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Study of spin dynamics in *trans*-polyacetylene at 2 mm waveband EPR

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Abstract

Electron spin–lattice, T_1, and spin–spin, T_2, relaxation times in polyacetylene samples have been measured by a saturation method at 2 mm waveband EPR at 90–330 K. Temperature dependences of the intrachain diffusion and interchain hopping rates in *trans*-$(CH)_x$ are evaluated. Spin dynamics in pristine *trans*-$(CH)_x$ does not agree with the predictions of the soliton model, but it is in a good agreement with the intersoliton isoenergetic electron hopping model of charge transport predicted by Kivelson.

Introduction

Particular interest in studying *trans*-polyacetylene (*trans*-$(CH)_x$) has been generated by the idea that the domain wall kinks in the electron charge density wave (solitons) are responsible for their transport properties [1, 2]. In the framework of soliton theory the domain walls are spread about 15 lattice sites and its electronic level is situated near mid-gap. They possess a spin–charge inversion in *trans*-$(CH)_x$. If the bound state contains one electron, the soliton is neutral and paramagnetic with spin $\frac{1}{2}$. If the bound state is empty or doubly occupied, then the soliton is positively or negatively charged, respectively, and it is diamagnetic with zero spin.

According to the approach of Su *et al.* [1, 2], the soliton in *trans*-$(CH)_x$ does not dissipate with time and is characterized by high mobility. The intrachain diffusion rate, $\nu_{1D} = D_{\|}/c_{\|}^2$ (where $D_{\|}$ is the 1-D diffusion coefficient and $c_{\|}$ is the intrachain hopping length of the soliton), was first evaluated [3, 4] using the Wada and Schrieffer relation [5] for 1-D Brownian motion of soliton-like domain walls interacting with thermal phonons. This value possesses a T^2 temperature dependence and it is equal to 6×10^{14} s^{-1} at room temperature. In the frame of the Maki approach [6], the ν_D value has $T^{-0.5}$ and $T^{0.5}$ temperature dependences for optical and acoustic phonon scattering, respectively.

To realize 1-D motion the spin diffusion should be extremely anisotropic in *trans*-$(CH)_x$, because the soliton (as a topological excitation)

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cannot hop from one chain to another. Nevertheless, in real systems the soliton may hop between chains with frequency ν_{3D}. The spin diffusion anisotropy in *trans*-(CH)$_x$, ν_{1D}/ν_{3D}, varies approximately in the range 10^5–10^8 [7–9].

Nechtschein *et al.* [3, 10, 11] have studied the dynamics of neutral solitons by ^{1}H NMR T_1 and Overhauser experiments. From the $\omega_e^{0.5}$ operating frequency dependence of ^{1}H NMR T_1 they concluded that the spin in *trans*-(CH)$_x$ diffuses mainly along the polymer chain with a rate of $\nu_{1D} \geqslant 10^{13}$ s^{-1} at room temperature. However, the dual interpretation of NMR T_1 results of partially deuterated *trans*-(CH)$_x$ by Glover *et al.* [12] showed an ambiguity in this approach for 1-D spin diffusion in *trans*-(CH)$_x$.

The spin dynamics in *trans*-(CH)$_x$ has also been studied by cw [9, 13–15] and spin echo [16] EPR methods. From T^{-2} temperature and $\omega_e^{0.5}$ frequency dependences of the EPR linewidth as well as from T_1 analyses, the 1-D spin diffusion moving with a rate of $\nu_{1D} \geqslant 10^{13}$ s^{-1} and a high anisotropy of 10^6–10^8 at room temperature have been demonstrated. These dependences are similar to those deduced from ^{1}H NMR T_1 analyses [3, 10, 11]. However, detailed spin echo and cw EPR measurements on both the *trans*-(CH)$_x$ and its deuterated analogue *trans*-(CD)$_x$, carried out by Shiren *et al.* [16], show relatively low 1-D spin diffusion with $\nu_{1D} \leqslant 10^{11}$ s^{-1}. This result is incompatible with the condition of 1-D diffusive spin motion [11] $\nu_{1D} \geqslant 6.8 \times 10^8 \pi \gamma_e \gamma_I^{-1} = 1.4 \times 10^{12}$ rad s^{-1} (where γ_e and γ_I are the hyromagnetic ratios of a electron and proton, respectively) and, hence, with soliton theory of charge transport in pristine *trans*-(CH)$_x$. Some data concerning spin dynamics determined by NMR and EPR as well as by cw and spin echo EPR methods were shown to be incompatible [17]. In order to explain the discrepancy between results determined by complimentary magnetic resonance methods, Holczer *et al.* [10] suggested the existence of two kinds (diffusive and localized) of paramagnetic centres (PCs) in *trans*-(CH)$_x$.

In this article we present the experimental results on the electron spin dynamics and its dimensionality in pristine and lightly iodine doped *trans*-(CH)$_x$. The success of our experiment is largely due to the first attempt of high frequency ($\sim$140 GHz) EPR and the first registration of T_1 and T_2 independently for localized and mobile electron spins in *trans*-(CH)$_x$ by the saturation method. From $T_1 \propto \nu_e^{0.5} T^2$ dependence (where ν_e is the MW frequency, T is the absolute temperature) we conclude that the relaxation process in *trans*-(CH)$_x$ is the superposition of Raman modulation of 1-D and 3-D spin–lattice interactions of the immobilized and 1-D diffusion motion of the delocalized centres. From the concentration dependence of T_1 the relaxation mechanism of paramagnetic centres in *trans*-(CH)$_x$ was determined as dipole and hyperfine couplings modulated by the interactions mentioned above. The data obtained at 2 mm waveband EPR concerning the spin dynamics in pristine and doped *trans*-(CH)$_x$ are not consistent with predictions by Su *et al.* [1, 2] for the soliton model and are in good agreement with the intersoliton isoenergetic electron hopping model of charge transport in *trans*-(CH)$_x$ predicted by Kivelson [8, 18].

Experimental

The *cis*-$(CH)_x$ films of 90–350 μm thickness were prepared by a Shirakawa method using a Ziegler–Natta catalyst [19]. Thermal isomerization was made in an oil bath at approximately 440 K in an evacuated tube for several minutes. The samples were doped in iodine vapour in an X-band spectroscopic cavity in order to register the variation in spin concentration of $(CH)_x$. The estimated dopant concentration was $y \leqslant 0.01$.

Samples were studied using a 2 mm EPR spectrometer [20] at 90–330 K. The setting of the LF modulation and MW field phases was made with the help of the single crystal $(DBTTF)_3PtBr_6$ lateral standard attached to the MW cavity plunger as described in ref. 21. The evaluation of the magnetic component of the MW oscillation H_1 in the sample location gave 20 μT in the whole temperature range [21]. The measurement of spin–lattice and spin–spin relaxation rates in the temperature range 90–330 K were performed simultaneously using a successive saturation method at a MW frequency of $\nu_e \approx 140$ GHz and LF frequency of 100 kHz as described earlier in ref. 22. In this case the MW section was tuned for the detection of the real part of the paramagnetic susceptibility χ'.

Results and discussion

Nature of paramagnetic centres in trans-$(CH)_x$

According to the Portis formalism [23], the spin packets are specified by their spin–lattice relaxation time T_1, width equal to $\gamma_e^{-1} T_2^{-1}$, resonant frequency ν_i and spin–spin exchange frequency ν_{ex}. In a strong magnetic field $H_0 \geqslant 1.2$ T, the spectral resolution increases and the conditions $\nu_{ex} \leqslant \Delta\nu_{ij}$ and $\nu_{ex} \leqslant \gamma_e \Delta H_{pp}$ (where ΔH_{pp} is the EPR linewidth between peaks) can be realized. In this case the ΔH_{pp} value both of *cis*-$(CH)_x$ and *trans*-$(CH)_x$ increases according to the equation [24] $\Delta H_{pp} = \gamma_e^{-1} T_2^{-1} + \Delta\nu_{ij}^2 / 8\nu_{ex}\gamma_e$. The computer analysis of the 2.0–0.7 mm waveband EPR spectra [25] has shown the presence of two types of PC in *trans*-$(CH)_x$ — a localized one with anisotropic g factor of 2.002 67 ($g_\perp = 2.002\ 83$ and $g_\parallel = 2.002\ 36$) and $\nu_{ex} = 3.0 \times 10^7$ s^{-1}, and a mobile one with $\nu_{ex} = 1.2 \times 10^8$ s^{-1} and with a motionally averaged g factor of $\{g\} = 2.002\ 68$. The ratio of mobile to localized PCs in *trans*-$(CH)_x$ was unexpectedly equal to 1:20 in the whole operating temperature interval. Investigation of the *trans*-$(CH)_x$ samples doped by iodine vapour up to $\sigma_{dc} \sim 10^{-1}$ S cm^{-1} shows the spectral shape as well as the ratio mentioned above to be non-varying with doping. This fact confirms the assumption proposed by Nectschein *et al.* [11] of the existence of both mobile and fixed PCs on short conjugated chain solitons, that become charged and diamagnetic under the doping process. Thus, during *cis–trans* isomerization in pristine $(CH)_x$ the concentration of localized (sp^3-defects and trapped solitons) PCs increases remarkably and mobile PCs appear. This process leads to increase in conductivity on the same order of magnitude [26], probably because of mobile PCs. The difference in $\Delta\nu_{ij}$ and ν_{ex} values for both kinds of PCs leads to the sharp narrowing in the low frequency EPR spectrum (e.g., 4–5 times at $\nu_e \leqslant 10^{10}$ s^{-1}) through this transformation. This fact disagrees with a general assumption that such a transformation in spectrum shape appears in *trans*-$(CH)_x$ EPR spectra due to highly mobile neutral solitons [26] only.

Passage effects in $(CH)_x$

The probability of cross-relaxation between spin packets $W_{cr} \propto \exp(-kH_0^2)$ (where k is the constant and H_0 is the magnetic field strength) [27] at $H_0 \geqslant 1.5$ T is sufficiently decreased, spin packets in $(CH)_x$ become non-interactive and therefore may be saturated even at low MW power. Such a case is realized and the passage effects are registered in EPR spectra of $(CH)_x$ at $H_0 \approx 5$ T [22].

The first derivative of the dispersion signal can be written as [28]

$$U = U_1 \sin(\omega_m t) + U_2 \sin(\omega_m t - \pi) + U_3 \sin(\omega_m t - \pi/2) \qquad (1)$$

where ω_m is the angular LF modulation frequency. The two latter terms in eqn. (1) are determined by the delayed response of the electron magnetization vector M on LF modulation field H_1 vector inversion with angular frequency ω_m. In *cis*-$(CH)_x$ and *trans*-$(CH)_x$ the $\omega_m T_1$ product becomes greater and smaller than unity, respectively, and the U value is therefore mainly defined for these samples by U_2, U_3 and U_1, U_3 terms of eqn. (1), respectively [22].

We have calculated independently the T_1 and T_2 values for eight *cis*-$(CH)_x$ and *trans*-$(CH)_x$ samples of 90–350 μm thickness using the saturation method at $\nu_e \approx 1.4 \times 10^{11}$ s^{-1} as described in ref. 22. The temperature dependences of T_1 and T_2 values for *cis*-$(CH)_x$ and *trans*-$(CH)_x$ (the sample with the highest PC concentration) isomerized from the former are presented in Fig. 1. One can clearly see that the spin–lattice relaxation time of both $(CH)_x$ isomers is a function decreasing monotonically with temperature, thereby the T_2 value demonstrates the different temperature dependences in *cis*-$(CH)_x$ and *trans*-$(CH)_x$ samples.

Relaxation processes and the influence of impurities on these processes in trans-$(CH)_x$

The spin–lattice relaxation rate may be written as $T_1 = An^{-1}\omega_e^{\alpha}T^{\beta}$, where A is a constant, n is the total concentration of the PCs, α is equal to 3 and -0.5 for *cis*-$(CH)_x$ and *trans*-$(CH)_x$, respectively, and β varies from -1.5 to -3.5 as a function of sample thickness. This relation indicates mainly the two-phonon Raman relaxation process [29] in *cis*-$(CH)_x$ and the more complicated spin–lattice interaction in *trans*-$(CH)_x$. The dependence mentioned above for the latter sample is probably due to the mixture of 1-D Raman modulation as well as 3-D spin–lattice interaction of the immobilized spins with total probability $W_R \propto A_1 \omega_e^{-2} T^2 + A_2 \omega_e^2 T$ [29], and also to the

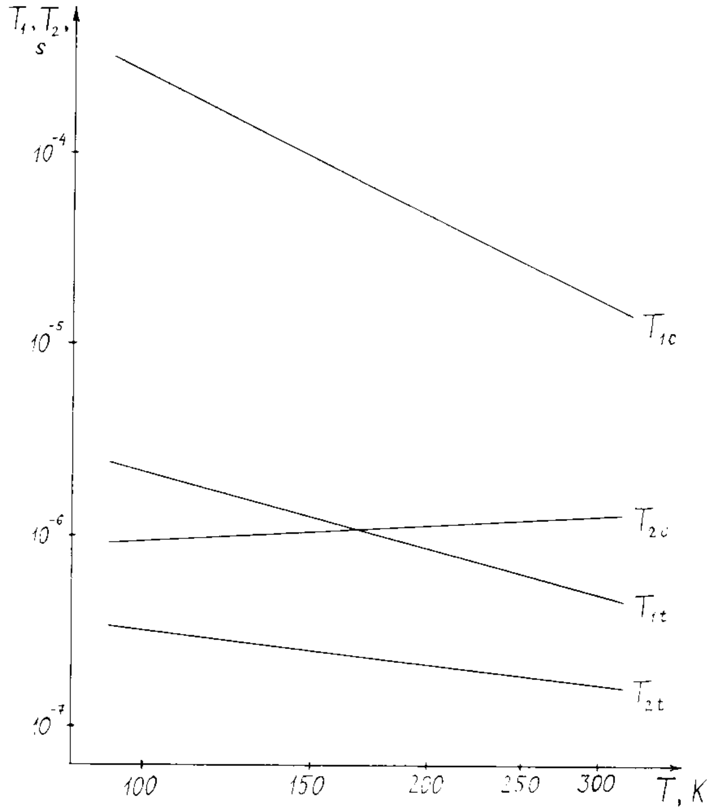

Fig. 1. Temperature dependences of spin–lattice T_1 and spin–spin T_2 relaxation times for *cis*-$(CH)_x$ and *trans*-$(CH)_x$ samples.

diffusive modulation of spin–lattice interaction by 1-D motion of delocalized centres with probability $W_D \propto \omega_e^{-0.5}$ [30].

It should be noted that a light (up to 0.1 S cm^{-1}) doping of the *trans*-$(CH)_x$ sample by iodine vapour leads to a reduction in total spin concentration by a factor of four and in spin–lattice relaxation time by an order of magnitude approximately. Smaller changes (by a factor two) in the latter value occurs in the presence of oxygen in the $(CH)_x$ matrix [21]. Taking into consideration the $T_1 \propto n^{\alpha}$ concentration dependence, where α varies from -0.7 to -1.0 in the temperature range 330–90 K, we can postulate that molecules of both I_3^- and O_2 do not act as traps for the delocalized PCs but rather expand the $(CH)_x$ matrix.

Calculation of the electron relaxation rates, T_1^{-1} and T_2^{-1}, of trans-$(CH)_x$

In order to compare our experimental results with the soliton theory and with results already reported [3, 4, 7–16], we assume the intrachain 1-D diffusive motion of delocalized PCs in *trans*-$(CH)_x$ within the restrictions of a quasi 1-D model with rate ν_{1D} and its cutoff by 3-D Lorentzian hopping between chains with frequency ν_{3D}. In this case the translation propagator of the spin motion along the chain, i.e., the probability of finding an electron spin in position r at time t, may be written as [31]

$$P_{1D}(r, r_0, t) = (1 + 4\pi\nu'_{1D}|t|)^{-0.5} \exp\left[-\frac{(r-r_0)^2}{4\nu'_{1D}t}\right] \tag{2}$$

The independence of the spin probability of the position of the interchain hopping between chains is assumed to have single exponential decay

$$P_{3D}(t) = \exp(-2\pi\nu_{3D}t) \tag{3}$$

The total probability of spin fluctuation is

$$P = P_{1D}(r, r_0, t)P_{3D}(t) \tag{4}$$

If the approximation $\nu_{1D} \gg \nu_e \gg \nu_{3D}$ is assumed, eqn. (1) becomes independent of variable r and has the same form as the Fourier transform of spectral density used by Holczer *et al.* [10], Nechtschein *et al.* [3, 11] and Mizoguchi *et al.* [9, 15] in order to analyse their EPR and NMR data. For the Fourier fluctuation power spectrum of 1-D electron spin motion $\phi(\nu_{1D}\,\nu_e)$ one obtains [32] $(4\pi\nu'_{1D}\,\nu_e)^{-0.5}$ at $\nu_{1D} \gg \nu_e \gg \nu_{3D}$ and $(4\pi\nu_{3D}\,\nu_e)^{-0.5}$ at $\nu_{1D} \gg \nu_{3D} \gg \nu_e$. The spectral density of this motion may be expressed as [31]

$$\begin{aligned} J(\nu_e\,\nu_D) &= n\sum_{r_1r_2} A^*(r_1)A(r_2)\phi(\nu_e, \nu_D) \\ &= an(4\pi\nu_e\,\nu_D)^{-0.5}\sum_{r_1r_2}\frac{P_2 \cos\vartheta_{1,2}}{r_1^3r_2^3} \end{aligned} \tag{5}$$

where n is the probability for the electron spin location at position r_1 and at the initial time, which is equal to delocalized spin concentration per C atom, A is the random interaction function modulated by intrachain diffusive motion of the electron spin, ϑ is the angle between vectors $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$, and a is a constant.

The electron spin relaxation rates, T_1^{-1} and T_2^{-1}, are defined mainly by dipole interaction and to a certain extent by hyperfine interactions between delocalized and fixed spins through one-dimensional diffusive motion along the molecular chain. These values for electronic dipolar modulation by 1-D diffusion, when the condition $\gamma_e \neq \gamma_I$ holds, are expressed [31] by

$$T_{1_d}^{-1} = \frac{1}{5}\left(\frac{\mu_0}{4\pi}\right)^2 \gamma_e^4\hbar^2 S(S+1)n\sum_{r_1r_2}\frac{P_2 \cos\vartheta_{1,2}}{r_1^3r_2^3}\,[\varphi_1(\omega) + 4\varphi_2(2\omega)] \tag{6a}$$

and

$$T_{2_d}^{-1} = \frac{1}{10}\left(\frac{\mu_0}{4\pi}\right)^2 \gamma_e^4\hbar^2 S(S+1)n\sum_{r_1r_2}\frac{P_2 \cos\vartheta_{1,2}}{r_1^3r_2^3}\,[3\varphi_0(0) + 5\varphi_1(\omega) + 2\varphi_2(2\omega)] \tag{6b}$$

For anisotropic hyperfine coupling the following expressions can be applied:

$$T_{1_{\mathrm{hf}}}^{-1}=\frac{1}{15}\left(\frac{\mu_0}{4\pi}\right)^2\gamma_{\mathrm{e}}^2\gamma_{\mathrm{I}}^2\hbar^2J(J+1)\sum_{r_1r_2}\frac{P_2\cos\vartheta_{1,2}}{r_1^3r_2^3}$$
$$\times[\varphi_0(\omega_{\mathrm{e}}-\omega_{\mathrm{I}})+3\varphi_1(\omega_{\mathrm{e}})+6\varphi_2(\omega_{\mathrm{e}}+\omega_{\mathrm{I}})]$$
$$+\frac{1}{15}\left(\frac{\mu_0}{4\pi}\right)^2\gamma_{\mathrm{e}}^2\gamma_{\mathrm{I}}^2\hbar^2S(S+1)k\sum_{r_1r_2}\frac{P_2\cos\vartheta_{1,2}}{r_1^3r_2^3}$$
$$\times[-\varphi_0(\omega_{\mathrm{e}}-\omega_{\mathrm{I}})+6\varphi_2(\omega_{\mathrm{e}}+\omega_{\mathrm{I}})] \qquad (7a)$$

and

$$T_{2_{\mathrm{hf}}}^{-1}=\frac{1}{30}\left(\frac{\mu_0}{4\pi}\right)^2\gamma_{\mathrm{e}}^2\gamma_{\mathrm{I}}^2\hbar^2J(J+1)\sum_{r_1r_2}\frac{P_2\cos\vartheta_{1,2}}{r_1^3r_2^3}$$
$$\times[4\varphi_0(0)+\varphi_0(\omega_{\mathrm{e}}-\omega_{\mathrm{I}})+3\varphi_1(\omega_{\mathrm{e}})+6\varphi_1(\omega_{\mathrm{I}})+6\varphi_2(\omega_{\mathrm{e}}+\omega_{\mathrm{I}})] \qquad (7b)$$

where

$$k=\frac{\langle J_z\rangle-J_0}{\langle S_z\rangle-\mathrm{S}_0}$$

Finally, the isotropic hyperfine terms may be written as

$$T_{1_{\mathrm{i}}}^{-1}=\tfrac{1}{3}Q^2\gamma_{\mathrm{e}}^2J(J+1)\varphi_1(\omega_{\mathrm{e}}) \qquad (8a)$$

and

$$T_{2_{\mathrm{i}}}^{-1}=\tfrac{1}{6}Q^2\gamma_{\mathrm{e}}^2J(J+1)[\varphi_0(0)+\varphi_1(\omega_{\mathrm{e}})] \qquad (8b)$$

The value of n in eqns. (6a) and (6b) is equal to $n_1+n_2/\sqrt{2}$, where n_1 and n_2 are the spin concentrations of localized and mobile PCs per carbon atom, respectively, and ω_{s} and ω_{I} are the angular frequencies of the electron and nuclear spin precessions, respectively. The coefficient $2^{-0.5}$ in the relation for n is used because two solitons diffuse independently, relative to each other. The probability of interaction between the electron and nuclear spins in *trans*-$(\mathrm{CH})_x$ is always equal to unity, so $n=1$ in eqns. (7a) and (7b).

Since pinned PCs predominate in *trans*-$(\mathrm{CH})_x$, the contribution of librations in their chain segments into the relaxation mechanism should also be taken into account. We have recently shown [25] that the disposition of the librations of the chain segments is almost unchanged at *cis–trans* isomerization of $(\mathrm{CH})_x$. In order to neglect these librations we must therefore subtract the respective relaxation rates of *cis*-$(\mathrm{CH})_x$ from that of *trans*-$(\mathrm{CH})_x$.

Using the values $\nu_{\mathrm{e}}=1.4\times10^{11}\ \mathrm{s}^{-1}$, $\Sigma_{r_1r_2}P_2\cos\vartheta_{1,2}/r_1^3r_2^3$ equal in eqns. (6a) and (6b) to $2\times10^{58}\ \mathrm{m}^{-6}$ and in eqns. (7a) and (7b) to $2.8\times10^{59}\ \mathrm{m}^{-6}$ [9], $Q=2.34$ mT and $k=0.078$ [9], we can simplify eqns. (6)–(8) to

$$T_{\mathrm{I}}^{-1}=\frac{3.4\times10^{10}}{(\nu'_{\mathrm{1D}})^{1/2}}(2.7\times10^4n+1)+T_{1_{cis}}^{-1} \qquad (9a)$$

and

$$T_2^{-1} = \frac{1.8\times10^{10}}{(\nu'_{1D})^{1/2}} \left(\frac{7.6\times10^9 n + 3.4\times10^5}{(\nu_{3D})^{1/2}} + 4.3\times10^4 n + 1 \right) + T_{2cis}^{-1} \qquad (9b)$$

The derived temperature dependence of diffusive intrachain rate, ν'_{1D}, estimated from eqn. (9a) and data of Fig. 1 for one of the *trans*-$(CH)_x$ samples with highest spin–lattice time and spin concentration is shown in Fig. 2. The $T^{-2.4}$ dependence of ν'_{1D} disagrees with the theoretical predictions of the soliton model [1, 2, 5, 6]. The Figure shows the maximum ν'_{1D} value to be not higher than 4×10^{10} s^{-1} at room temperature. If one takes into account the spin delocalization over a soliton with a half-width N of seven sites, then $\nu_{1D} = \nu'_{1D}N^2 \leqslant 2\times10^{12}$ s^{-1}. In comparison with the values expected from soliton theory and derived from NMR and EPR measurements [3, 4, 7–15], the obtained value is at least two orders of magnitude lower for this sample (and it is still smaller for the other samples).

The analysis of experimental T_2 values on the dimensionality of spin dynamics was also carried out. The temperature dependence of the interchain spin hopping frequency, ν_{3D}, of the sample mentioned above, calculated from eqn. (9b) and the data of Fig. 1, is presented in Fig. 2. The Figure shows the ν_{3D} values to be $T^{1.0}$ dependent at 90–330 K for this sample. Consequently, the room temperature anisotropy of spin motion is $\nu_{1D}/\nu_{3D} \leqslant 10^3$ for this sample, varies from 10 to 10^4 for other samples and is lower than those

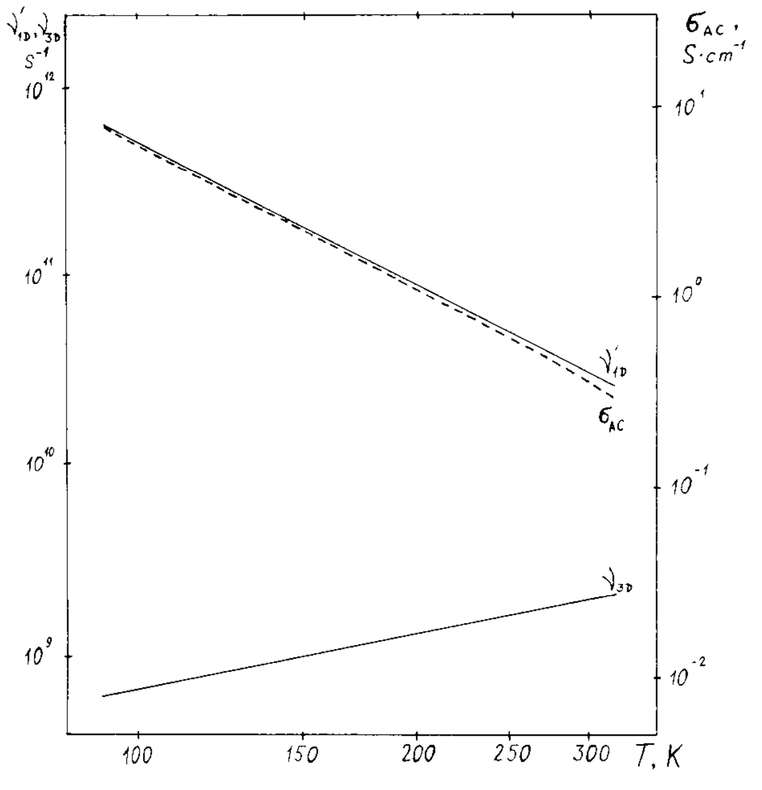

Fig. 2. Intrachain diffusion ν'_{1D} and interchain hopping ν_{3D} rates and a.c. conductivity σ_{ac} at 140 GHz vs. temperature for pristine *trans*-$(CH)_x$. The σ_{ac} value has been calculated using equation $\sigma_{ac} = 3\times10^{-15}\nu_e T^{-1}[\ln(10^{24}\nu_e T^{-10.5})]^4$.

determined in refs. 7–9. If one can write the intra- and interchain spin hopping rates as $\nu_{1D} = AT^{\alpha}$ and $\nu_{3D} = BT^{\beta}$, the decrease in α values from -2 to -5 is accompanied by an increase in β value from 0.4 to 7 and by decrease in anisotropy at room temperature from 10 to 10^4 for different samples. This fact rejects once more the supposition of 1-D diffusive and 3-D hopping spin motion in different contributions in various *trans*-$(CH)_x$ samples.

Now we can extract the temperature dependences of relaxation rates for delocalized PCs in the above *trans*-$(CH)_x$ sample to be $T_1^{-1} = 240T^{1.2}$ and $T_2^{-1} = 1.1 \times 10^4 T^{0.8}$.

According to the Einstein relation, $\sigma = n_2 De^2 k^{-1} T^{-1}$, where $n_2 = 4 \times 10^{22}$ m^{-3} is the highest spin carrier volume concentration in *trans*-$(CH)_x$ under study, e is the elementary charge and k is the Boltzmann constant, the d.c. conductivity of doped *trans*-$(CH)_x$ should be equal to $\sigma_{dc} \leqslant 10^{-4}$ S cm^{-1} at room temperature, even if all solitons were participating in the charge conduction in spite of increased disorder and coulomb pinning. This value is the same number of orders of magnitude smaller than that usually achieved for highly doped *trans*-$(CH)_x$. Moreover, the light doping of *trans*-$(CH)_x$ causes a decrease in 1-D spin diffusion and an increase in 3-D hopping rates as shown in Fig. 3. Therefore, it is impossible to provide *trans*-$(CH)_x$ with high conductivity by solitons and to explain charge transport in *trans*-$(CH)_x$ within the soliton theory only. So another acceptable mechanism of charge transport is required.

A more acceptable spin dynamic process may be proposed within the Kivelson formalism [8, 18] associated with the phonon-assisted hopping of electrons between soliton sites. In this model charged mobile solitons are coulombically bound to charged impurity sites. The excess charge on the

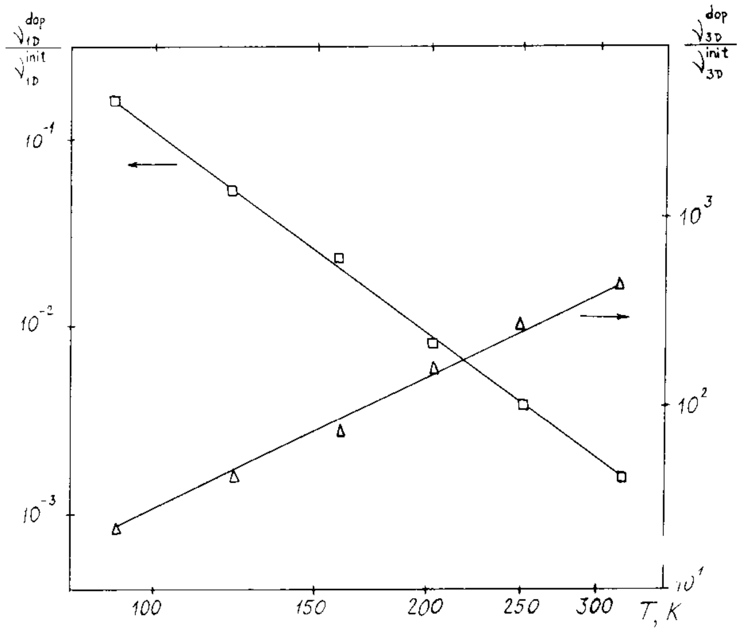

Fig. 3. Temperature dependences of the ratio of ν'_{1D} and ν_{3D} values of pristine *trans*-$(CH)_x$ to that of a doped (up to 0.1 S cm^{-1}) sample.

soliton site makes a phonon-assisted transition to a neutral soliton on another chain. If this neutral soliton is near another charged impurity, the energy of the charged soliton before and after the hop is unchanged. The rate of such an electron transition is then determined by the probability W that the neutral soliton is near the charged impurity and that the initial and final energies are within kT of each other [18], $W \sim [\ln(T^{-n-1})]^4/kT$, where $n \approx 10$. The temperature dependence of a.c. ($\nu_e \approx 1.4 \times 10^{11}$ s^{-1}) conductivity of *trans*-(CH)$_x$ calculated using equation $\sigma_{ac} = k'\nu_e T^{-1}[\ln(10^{24}\nu_e T^{-n-1})]^4$ [33, 34], where $k' = 3 \times 10^{15}$ s K S cm^{-1} and $n = 9.5$, is presented as a dotted line in Fig. 2. The data in the Figure show both $\nu_{1D}(T)$ and $\sigma_{ac}(T)$ functions to be comparable in the operating temperature region. The room temperature value of σ_{ac} is nearly 10^{-1} S cm^{-1}. The d.c. conductivity of *trans*-(CH)$_x$ is approximately equal to 10^{-5} S cm^{-1} [34], so that the value $\sigma_{ac}/\sigma_{dc} \approx 10^4$ is in good agreement with the isoenergetic electron hopping mechanism proposed by Kivelson.

Thus, we can assume the following dynamic process in *trans*-(CH)$_x$. The mobility of the part of trapped solitons increases in (CH)$_x$ at *cis–trans* isomerization. The number of mobile and trapped PCs decreases during doping and, hence, the paramagnetic susceptibility of *trans*-(CH)$_x$ also decreases. The electrons are trapped by mobile solitons and are carried by them along the chain up to certain points where the probability of the isoenergetic electron hopping (tunnelling) from one chain to another is higher. Because the solitons play an auxiliary role, this mechanism may be correct, however, at light doping levels. As the doping level increases, the intersoliton electron hopping propagation is unlikely to be the dominant charge transport mechanism and the conductivity is determined mainly by spinless charge carriers.

Conclusions

The high spectral resolution as well as the slow interaction between spin packets in a strong magnetic field of strength 5 T allow the determination of the nature of different PCs, their spin–lattice and spin–spin relaxation rates separately, the influence of different factors on these values and other peculiarities of the (CH)$_x$ samples. The most important result of this article concerning spin dynamics in *trans*-(CH)$_x$ is the discrepancy between our experimental data and soliton theory. We consider it as evidence that the mobile solitons are not the dominant type of defects and soliton propagation is unlikely to be the dominant charge transport mechanism in *trans*-(CH)$_x$. The data obtained demonstrate the application of the Kivelson phenomenological formalism, not only in low and submillimetre wavebands, but also in 2 mm waveband EPR.

A possible modification of the (CH)$_x$, the spin relaxation rates and dynamic peculiarities in mechanically stretched (CH)$_x$ are very interesting not only experimentally [15, 35] but also theoretically [36]. We are now undertaking this experiment with $(CH)_x$ synthesized by the Shirakawa method as well as other $(CH)_x$ samples to discuss these questions in future publications.

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