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Non-linear 2-mm waveband EPR spectroscopy of spin/charge excitations in organic semiconductors

V.I. Krinichnyi*

Institute of Problems of Chemical Physics, 16 Institutski Prospect, Chernogolovka, MD, 142432 Russia

Abstract

This report summarizes the basic aspects of an investigation at 2-mm waveband EPR of magnetic, relaxation and dynamics parameters of various low-dimensional solid-state organic semiconductors with mobile paramagnetic impurities. At high-registration frequency, all components of the g-tensor of such paramagnetic centers are determined. Relaxation and diffusion rates of paramagnetic impurities with different mobilities are determined by the method of steady-state saturation of spin packets. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: EPR; Organic semiconductors; Relaxation; Dynamics

1. Introduction

The recent years are characterized by a great attention to the synthesis and investigation of new electronic low-dimensional systems, organic polymer and fullerene semiconductors [1]. This happened since the investigation of these systems has generated entirely new scientific conceptions and a potential for its perspective application in molecular electronics.

Normally, these systems contain paramagnetic centers (PC) localized or/and delocalized along molecules, therefore EPR spectroscopy is a powerful method for investigation of different properties of organic semiconductors. However, at the usually used centimeter wavebands EPR, the signals of organic free radicals are registered in a narrow magnetic field range that leads to the overlapping of the lines of complex spectrum or spectra of different radicals with similar g-factors [1]. It was shown earlier [2], that transition to 2-mm waveband EPR and use of saturation methods enable the profound investigation of the structure, dynamics, other specific characteristics of paramagnetic impurities and their local environment, and charge transfer processes in different solid-state systems.

This report is devoted to the potentialities of non-linear 2-mm waveband EPR spectroscopy in the investigation of relaxation and dynamics properties of PC in various organic low-dimensional semiconductors, e.g. polyaniline, $(\text{–}C_6H_4\text{–}NH\text{–})_x$ (PANI) slightly doped with sulfuric acid and in triphenylamine fullerene complex ($C_{60}^{-}TPA^{+}$) irradiated by light with $\lambda > 400$ nm.

2. Polyaniline

Nearly symmetric Lorentzian signals are observed in the 3-cm EPR spectrum of the polyaniline slightly doped with sulfuric acid (Fig. 1a). At 2-mm waveband EPR, this sample demonstrates a more informative spectrum (Fig. 1b). Computer simulation of these EPR spectra showed that at least two types of PC are stabilized in the polymer semiconductor, namely localized polarons R_1 with $g_{xx} = 2.00535$, $g_{yy} = 2.00415$, $g_{zz} = 2.00238$, $A_{xx} = A_{yy} = 0.33\,\text{mT}$, and $A_{zz} = 2.3\,\text{mT}$, and polarons R_2 with $g_{\text{eff}} = 2.00395$ moving along polymer chains with a minimum rate $\nu_{1D}^0 \geqslant (g_{xx} - g_e)\mu_B B_0/2\pi\hbar \cong 5.7 \times 10^7\,\text{s}^{-1}$.

In both the dispersion components, the bell-like signals are detected due to an adiabatically fast passage of the inhomogeneously broadened line (Figs. 1c and d). This effect was not detected earlier at lower magnetic

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*Tel.: +7-95-524-5035; fax: +7-96-524-9676.

E-mail address: kivi@cat.icp.ac.ru (V.I. Krinichnyi).

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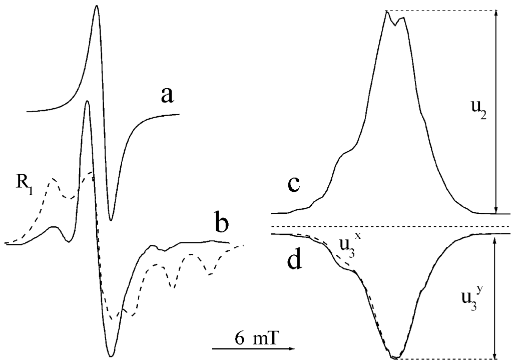

Fig. 1. In phase (a–c) and $\pi/2$-out-of-phase (d) absorption (a,b) and dispersion (c,d) spectra of polyaniline base detected at 3-cm (a) and 2-mm (b-d) wavebands EPR. Dotted lines show shown calculated PC R_1 and dispersion component u_3 registered at low temperature. The dispersion components u_2 and u_3 are shown.

fields. Indeed, the probability of interaction of the spin packets $P \propto \exp(-\hbar\omega_e/kT)$ decreases strongly at 2-mm waveband EPR such that the spin-packets become non-interacting and are saturated at lower RF power. This type of components is a result of rapid passage of PC as the conditions of the spin packets saturation $\gamma_e B_1 \sqrt{T_1 T_2} > 1$ and adiabatic passage of resonance $dB/dt = B_m\omega < \gamma_e^2 B_1^2$ hold (here T_1 and T_2 is, respectively, the spin–lattice and spin–spin relaxation time, dB/dt is the rate of passage of resonance, B_m and ω_m are the amplitude and angular frequency of magnetic field modulation, respectively, and B_1 is the magnetic component of the polarizing RF field. In this case, the dispersion signal consists of one linear and two nonlinear terms [3]:

$$U = u_1 \sin(\omega_m t) + u_2 \sin(\omega_m t - \pi) + u_3 \sin(\omega_m t - \pi/2). \tag{1}$$

The dispersion signal of PANI is determined mainly by the two later terms of Eq. (1), so that both the relaxation times can be calculated from the u_2 and u_3 terms of Eq. (1) as was described earlier [4].

The relaxation times calculated from the dispersion spectra of PC in PANI sample are shown in Fig. 2 as a function of temperature.

The amplitude and shape of the components of the dispersion signal depend not only on the intensity of spin exchange and the rate of electronic relaxation, but also on the relatively slow macromolecular reorientations or torsional librations in the polymer semiconductor. Such motions are usually studied by the saturation transfer EPR spectroscopy (ST-EPR) [5]. Fig. 1 shows that the shape of the u_3 component changes with temperature. It is a typical manifestation of intensification of superslow anisotropic librations of macromolecules with localized R_1 radicals near the main X-axis. The correlation time of such PC motions in PANI was determined from the equation $\tau_c^x = \tau_c^0 (u_3^x/u_3^y)^{-4.8}$ to be $2.7 \times 10^{-7} \exp(0.045 eV/kT)$. The calculated activation energies of macromolecular librations correspond to the energies of optical phonons and are close to the value obtained for poly(tetrathiafulvalene) and poly(bis-alkylthioacetylene) [2].

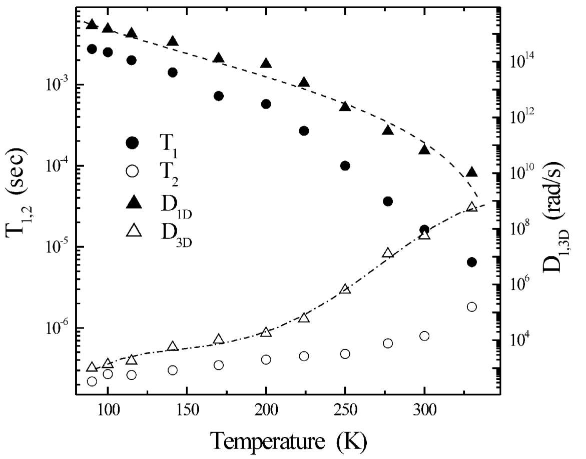

Fig. 2. The temperature dependences of the effective relaxation times, the 1D and 3D translative diffusion coefficients of PC in polyaniline slightly doped with sulfuric acid. The dependences $D_{1D}(T) \propto \ln^4(10^{25} T^{-9.8})$ and $D_{3D}(T) \propto k_1 T \exp(-0.025\, eV/kT) + k_2 T \exp(-0.048\, eV/kT)$ are shown by a dashed and dash-dotted lines, respectively.

The experimental data obtained can be explained by the modulation of electron relaxation by 1D diffusion of mobile polarons along the polymer chains and by their 3D hopping between the chains with the diffusion coefficients D_{1D} and D_{3D}, respectively. Such spin motions induce an additional magnetic field at the sites of other PC. This leads to the increase of effective relaxation rates of the spin ensemble [6]

$$T_1^{-1} = \langle \omega^2 \rangle [2J_1(\omega_e) + 8J_2(2\omega_e)], \tag{2a}$$

$$T_2^{-1} = \langle \omega^2 \rangle [3J(0) + 5J_1(\omega_e) + 2J_2(2\omega_e)], \tag{2b}$$

where $\langle \omega^2 \rangle$ is the second momentum of the line, and $J(\omega_e) = (D_{1D}\omega_e)^{-1/2}$ at $D_{3D} \leqslant \omega_e \leqslant D_{1D}$ and $J(\omega_e) = (D_{1D}D_{3D})^{-1/2}$ at $\omega_e \leqslant D_{3D}$ are the spectral density functions at the spin precession frequency ω_e.

1D spin dynamics in PANI can be interpreted in the framework of the Kivelson–Heeger model [7] of isoenergetic electron transfer between the polymer chain involving optical phonons. According to this model, polarons should diffuse along the chain with a diffusion coefficient of

$$D_{1D}(T) \propto D_{1D}^0 \ln^4[k_1 T^{-n-1}], \tag{3}$$

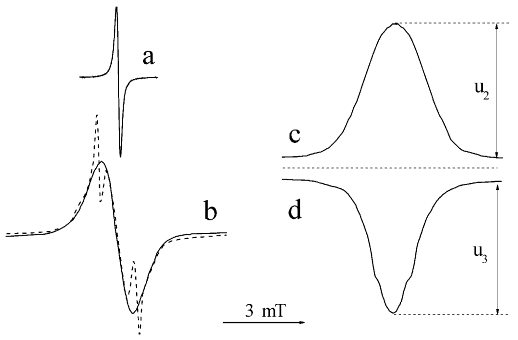

Fig. 3. In phase (a–c) and $\pi/2$-out-of-phase (d) absorption (a,b) and dispersion (c,d) spectra of $C_{60}^{-}TPA^{+}$ complex detected at 3-cm (a) and 2-mm (b–d) wavebands EPR. The first derivative of quadrature dispersion signal (insert d) is shown by a dashed line (insert b). The dispersion components u_2 and u_3 are shown.

where k_1 is constant and $n \cong 10$. Fig. 2 shows that this function $k_1 = 10^{25}\,K^{9.8}$ and $n = 8.8$ fit well with the experimental data.

As in case of inorganic semiconductors, 3D spin dynamics in PANI can be explained by activated hopping through a barrier E_a, $D_{3D}(T) \propto T \exp(-E_a/kT)$. It is seen from Fig. 2, that spins and charges hop between polymer chains with $E_a = 0.025\,eV$ at $T \leqslant 200\,K$ and with $E_a = 0.048\,eV$ at higher temperatures. The latter value lies near the energy of lattice phonons determined above. This leads to a conclusion of modulation of interchain spin/charge transfer by macromolecular motion.

3. Fullerene complex

PC in $C_{60}^{-}TPA^{+}$ demonstrate a single spectrum with $g = 2.0023$ and linewidth of 0.15 and 1.18 mT at 3-cm and 2-mm wavebands EPR, respectively (Fig. 3). At 2-mm waveband, the EPR linewidth decreases down to 1.08 mT for the temperature decreasing down to 100 K. The spin susceptibility follows the Curie law for 100–250 K and it decreases sharply at higher temperatures (Fig. 4).

As in the case of PANI, in both dispersion components, the bell-like signal are detected due to an adiabatically fast passage of the inhomogeneously broadened line (Figs. 3c and d), so that the relaxation times of the sample can be determined from its dispersion components as well.

The temperature dependencies of the effective relaxation times of PC in $C_{60}^{-}TPA^{+}$ are present in Fig. 4. The figure shows that $T_1(T)$ and $T_2(T)$ functions differ on those of some metals and compounds of lower 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 closer to that of phase transition in C_{60} single crystal. It is accompanied with the librative reorientation of preferable axis of some C_{60} molecules by 22° and the change of the crystal unit volume.

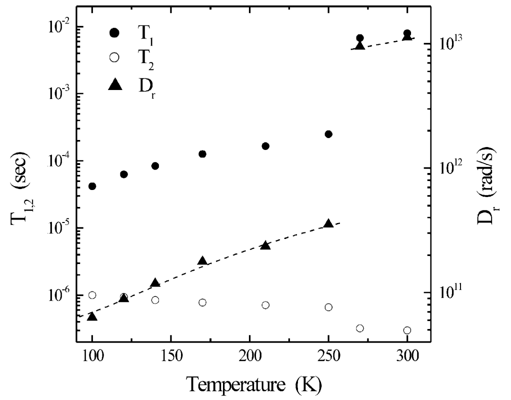

Fig. 4. The temperature dependences of the effective relaxation times, the rotational diffusion coefficient and relative susceptibility of PC in $C_{60}^{-}TPA^{+}$ complex. The dependence $D_r = D_r^0 + k_1 T \exp(-0.027/kT)$ is shown by dashed line.

The temperature dependence of the D_r value calculated for $C_{60}^{-}TPA^{+}$ from Eq. (2) with $J(\omega_e) = 2D_r/(D_r^2 + \omega_e^2)$ is also shown in Fig. 4. The figure shows that the spin rotation frequency increases monotonicaly with the temperature increase from 100 K up to $T_c \cong 250\,K$ and then increases sharply up to $\sim 10^{13}\,s^{-1}$ 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 sample 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 D_r value was determined to be $D_r = D_r^0 \exp(-0.024/kT)$ at $T \leqslant T_c$. $D_r^0 = 1.2 \times 10^{12}\,rad\,s^{-1}$ corresponds to an upper frequency limit for optical phonons in solids. The activation energy E_a is near to the phonon energy of C_{60} single crystal, 0.025 eV [8]; however, it is less than that of C_{60} rotation, 0.052 eV determined by X-ray structure analysis [9]. Such a discrepancy can be explained by the larger size of elemental unit of $C_{60}^{-}TPA^{+}$ complex that should lead to a decrease in the rotational barrier for PC.

The first derivative of $\pi/2$-out-of-phase component of the dispersion signal shown in Fig. 3d is presented by a dotted line in Fig. 3b. The comparison of this spectrum with the normal absorption one (Fig. 3b) shows that, two PC, R_1 and R_2 with ratio 80 : 1 and equal g-factors but with different relaxation and dynamics parameters are stabilized in the complex. The singlet attributed to radical R_1 has $\Delta B_{PP} = 1.08\,mT$, whereas PC R_2 demonstrates a doublet with $\Delta B_{PP} = 0.19\,mT$ splitted by $D = 1.37\,mT$ (Fig. 3b). 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, $D = 1.5\gamma_e \hbar r_{12}^{-3}$to be 1.22 nm. This value is lesser than the distances between C_{60}^{-} anions (1.8334 nm) and that between C_{60}^{-} anion and TPA^{+} cation (1.5394 nm), however, but exceeds another anion–cation distance (0.9953 nm) obtained for the complex by X-ray spectroscopy. This discrepancy can be explained by a more planar conformation of cation in triplet pairs.

As Fig. 3 shows, the spectrum of PC R_2 is manifested only in $\pi/2$-out-of-phase dispersion signal. 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 D_r from Eq. (2) with $\langle \omega^2 \rangle = 1/30\gamma_e^2 D^2$ for the triplet radical pair [10] gives $D_r \sim 10^{15}\,s^{-1}$ at room temperature that is higher than that estimated for R_1 radical with higher linewidth.

4. Conclusions

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

The data obtained show the evident advantages of non-linear 2-mm waveband EPR spectroscopy in the investigation of different organic semiconductors of low dimensionality. The method allows to analyze completely and correctly the magnetic and relaxation parameters of PC of different mobilities in order to obtain fine peculiarities of molecular and spin dynamics in these and other systems.

Acknowledgements

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