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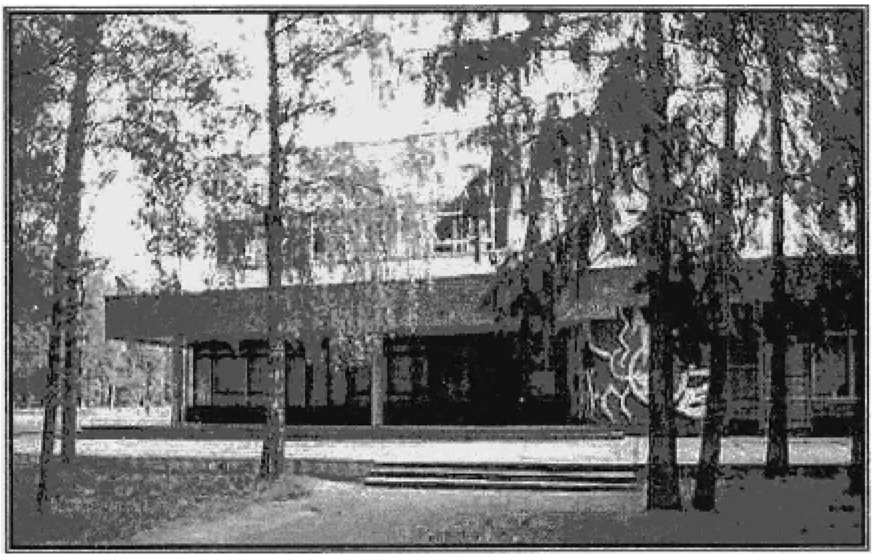

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High-Field Saturation Transfer EPR Method in the Study of Conducting Polymers

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Conducting polymers attract considerable attention due to unusual electronic properties suitable for their perspective application in molecular electronics [1]. The charge in such systems is transferred by non-linear excitations, polarons, characterizing by spin $S = ½$ and fast diffusion along polymer chains. Paramagnetic centers (PC) in most of conducting polymers are localized near heteronucleus involving into backbone that causes small anisotropy of their magnetic resonance parameters. Earlier, it was demonstrated [2, 3] that all terms of anisotropic magnetic parameters of different organic radicals can be registered separately at the increasing of the electron precession frequency $\omega_e/2\pi$ up to 140 GHz (D- or 2-mm waveband) because spectral resolution Δg growths proportional to with ω_e.

Another main advantage of D-band EPR is that it offers the opportunity to investigate the macromolecular mobility of PC with anisotropic magnetic parameters. Such motion is *a priori* realized with correlation times in the range of $\tau_c > 10^{-7}$ s [4]. Except correlation time, PC are characterized also by the anisotropy of the magnetic interaction $\Delta\omega$ and the spin-lattice relaxation time T_1, so then the inequalities $\Delta\omega\tau_c>>1$, $100T_1>\tau_c>0.01T_1$ should be fulfilled for the region of their superslow tumbling domain. The first inequality shows that the absorption EPR spectrum is the same as that obtained by using a rigid powder. The second inequality leads to a spectral diffusion of saturation across the spectrum, since rotational diffusion is comparable to T_1^{-1}. This inequality is valid for PC characterizing by comparatively high spin-orbit coupling and correlation time $10^{-3} > \tau_c > 10^{-7}$ s. Such molecular motions are usually studied by the saturation transfer EPR method (ST-EPR) [5] which broadens the range of correlation time of organic radical rotation up to 10^{-3} s.

Earlier, we shown [6] that at the D-band it becomes possible to use the ST-EPR method in the study of anistropic superslow molecular dynamics in organic solids. In contrast with the nitroxide radicals usually used as a spin probe or spin label introduced into condensed systems, the native polarons with anisotropic magnetic parameters stabilized in conducting polymers become themselves a stable spin labels. Therefore, the nearest environment of such PC remains undisturbed and the results obtained from the study of their molecular and dynamics properties become more accurate and complete. Besides, the sensitivity of both the EPR and ST-EPR methods increases with ω_e, so the methods should be used more efficiently in the study of structure, conformation and macromolecular dynamics of conductive polymers at D-band EPR.

In the present report is analyzed the possibility of the study by the D-band ST-EPR method of superslow anisotropic dynamics in such conducting polymers as polytetrathiafulvalene with phenyl (PTTF-Ph) and tetrahydroanthracene (PTTF-THA) bridges, poly(3-alkylthiophene) (P3AT), poly(*bis*-alkylthioacetylene) (PATAC), emeraldine base form of polyaniline (PANI-EB) including different heteroatoms in backbone.

Figure 1 shows D-band absorption and dispersion spectra of some organic conjugated polymers registered at room temperature. It is seen from the Figure that additional bell-like

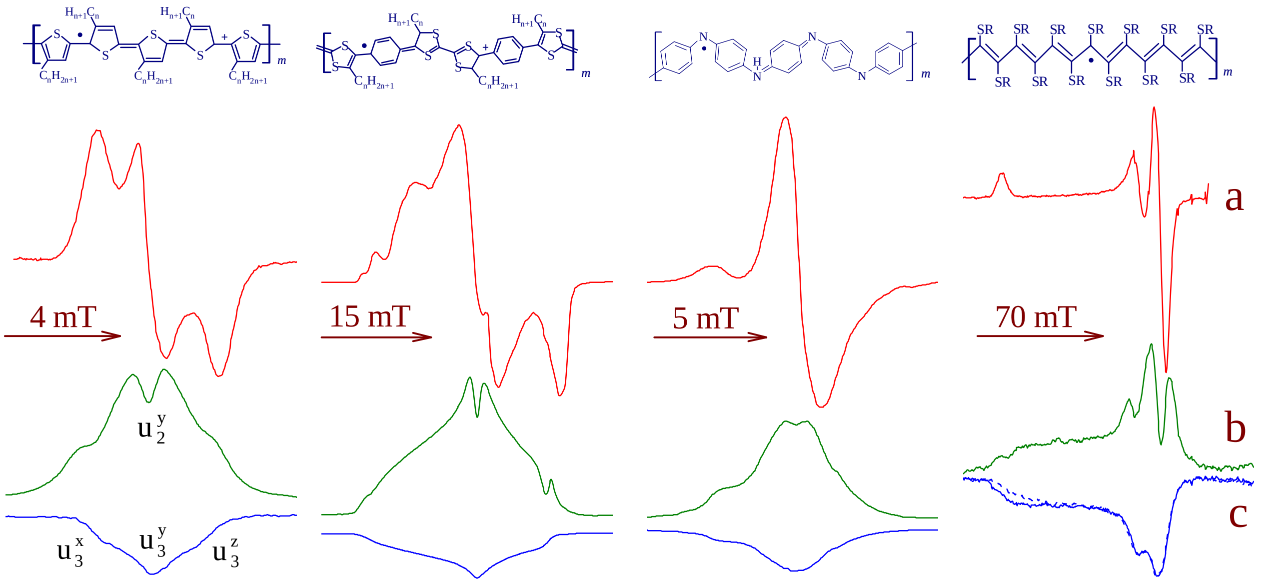

FIGURE 1. D-Band in-phase absorption (*a*) as well as in-phase (*b*) and π/2-out-of-phase (*c*) dispersion spectra of poly(3-alkylthiophene) (P3AT, *n* = 4, 6, 8, 12), polytetrathiafulvalene (PTTF-Ph, *n* = 1, 2), polyaniline (PANI) and poly(*bis*-alkylthioacetylene) (PATAC, *R* = C_nH_{2n+1}, *n* = 1, 2, 3) registered at room temperature.

contributions appear in both the in-phase and π/2-out-of-phase terms of the dispersion spectrum due to microwave adiabatic saturation, when $\gamma_e\omega_m B_m << \gamma_e^2 B_1^2$ (here γ_e hyromagnetic ratio for electron, ω_m and B_m are the angular frequency and amplitude of *ac* modulation field, respectively, and B_1 is the magnetic term of microwave polarizing field) conditions are fulfilled. In this case the first derivative of the dispersion signal is generally written as [7]

$$U = u_1 g^{|}(\omega_e)\sin(\omega_m t) + u_2 g(\omega_e)\sin(\omega_m t - \pi) + u_3 g(\omega_e)\sin(\omega_m t \pm \pi / 2) \qquad (1)$$

At the absence of microwave saturation both the u_2 and u_3 terms of Eq.() tend to zero and the spectrum transforms into classical shape $g^{|}(\omega_e)$. The saturation being realized, the relative intensity of u_1 and u_3 components is defined by the relationship between the relaxation time of a spin-packet and the rate of its resonance field passage.

We shown [8] that all the spin-lattice and spin-spin relaxation times of saturated PC in π-conducting polymers can be determined separately from the analysis of all the terms of Eq.(3). On the other hand, the analysis of the latter term of Eq.(1) allows one to determine the parameters of the PC superslow dynamics by using the principle of the ST-EPR method [5]. According to the method, the most sensitive to such molecular motions are the first harmonic dispersion of π/2-out-of-phase and the second harmonic absorption of π/2-out-of-phase spectra. The rotational diffusion of the radical leads to the diffusion of saturation across the spectrum with the average transfer rate [5]

$$\left\langle \frac{d(\delta B)}{dt} \right\rangle = \sqrt{\frac{2}{3\pi^2 T_1 \tau_c}}\, \frac{\sin\vartheta\cos\vartheta\left(B_\perp^2 - B_\parallel^2\right)}{\sqrt{\left(B_\perp^2\sin^2\vartheta + B_\parallel^2\cos^2\vartheta\right)}} \qquad (2)$$

where δB the average spectral diffusion distance, $B_\perp$ and $B_\parallel$ are the anisotropic EPR spectrum components arrangement along the field, ϑ is the angle between $\mathbf{B}_0$ and a radical axis. If the following inequality holds for a correlation time of radical rotation near main, e.g. *x*-axis [5]

$$\tau_c^x \le \frac{2}{3\pi^2 T_1 \gamma_e^2 B_1^4}\, \frac{\sin^2\vartheta\cos^2\vartheta\left(B_\perp^2 - B_\parallel^2\right)^2}{B_\perp^2\sin^2\vartheta + B_\parallel^2\cos^2\vartheta} \qquad (3)$$

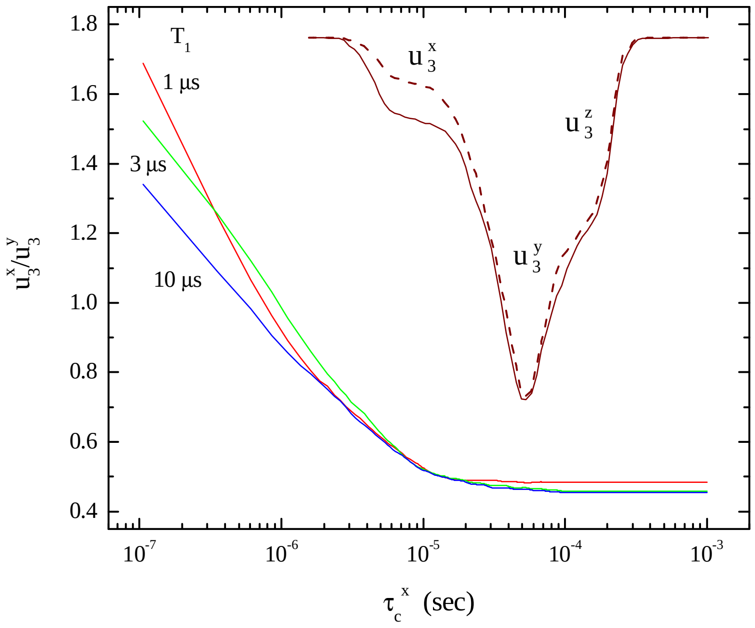

FIGURE 2. The dependence of the u_3^x/u_3^y ratio of the π/2-out-of-phase dispersion term components shown in the insert on the correlation time τ_c of PC motion near *x*-axis at different spin-lattice relaxation time T_1. In the insert by solid and dashed lines are shown ST-EPR spectra calculated respectively for slower and faster radical rotation near main molecular *x*-axis.

the adiabatic condition can be realized for the radicals oriented by *x*-axis along $\mathbf{B}_0$ and it can not be realized for the radicals of other orientations. This results in the elimination of the saturation of the spectra of radicals, whose *y* and *z* axes are oriented parallel to the field $\mathbf{B}_0$ and consequently to the decrease of their contribution to the total ST-EPR spectrum.

It is seen from Eqs. (2) and (3) that the increase in registration frequency ω_e should increase the saturation transfer rate across the spectrum and broad the range of relaxation times measured as well. Besides, the higher spectral resolution at higher ω_e allows one to analyze the affect of microwave saturation to all spectral components. Both the mobile charge carriers and those localized on polymer chains possess *x*-anisotropy of magnetic and dynamics parameters. Figure 2 shows the dependence of the u_3^x/u_3^y ratio on the correlation time of PC motion near *x*-axis at different T_1 value evaluated from data of [6]. This allowed us to determine correlation time from the following semiempirical equation [3],

$$\tau_c^x = \tau_{c0}^x \left(\frac{u_3^x}{u_3^y} \right)^{\alpha}, \qquad (4)$$

where α is a constant governed by the anisotropy of spin-orbit interactions. The preexponential factor τ_{c0}^x is the lowest limit for the correlation time in a respective polymer matrix.

The analysis of quadrature components of the dispersion spectra of the polymer samples shows the increase in the u_3^x/u_3^y ratio with temperature. This is evidence of the saturation transfer over their EPR spectra due to superslow macromolecular libration dynamics. The temperature dependences of τ_c^x determined from Eq. 4 for such motion in different conducting polymers are presented in Fig. 3. Assuming activation spin motion with appropriated correlations time

$$\tau_c^x = \tau_{c0}^X \exp\left(\frac{E_a}{k_B T} \right) \qquad (5)$$

and activation energy E_a, the latter values were determined from the slopes of the curves presented in Fig. 3.

The correlation time deduced for P3OT decreases with a temperature increase up to T_c ~ 150 K and then increases above this critical temperature. It should be noted that Masubuchi et al. [9] observed the proton nuclear magnetic resonance (^{1}H NMR) T_1 temperature dependence with the same critical temperature. This result was attributed to the motion of the alkyl chain end groups.

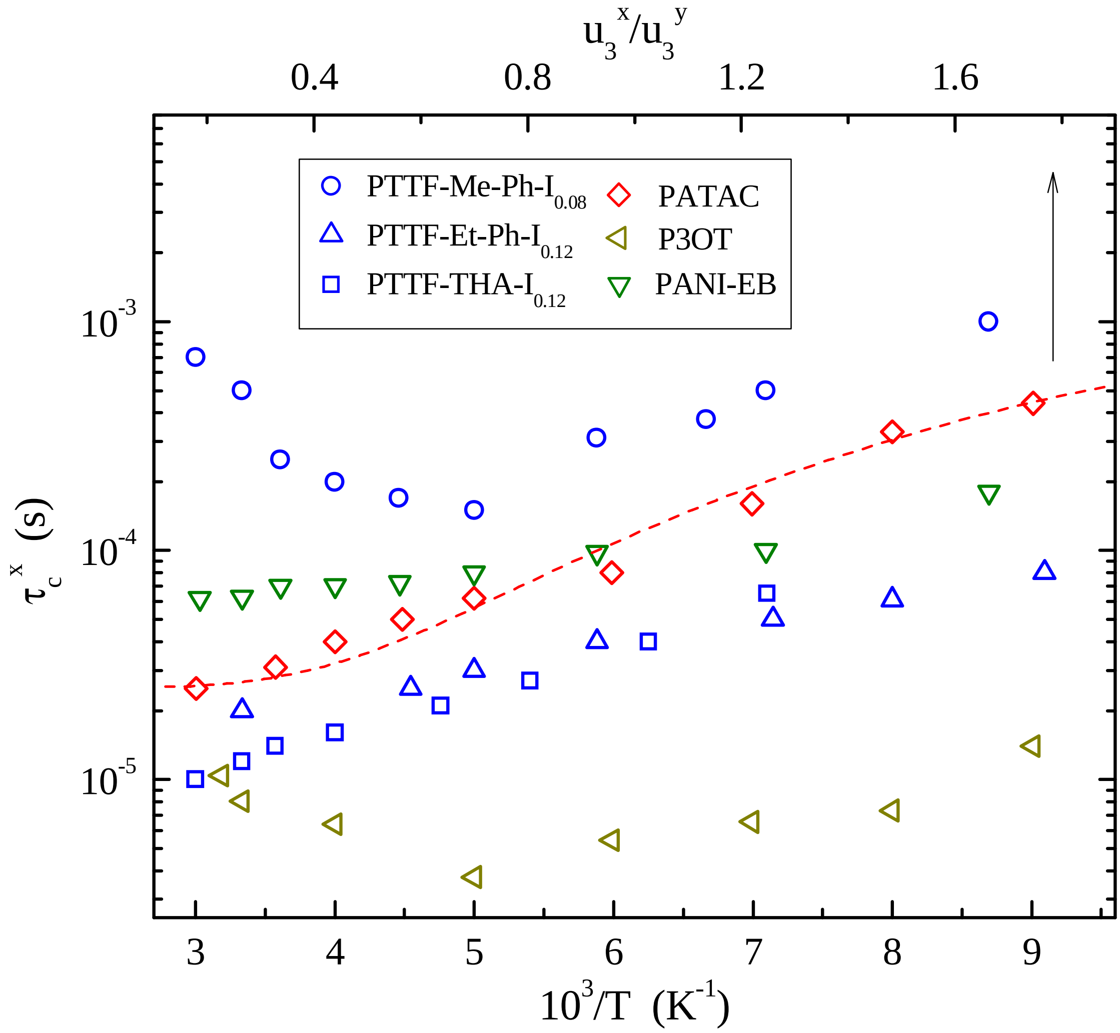

FIGURE 3. Arrhenius dependence of correlation times for superslow librations near the polymer main *x*-axis of polarons R_1 localized on polymer chain segments in some conductive polymers evaluated from their ST-ESR spectra (inset). In the inset, the typical Jl/2-out-of-phase dispersion spectra registered at 100 K (solid line) and 200 K (dashed line) are shown. The dependence calculated from Eq.(4) is shown by a dashed line.

The dependences obtained can be interpreted in the frame of the superslow 1D libration of the polymer chains together with polarons near their main *x*-axis at low temperatures, when $T < T_c$, whereas their high-temperature part can be explained by the collective 2D motion at $T > T_c$ with $E_a = 0.069$ eV.

Activation energy is governed by the modification, structure and doping level of a polymer. For example, treatment of the P3OT by annealing and by both recrystallization and annealing decreases (0.054 eV) and increases (0.073 eV) E_a value, respectively [10]. The E_a value was obtained for PANI-EB, laser-modified PATAC, iodine doped PTTF-Me-Ph, PTTF-Et-Ph, and PTTF-THA from the data summarized in Fig. 3 to be 0.015, 0.043, 0.036, 0.021, and 0.041 eV, respectively. Slight doping of an initial PTTF sample doubles the activation energy of macromolecular librations. The E_a values obtained at D-band EPR are comparable with those determined for interchain charge transfer in doped PTTF at a lower measuring frequency [11], indicating the interaction of pinned and mobile polarons in this polymer matrix. The upper limit for the correlation time registered by the ST-ESR method is $4\text{x}10^{-4}$ s at 66 K for P3OT and $1\text{x}10^{-4}$ s for PTTF-Me-Ph and PANI-EB at 75 and 125 K, respectively.

Thus, the EPR spectra of organic radicals become more informative D-band EPR, their interpretation is simplified and the possibility of a more accurate determination of their magnetic resonance parameters change under the effect of different factors, including the change of a radical structure and/or its microenvironment arises. Higher spectral resolution and easier microwave saturation at D-band EPR makes it possible to obtain more complete and correct qualitatively new information on magnetic, relaxation and dynamics parameters of paramagnetic centers, stabilized in the matrix under study, their interactions with own environment. These possibilities of the method are of an especial importance in the identification of the structure and dynamics of conducting polymers, whose properties depend on many factors and are defined by a greater number of parameters. This allows the establishment of the correlation between these parameters and the polymer structure for a synthesis of different organic elements with optimal and controllable properties suitable for molecular electronics.

At D-band EPR, an independent analysis of relaxation and dynamics changes in each spectral component and the anisotropic superslow molecular rotations study become possible. Macromolecular dynamics in conducting polymers is governed by their structure, crystallinity and treatment.

Acknowledgements

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