

## SPIN PROPERTIES OF PARAMAGNETIC CENTERS GENERATED UNDER IRRADIATION OF CRYSTALLINE COMPLEXES OF C<sub>60</sub> WITH TRIPHENYLAMINE

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EPR spectra of paramagnetic centers formed in crystals of C<sub>60</sub> complexes with triphenylamine exposed to visible light are recorded in three-centimeter and two-millimeter spectral ranges. Convincing evidence for the existence of two kinds of paramagnetic centers with different relaxation and dynamic parameters is gained. Rotation of C<sub>60</sub> molecules in C<sub>60</sub>/triphenylamine crystals at low temperatures is an activated process accelerating dramatically upon phase transition. This transition is accompanied by changes in electron relaxation and paramagnetic susceptibility of the system. Rotation frequency of the molecules depends on the size of a unit cell of the complex and on the triphenylamine conformation.

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Charge transfer complexes of fullerenes with electron-donating species hold considerable interest as novel materials evincing unusual conducting and magnetic properties [1, 2]. Single crystals of C<sub>60</sub> complexes with tertial aromatic amines, triphenylamine (TPA) and tetramethylparaphenylenediamine (TMPD), of composition C<sub>60</sub>:amine=1:1 synthesized in our laboratory were the subject of recent investigation into their spectra in the IR and visible spectral ranges and molecular structure [3, 4]. Photoinduced electron transfer and the dependence of the lifetime of radical-ion pairs formed in charge transfer complexes of C<sub>60</sub> with tertial aromatic amines in solutions on the energy gap width were studied in [5-7]. The recorded spectra suggest that in crystals, as well as in solutions, C<sub>60</sub> and amine are coupled by donor-acceptor interaction, and electron is partly transferred from amine to C<sub>60</sub>. Electronic properties of these crystals and, in particular, their spin dynamics sensitively depends on the structure and molecular dynamics of the lattice. The most comprehensive information about the molecular dynamics is

available in the literature for crystalline fullerites. NMR studies have revealed orientational rotation of C<sub>60</sub> molecules in crystals occurring with a frequency of 10<sup>10</sup> Hz at  $T = 300$  K and having an activation energy of 0.024 eV at  $T = 90 - 260$  K and 0.24 eV at  $T > 260$  K [8–11]. Certain fullerene systems generate detectable paramagnetic signals and, therefore, can be studied by the method of electron paramagnetic resonance (EPR). These studies usually cover the conventional three-centimeter EPR range (detection frequency  $\nu_e \cong 10$  GHz) [1, 2]. By using this method, e.g., it has been found that certain systems contain paramagnetic centers (PCs) with a spin of  $S = 1/2$  and  $g$ -factors close to that of a free electron ( $g_e = 2.00232$ ), showing themselves as a single poorly informative line of the order of a few gauss in width. The origin of these PCs is still inadequately understood [1, 2]. Radical pairs were found to occur in some samples (e.g., see [12–16]), and the separation between PCs in them was assessed from their doublet spectra. In going to the two-millimeter range of EPR measurements ( $\nu_e \cong 140$  GHz), the accuracy and information content of EPR measurements of structural and dynamic parameters of condensed systems are vastly improved [17, 18]. High spectral resolution in this EPR range ensures reliable measurement of a full set of magnetic parameters of organic PCs differing in mobility. Weak interaction of spin packets in higher magnetic fields makes it possible to apply the method of continuous microwave saturation of spin packets for studying their relaxation and dynamic parameters in this range. This method was invoked previously to elicit the structure and conformation of certain organic polymeric semiconductors and the dynamics of charge carriers in these compounds [18–20]. Up to this point, EPR technique has never been used in studies of the molecular and spin dynamics of crystals on the basis of fullerenes, and therefore, the effect of intra- and intermolecular motions on the spin dynamics of these compounds remains unexplored [1, 2].

This study is concerned with paramagnetic centers formed in irradiated C<sub>60</sub>/TPA crystals and with spin properties of these crystals measured by means of EPR spectroscopy of two-millimeter and three-centimeter ranges.

## EXPERIMENTAL

Crystals of C<sub>60</sub>/TPA complexes were synthesized by the procedure described in [3] through slow evaporation of solutions saturated with both reagents and subsequent removal of impurities from single crystals of C<sub>60</sub>/TPA. The so prepared black crystals were ground before irradiation in order to increase the surface-to-volume ratio, for the absorption coefficient of the crystals is relatively high —  $3 \cdot 10^4$  cm<sup>-1</sup>. The crystals

were irradiated with the light of a Xe lamp restricted by light filters to the wavelength range of  $\lambda = 450 - 600$  nm.

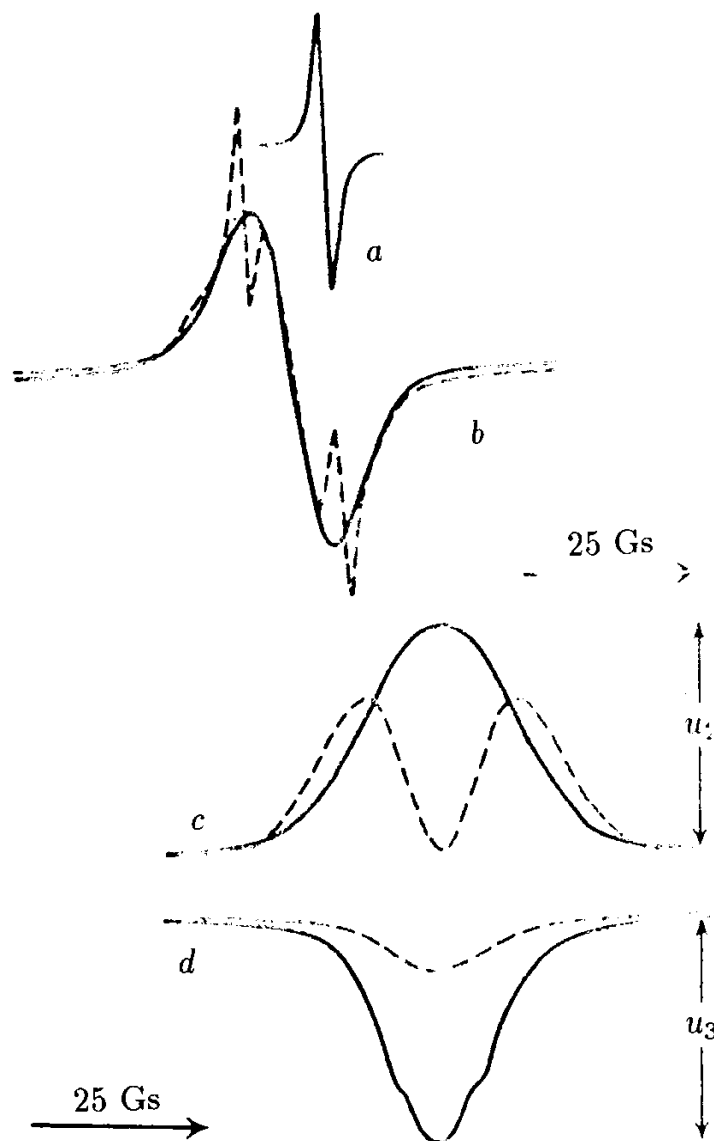


FIGURE 1. In-phase (*a-c*) and quadrature (*d*) components of the first derivative of the absorption (*a, b*) and dispersion (*c, d*) signals from  $C60^-/TPA^+$  recorded in the three-centimeter (*a*) and two-millimeter (*b-d*) EPR ranges. The first derivative of the quadrature component of the dispersion signal shown as a solid curve in Fig.1*d* is marked by a dashed line in Fig.1*b*. The spectra recorded at  $H_1=0.2$  mT (solid curves) and  $H=H_{10}$  (dashed curves) are displayed in Fig.1*c, d* together with the measured components of the dispersion signal ( $u_2$  and  $u_3$ ).

Solid-phase  $C60/TPA$  complex was examined by the EPR method using EPR spectrometers of three-centimeter (PS 100.X) and two-millimeter ranges (EPR5-01) with high-frequency (100 kHz) modulation of the scanning field. In the two-millimeter EPR range, we recorded both components of the complex-valued paramagnetic susceptibility at temperatures from 100 to 300 K by the procedure proposed in

[21]. The concentration of paramagnetic centers was assessed through double integration of the EPR lines of the test sample and a single crystal of diphenylpicrylhydrazyl which served as a lateral reference.

## RESULTS AND DISCUSSION

On exposure of the crystals to visible light, a single almost symmetric EPR spectrum with  $g = 2.0023$  and the separation between peaks of  $\Delta H_{PP} = 1.5$  Gs was observed in the three-centimeter range (Fig.1a). The formed PCs persisted long — several days. The concentration of PCs decays dramatically upon further irradiation of the crystals with IR light. Dissolution of the PC-containing crystals under anaerobic conditions in such solvents as toluene and chlorobenzene also results in disappearance of the EPR signal. From these experiments follows that PC carriers generated under irradiation recombine. This behavior of the system qualitatively agrees with the results of laser photolysis studies of the kinetics of photoinduced electron transfer in complexes: formation of a radical-ion pair is followed by recombination of charges in solutions. The difference in the behavior of the system in crystals and in solutions is that no long-lived radical-ion states form in solutions. Given the PC concentration in the sample, which can be as high as  $N = 1.2 \cdot 10^{20}$  spin/g (which approximately amounts to one spin per five molecules of the complex), the second moment of the Gaussian line of a polycrystalline sample can be calculated as [22]

$$M_2 = \frac{3\pi}{10} \left( \frac{\mu_0}{4\pi} \right)^2 \gamma_e^2 N \hbar r_0^{-3}, \quad (1)$$

where  $\mu_0$  is the permittivity in vacuum,  $\gamma_e$  is the gyromagnetic ratio for an electron, and  $r_0$  is the separation between spins.  $M_2$  measures  $8.96 \text{ Gs}^2$  at  $r_0 = 18.334 \text{ \AA}$  and  $N = 1.7 \cdot 10^{20} \text{ cm}^{-3}$ , which corresponds to an individual spin-packet  $\Delta_{SP} = (M/3)^{1/2} = 1.7 \text{ Gs}$  wide at 300 K. This quantity somewhat exceeds  $\Delta H_{PP}$ , which is presumably associated with the spin dynamics of the complex.

In the two-millimeter range, the sample exhibits a symmetric Gaussian EPR line (Fig.1b) with  $g = 2.00231$ , the width of which,  $\Delta H_{PP}$  varies from 10.8 to 11.7 Gs, as the temperature is increased from 100 to 300 K. The signal intensity approximately follows the Curie law over the temperature range from 100 to 250 K and decays drastically at higher temperatures (Fig.2). The in-phase and quadrature components of the dispersion signal (Fig.1c,d, respectively) involve dome-like components with a Gaussian distribution of spin packets owing itself to the effects of fast adiabatic passage through the inhomogeneously broadened line [23]. Never was an EPR line of this shape observed in the

previous studies of fullerene systems in lower magnetic fields [1, 2, 13–16]. As the detection frequency increases, the probability of interaction between spin packets  $P$  decreases as  $P \sim \exp(-h\nu_e/kT)$  [24]. This interaction reduces so dramatically in the two-millimeter range of EPR measurements that individual spin packets can be reckoned as being noninteracting. This results in broadening of the line which therewith changes its shape and in saturation of the PC spectrum, as happens with other solid organic systems of reduced dimensionality [18–20].

The derivative of the quadrature component of the dispersion signal shown in Fig. 1c is plotted in Fig. 1b (dashed curve). When this spectrum is compared with the initial absorption spectrum, it becomes evident that two kinds of PCs are stabilized in the complex exposed to visible light,  $R_1$  and  $R_2$ , possessing identical  $g$ -factors but different relaxation and dynamic parameters. Radical  $R_1$  exhibits a single symmetric Gaussian spectrum with  $\Delta H_{PP} = 10.8$  Gs, and radical  $R_2$ , a doublet Lorentzian spectrum with  $\Delta H_{PP} = 1.9$  Gs and splitting  $\delta H = 13.7$  Gs between the components (Fig. 1b). The structure and shape of the EPR spectrum of radical  $R_2$  testify to stabilization of a triplet radical pair C60/TPA which is more mobile than  $R_1$ . The separation between PCs of this pair,  $r_{12}$ , can be calculated from the equation

$$D = \delta H = \frac{3}{2} \left( \frac{\mu_0}{4\pi} \right)^2 \gamma_e \hbar r_{12}^{-3} \quad (2)$$

derived in the approximation of interaction of two point-like dipoles. Separation  $r_{12} = 12.2$  Å assessed from Eq.(2) is shorter than the separation between anions C60<sup>-</sup> (18.334 Å) and between anion C60<sup>-</sup> and cation TPA<sup>+</sup> (15.394 Å, however, it exceeds the distance between C60 and TPA molecules in the complex (9.953 Å). This discrepancy is explainable on the following basis. On exposure of the initial sample to visible light, an electron is transferred from TPA to C60 with the result that there forms a triplet pair of radical-anions and radical-cations C60<sup>-</sup> and TPA<sup>+</sup>. The TPA conformation changes from pyramidal to planar, as the molecule goes from the diamagnetic (TPA) to the paramagnetic state (TPA<sup>+</sup>). This is presumably the reason for the aforesaid variation of  $r_{12}$  from the intermolecular separations in the complex assessed from X-ray data.

The intensity and shape of dome-like components depend on the amplitude  $H_m$  and frequency  $\omega_m$  of high-frequency modulation, on the magnetic component of the microwave field  $H_1$ , and on the times of spin-lattice ( $T_1$ ) and spin-spin ( $T_2$ ) relaxation of PCs. Saturation signals make their appearance upon saturation of spin packets and adiabatic passage through their envelope, i.e., at  $\gamma_e H_1 \cdot (T_1 T_2)^{1/2} \gg 1$  and  $\gamma_e \omega_m H_m \ll \gamma_e^2 H_1^2$ . When these inequalities are true, magnetization

vector  $M$  follows a steady-state trajectory, and the dispersion signal  $U$  with a shape function  $g(\nu_e)$  involves the following components [25] (Fig.1c,d):

$$U = u_1 g'(\nu_e) \sin(\omega_m t) + u_2 g(\nu_e) \sin(\omega_m t - \pi) + u_3 g(\nu_e) \sin(\omega_m t - \pi/2). \quad (3)$$

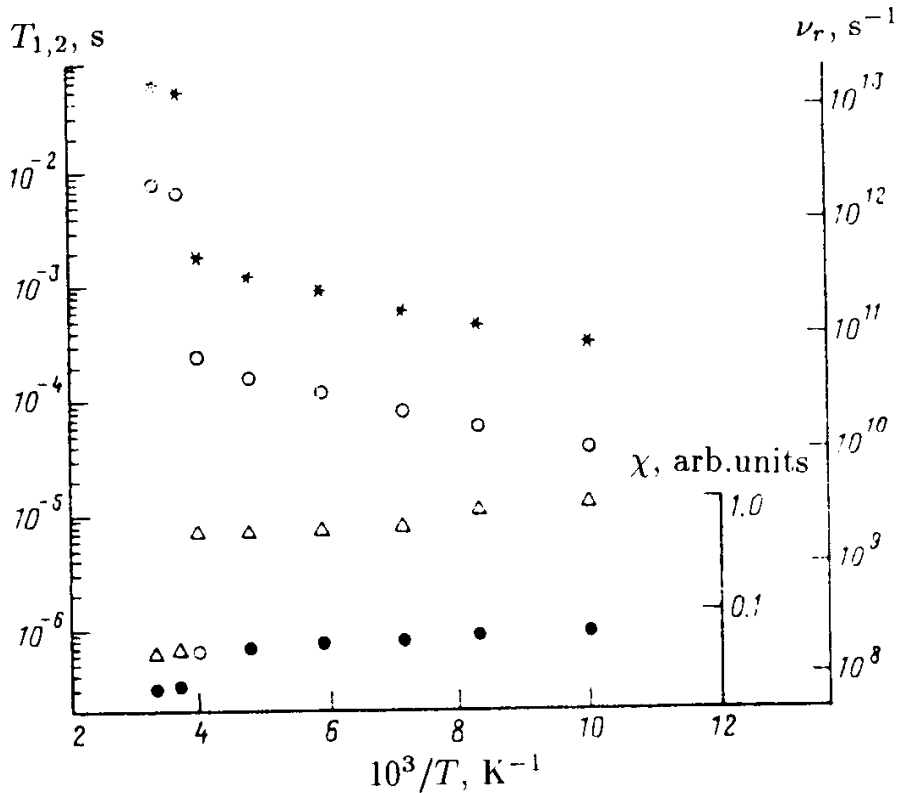


FIGURE 2. Arrhenius dependences of the effective times of (o) spin-lattice ( $T_1$  and (•) spin-spin ( $T_2$ ) relaxation of (\*) the rotation frequency  $\nu_r$  and ( $\Delta$ ) relative susceptibility  $\chi$  of paramagnetic centers in  $C60^-/TPA^+$  complexes.

For a radical-ion pair in a  $C60^-/TPA^+$  crystal,  $\omega_m T_1 > 1$ , and therefore, the dispersion signal is dominated by the last two terms of Eq.(3). As revealed by calculations [26], the relaxation times can be calculated in this case from the ratio of the central amplitudes of these components of the dispersion spectrum:

$$T_1 = 3\omega_m(1 + 6\Omega)/[\gamma_e^2 H_{10}^2 \Omega(1 + \Omega)], \quad (4a)$$

$$T_2 = \Omega/\omega_m, \quad (4b)$$

where  $\Omega = u_3 u_2^{-1}$ , and  $H_{10}$  is the magnetic component of the polarizing field  $H_1$  at which  $u_1 = -u_2$  (Fig.1c).

Electron relaxation times are the effective parameters of radicals  $R_1$  and  $R_2$  with concentrations  $N_1$  and  $N_2$ , respectively. Therefore, when

dipole-dipole interactions of PCs prevail in the complex,

$$(N_1 + N_2)T_{1,2}^{-1} = N_1[T_{1,2}^{-1}]_1 + N_2[T_{1,2}^{-1}]_2. \quad (5)$$

This implies that the relaxation times of PCs of different mobility, present in the complex, can be calculated individually using measured values of  $T_1$ ,  $T_2$ ,  $N$ , and  $N_1/N_2$ . Since the amplitude of the quadrature component of the dispersion signal,  $u_3$ , mostly depends on  $T_1$ , the ratio between relaxation rates of paramagnetic centers  $R_1$  and  $R_2$  of different mobility can be derived from the shape of this component. This ratio approximately equals 80:1 and slightly varies with temperature.

Temperature dependences of the effective relaxation times assessed from two-millimeter EPR spectra of  $C60^-/TPA^+$  taken in a polycrystalline sample are shown in Fig.2. As viewed in Fig.2, the  $T_1(T)$  and  $T_2(T)$  curves diverge conspicuously from the appropriate dependences of certain metals and compounds of reduced dimensionality (e.g., see [17, 26, 27]) and experience a bend at  $T_c = 250$  K. This suggests that the system presumably undergoes structural and conformational transformations. Note that the value of  $T_c$  closely approximates the critical temperature of phase transition in single C60 crystals [1, 2, 8–11] accompanied with changes in the orientation of the preferred axes of certain C60 molecules by  $22^\circ$  and in the volume of a unit lattice cell of the crystal.

Joint rotational motion of a spin and  $C60^-$  molecule with the characteristic time  $\tau_r = \nu_r^{-1}$  induces a local magnetic field  $H_{loc}(t)$  at the locations of other electron and nuclear spins and thereby alters their electron relaxation times. This mobility is characterized by the appropriate spectral density function  $J(\omega_e) = 2\nu_r/(\nu_r + \omega_e^2)$  [28]. It would be pertinent to note that a similar  $J(\omega_e)$  was used previously in analyzing the spin dynamics of C60 [8] and polycrystalline benzo-1,2,3-trithiols [29]. The spin dynamics of  $C60^-/TPA^+$  complexes to a larger extent depends on anisotropic dipole interaction and to a lesser, on isotropic scalar hyperfine interaction of electron and nuclear spins. Therefore, the equations for the electron relaxation rates under the assumption of dipole interaction of equivalent spins ( $S = 1$ ) in this polycrystalline sample can be written as [30]

$$T_1^{-1} = \frac{1}{3}\gamma_e^2 M_2 P [J(\omega_e) + 4J(2\omega_e)], \quad (6a)$$

$$T_2^{-1} = \frac{1}{6}\gamma_e^2 M_2 P [3J(0) + 5J(\omega_e) + 2J(2\omega_e)], \quad (6b)$$

where  $P$  is the probability of spin location at each lattice point.

The temperature dependence of the rotational spin diffusion rate ( $\nu_r$ ) calculated from Eq.(6a) for a C60<sup>-</sup>/TPA<sup>+</sup> complex at  $\omega_e\tau_r \ll 1$  is displayed in Fig.2. From this curve it is obvious that the frequency of spin rotation first increases monotonically with temperature in the temperature range from  $T = 100$  K to  $T_c = 250$  K and then increases steeply to  $1.5 \cdot 10^{13}$  s<sup>-1</sup> at 300 K. This upsurge of frequency is presumably associated with a phase transition in the C60<sup>-</sup>/TPA<sup>+</sup> complex, accompanied, as in the case of C60 [31], with variation of the unit cell size. This variation lowers the energy barrier to rotation and thus entails an increase in the molecular mobility.

The activation energy for rotation was assessed from the slope of the low-temperature dependence of  $\nu_r$ ,  $E_a = 0.024$  eV. Thus, the rotation frequency varies by the activation mechanism as  $\nu_r = 1.2 \cdot 10^{12} \exp(-0.024/kT)$  [s<sup>-1</sup>]. The preexponential factor is of the same order as the cutoff frequency of optical phonons in solids [32]. The above  $E$  value is close to the energy of lattice phonons ( $h\nu_{ph} = 0.025$  eV) in single crystals of C60 [33], however, it is lower than the activation energy for C60 rotation ( $E_a = 0.052$  eV) determined by X-ray analysis [34]. A lower value of  $E_a$  for a C60<sup>-</sup>/TPA<sup>+</sup> complex can be attributed to a larger size of its unit cell, owing to which the barrier to its rotation is lower.

The doublet spectrum of  $R_2$  shows up only in the quadrature component of the dispersion signal (Fig.1d), and no such spectrum was detected in the in-phase components of the dispersion and absorption signals. This suggests that the effective relaxation rate and, hence, the rotation frequency of this radical exceed the appropriate parameters of  $R_1$  at least by order of magnitude. Indeed, Eq.(6a) for a radical pair in the complex can be recast as [16]

$$T_1^{-1} = (1/15)\gamma_e^2 D^2 P[J(\omega_e) + 4J(2\omega_e)]. \quad (7)$$

Using Eq.(7) we obtained the following estimate of the rotation frequency of the molecule in a radical pair:  $\nu_r \sim 10^{15}$  s<sup>-1</sup>. The above assumption is supported by an almost ten-fold difference in width between the EPR lines of the two radicals (Fig.1b). This acceleration of rotation of a C60 molecule in a radical pair is explicable on the basis of an increase (by 2.3 Å) in the minimum intermolecular separation due to singlet-triplet transformation and a change-over to the planar conformation of the cation in a C60<sup>-</sup>/TPA<sup>+</sup> complex, which further reduces the energy barrier to C60 rotation.

Thus, two types of paramagnetic centers differing in relaxation and dynamic parameters are stabilized in irradiated C60/TPA complexes. Rotation of C60 molecules at low temperatures is an activated process



which accelerates dramatically upon phase transition. This process is accompanied with changes in the parameters of electron relaxation and paramagnetic susceptibility of the system. The rotation frequency also changes conspicuously under changes in the conformation of the cationic constituent of the complex.

The data obtained clearly prove the benefits of applying EPR spectroscopy of the two-millimeter range to fullerene-based complexes C60/TPA. This method ensures reliable measurement of magnetic and relaxation parameters of paramagnetic complexes of different mobility and furnishes information about fine details of the molecular and spin dynamics of this complex. This method can obviously be used to advantage for studying other fullerene-based compounds.

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