b. The comparison of this spectrum with the absorption signal (Fig.1,b) shows that two PC, R_1 and R_2 with equal g-factors but different relaxation and dynamics parameters are stabilized in the complex after illumination by the visible light. The singlet attributed to radical R_1 has ΔB_{PP}=1.08 mT, whereas PC R_2 demonstrates doublet with ΔB_{PP}=0.19 mT splitted by D=1.37 mT (Fig.1,b). The shape of the latter spectrum should be attributed to triplet pairs stabilized in the sample. The distance r_{12} between PC in this triplet can be calculated in the framework of an interaction of two point-like dipoles from the equation

$$D = \frac{3}{2}\gamma_e \hbar r_{12}^{-3} \tag{4}$$

to be 1.22 nm. This value is less than the distances between C_{60}^{-} anions (1.8334 nm) and between C_{60}^{-} anion and TPA^{+} cation (1.5394 nm), however, exceeds another anion-cation distance (0.9953 nm) obtained for the complex by X-ray spectroscopy. This discrepancy could be explained by more planar conformation of cation in triplet pairs.

The u_3 value is determined mainly by spin-lattice relaxation, therefore the ratio of the effective relaxation rates of R_1 and R_2 radicals can be estimated from the analysis of sum $\pi/2$-out-of-phase dispersion spectrum. This ratio depends weakly on temperature. It is approximately equal to 1:80.

As Fig.1 shows, the spectrum of PC R_2 is manifested in $\pi/2$-out-of-phase dispersion signal only. This means that the effective relaxation and consequently the rotation rate of this center exceeds at least by order of the value for R_1. Indeed, the evaluation of ν_r from modified Eq.(3) for the triplet radical pair [5]

$$T_1^{-1} = \frac{1}{15}\gamma_e^2 D^2 P\left[J\left(\omega_e\right) + 4J\left(2\omega_e\right)\right] \tag{5}$$

gives $\nu_r \sim 10^{15}$ s^{-1} at room temperature that is higher than that estimated for R_1 radical. This leads to a strong narrowing of R_2 linewidth as compared with R_1 center (Fig.2,b).

Conclusions

Two PC with different relaxation and dynamics parameters are stabilized at irradiation of $C_{60}^{-}TPA^{+}$ complex. C_{60} molecules rotate activatively at low temperatures and the rate of this motion increases sharply at phase transition. This is accompanied with the change in the electron relaxation and in the paramagnetic susceptibility of the system. The change in the conformation of the complex cation also leads to the considerable increase in the rotation frequency.

The data obtained show the evident advantages of 2-mm waveband EPR spectroscopy in the investigation of the fullerene complex $C_{60}^{-}TPA^{+}$. The method allows to analyze more completely and correctly the magnetic and relaxation parameters of paramagnetic centers of different mobility, to obtain fine peculiarities of molecular and spin dynamics in this complex. Undoubtedly, this method can be successfully used also in the investigation of other fullerene compounds.

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