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The Temperature Dependence of Electron Spin-Lattice Relaxation Data in Trans-Polyacetylene and the Evidence for a Soliton-Phonon Interaction

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THE TEMPERATURE DEPENDENCE OF ELECTRON SPIN-LATTICE RELAXATION DATA IN TRANS-POLYACETYLENE AND THE EVIDENCE FOR A SOLITON-PHONON INTERACTION

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Abstract The temperature and frequency dependence of the electron spin-lattice relaxation rate $\bar{R}_1$ for the paramagnetic defects in pristine transpolyacetylene is analyzed in terms of a model in which the electron-electron dipolar interaction between spins is modulated by one-dimensional diffusion induced by phonon scattering of the spins. According to this model, at room temperatures $\bar{R}_1$ has a $T^{1/2}$ temperature dependence; at low temperatures $\bar{R}_1$ has a T^2 or $T^{5/2}$ temperature dependence. $\bar{R}_1$ is described by a $\omega^{-1/2}$ frequency dependence. The model shows the symmetry between moving and stationary solitons scattered by phonons. The soliton wave function obtained from experimental ENDOR data is used to obtain analytical results. We discuss the possible temperature and frequency limitations of this model.

INTRODUCTION

One of the most puzzling results deriving from the study of the paramagnetic defect in the prototype conducting polymer, trans-polyacetylene (t-PA), has been the frequency and temperature dependence of the electron spin-lattice relaxation data.[1,2] Dalton and coworkers[3] suggested that electron spin-lattice relaxation might be determined by electron tunneling envisioned in the Two-Level System (TLS) model of Phillips.[4] However, the fit to high temper-

ature data employing the TLS model is poor; moreover, an extensive investigation of the frequency dependence of the electron spin-lattice relaxation data over the range 35 MHz to 40 GHz reveals that the data over this entire range is best described by a fit to $\bar{R}_1 = a(\omega)^{-1/2}$ (see Fig. 2) and not by the more complicated dependence predicted by the TLS model.

The above dependence of $\bar{R}_1$ on ω implies a reciprocal dependence of $\bar{R}_1$ on the diffusion coefficient, $D_{\parallel}$. Therefore $\bar{R}_1$ cannot be qualitatively described by a simple activated process. We present an alternative model capable of explaining the temperature and frequency dependences of electron spin-lattice relaxation data in terms of phonon scattering from a stationary soliton.

EXPERIMENT

Samples of pristine polyacetylene were prepared as described previously.[5] Care was taken to minimize exposure to atmospheric oxygen; spectroscopic measurements were conducted on samples contained in sealed quartz or glass tubes. Electron spin-lattice relaxation measurements at frequencies of 9.5 and 16 GHz were performed with the three pulse inversion recovery method employing the electron spin echo spectrometer described by Thomann et. al.[6] Effects of spectral diffusion were investigated employing spectral diffusion quenching pulse procedures.

THEORY

The absence of a strong dependence upon isotopic composition (i.e., hyperfine interaction) and the absence of an ω^n (where $n \geq 3/2$) dependence where ω is the microwave frequency suggest that electron spin-lattice relaxation rates are dominated by modulation of an electron-electron dipolar interaction. The electron dipolar interaction between two spins is described by the Hamiltonian term

$$\mathcal{H} = \vec{S}^{(1)} \cdot \tilde{D} \cdot \vec{S}^{(2)} = \sum_{i,j} \sum_{q} F_{ij}^{(q)} A_{ij}^{(q)} \qquad (1)$$

where $F_{ij}^{(q)}$ is the lattice operator and $A_{ij}^{(q)}$ is the spin operator. This Hamiltonian leads to the following expression for the electron spin-lattice relaxation rate.[7]

$$R_1 = (\gamma_1\gamma_2\hbar)^2 N_s S(S+1)\left[\frac{3}{2}J^{(1)}(\omega_1) + \frac{3}{4}J^{(2)}(\omega_1+\omega_2)\right] \quad (2)$$

where the spectral density function $J(\omega)$ is the Fourier transform of the autocorrelation function.

Consider the simple classical model of two point dipoles illustrated in Fig. 1. In the case of two spins each undergoing one-dimensional diffusion, only the r dependence is important. Note that this model depends only upon local and not long range order. Since t-PA is macroscopically unordered, we average over all possible orientations:

$$\bar{R}_1 = \int R_1(\Omega)\, d\Omega$$

which gives the result that:

$$\bar{R}_1 = (\gamma_1\gamma_2\hbar)^2 N_s S(S+1)\left[\frac{3}{2}\overline{|f^{(1)}|^2}\, J(\omega_1) + \frac{3}{4}\overline{|f^{(2)}|^2}\, J(\omega_1+\omega_2)\right] \quad (3)$$

with

$$J(\omega) = \int_0^\infty e^{i\omega t} \left\langle \frac{1}{r(t)^3} \middle| \frac{1}{r(0)^3} \right\rangle dt \quad (4)$$

We now evaluate the spectral density function $J(\omega)$ for two spins traveling in parallel lines along the x axis with a distance of closest approach b (see Fig. 1). Each spin is assumed to move stochastically in one dimension, independently the other. Let $W(x,t|x_0,0)$ be the probability that a spin (either 1 or 2) is at position x at time t when it was at x_0 at time zero. This function is well known from the theory of one dimensional diffusion.[8]

$$W(x,t|x_0,0) = \frac{e^{-(x-x_0)^2/4D_{\parallel}t}}{(2\pi D_{\parallel} t)^{1/2}} \quad (5)$$

where $D_{\parallel}$ is the one-dimensional diffusion coefficient. Numerical evaluation of the autocorrelation function in equation 7 shows that

$$J(\omega) \simeq (Lb^4)^{-1} \left(\frac{\pi^3}{16\, D\, \omega}\right)^{1/2} \tag{6a}$$

Use of the spectral density function given in Eq. (4) permits the expression for spin lattice relaxation from electron dipolar modulation (Eq. (3)) to be simplified as

$$\overline{R}_1 \simeq 0.435(\hbar\gamma_e^2)^2 S(S+1)\left(\frac{N_e}{L}\right) b^{-4} (D_{\parallel}\omega)^{-1/2} \tag{6b}$$

Clearly this equation predicts the experimentally observed frequency dependence shown in Fig. 2. We now evaluate the temperature dependence of $D_{\parallel}$. The diffusion coefficient is related to the mean square displacement, $\langle \Delta x(t)^2 \rangle$, of the electronic spatial distribution as

$$D = \frac{1}{2} \frac{\partial \langle \Delta x(t)^2 \rangle}{\partial t} \tag{7}$$

The soliton has time dependent displacements due to interactions with phonons. The evaluation of such a quantity is too difficult

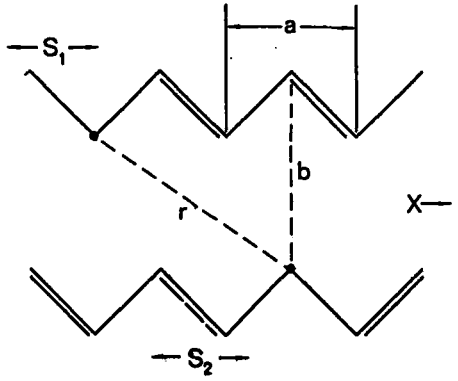

Figure 1. Two transpolyacetylene chains, each containing a paramagnetic defect, characterized by lattice constant a, interchain spacing b and spins separation r.

to be done by straight forward techniques. We therefore suggest that the displacements be replaced by a statistical or group velocity, $\langle V \rangle$, of the praticles and a lifetime, τ, for the soliton in the ground state. Then:

$$D_{//} = \frac{1}{2} \langle V^2 \rangle \tau \qquad (8)$$

In this sense then the velocity is the effective velocity of the spin in its ground state. We assume that $\langle V^2 \rangle$ can be estimated by equating the quantum and classical expressions for the momentum:

$mV = k\hbar$, where $k = \pi/a$, and is

given by the nodal structure for the soliton.

The lifetime, τ, may be estimated from the rate of transitions from the ground state according to Fermi's Golden Rule. We begin with the Hückel theory hamiltonian for valence π-electrons on a symmetric rigid lattice:

$$H = \sum_{r=1}^{N} \hbar\beta (b_r^{+} b_{r+1} + b_r^{+} b_{r+1}) = \sum_q \pi\, 2\beta \cos q\, (b_q^{+} b_q), \qquad (9)$$

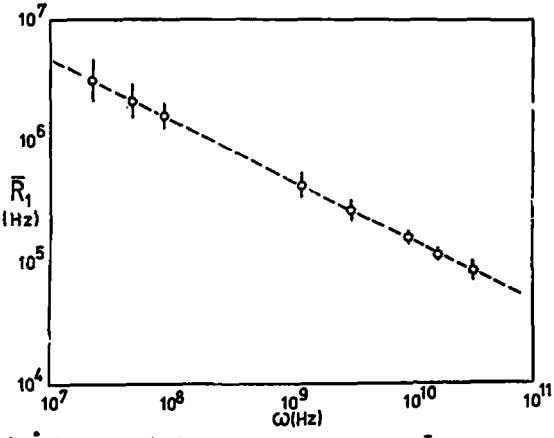

Figure 2. Electron spin-lattice relaxation rates, $\bar{R}_1$ (measured at ambient temperatures employing both pulse and cw methods), are plotted as a function of microwave frequency, ω. The experimental data are shown by circles with the error bars indicating the error associated with each measurement. An $\omega^{-1/2}$ dependence is indicated by the dashed line.

where cyclic boundary conditions have been applied, and the eigenstates are indexed by $q = 2\pi\, n/N$, $n = -N/2, \ldots N/2$. In the presence of phonons the β-parameters are altered. We account for this by expanding $\beta_{r,r+1}$ in terms of Taylor series in nuclear displacements from equilibrium. The total hamiltonian consists of a pure phonon term, an electron hamiltonian in which the nuclei are at their equilibrium positions and an electron-phonon interaction hamiltonian. The assumption the the soliton is confined to a region characterized by a uniform carbon-carbon bond length for 49 carbon atoms is consistent with the ENDOR data.[3] The Hückel hamiltonian for this system yields a simple set of one-particle electron eigenstates. The relaxation rate of the initial state, $1/\tau$, is then given by

$$\frac{\pi g^2}{\pi 2^7} \frac{c^3}{M |\beta|^4} \left[\left(\frac{T}{\theta}\right)^5 h_5\left(\frac{\theta}{T}\right) + \left(\frac{T}{\theta}\right)^4 h_4\left(\frac{\theta}{T}\right) \frac{4|\beta|\,(q-\pi)}{c} \frac{(q-\pi)}{2} + \left(\frac{T}{\theta}\right)^3 h_3\left(\frac{\theta}{T}\right) \frac{4\beta^2}{c^2} (q-\pi/2)^2 \right]$$

where $\theta = \hbar c\, \hat{q}_{max}/k_B$ is the Debye temperature and (10)

$$h_n(\theta/T) \equiv \int_0^{\theta/T} dx\, x^{n-1} (e^x - 1)^{-1} \tag{11}$$

This expression for τ may be compared with the expression for τ in a simple metal, where the pertinent relaxation time can be determined from the theory of electrical conductivity and is given by Haug.[9]

$$\tau(\zeta_o) = \frac{8}{3\pi} \frac{M\hbar\, K_B\theta}{m^* C^2} \left(\frac{\theta}{T}\right) \frac{1}{G(\theta/T)} \tag{12}$$

where

$$G(\theta/T) = 4\left(\frac{\theta}{T}\right)^4 \int_0^{\theta/T} \frac{s^5 e^{-s}}{(1 - e^{-s})^2} ds \tag{13}$$

m^* is the effective mass of the conduction electron; M is the mass of the lattice particle; ζ_o is the Fermi energy; and $C = (2/3)\zeta_o$ is a coupling constant.[9]

RESULTS

For simplicity we use equation 12 for τ and thereby obtain the temperature dependence of $\bar{R}_1$. Fig. 3 shows $\bar{R}_1$ as a function of temperature from 4.2K to ambient temperatures for two different data sets taken at different times for the same sample. The solid line is the fit of $\bar{R}_1$ to the temperature and frequency dependence given by

$$\bar{R}_1 = \alpha \left(\frac{\frac{T}{\theta} G(\theta/T)}{\omega/\omega_o} \right)^{1/2} \quad \text{where } \omega_o = 2\pi \cdot 10^9 \tag{14}$$

α is a least squares adjusted scale factor taking into account, for example, the variation in spin concentration. Similar results were obtained for the fit of electron spin-lattice relaxation data recorded at 16 GHz. α for the 16 GHz data is in excellent agreement with that obtained from the 9.5 GHz data. It is useful to consider how the temperature dependence of $\bar{R}_1$ changes as the temperature is reduced from high temperature where $\bar{R}_1 \simeq f \cdot T^{1/2}$. According to equation 14, the temperature is decreased from 200K to 5K, the functional dependence of $\bar{R}_1$ changes from $T^{1/2}$ to T^1 and finally to $T^{5/2}$. Clark and coworkers[2] have performed $\bar{R}_1$ measurements over temperature range 35 mK to 300 mK employing radiofrequency fields

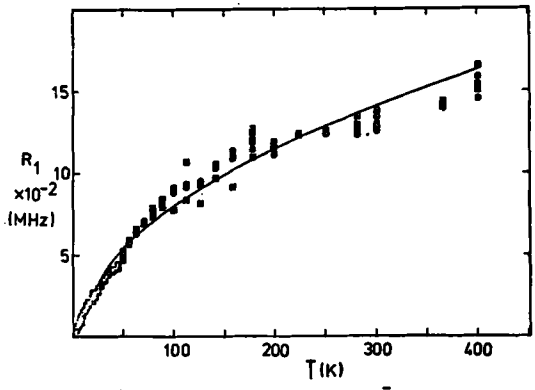

Figure 3. Electron spin-lattice relaxation rate, $\bar{R}_1$, as a function of temperature at a microwave frequency of 9.5 GHz is shown. The squares and circles are different experimental data sets. The solid line is a plot of Eq. (17) versus temperature for θ = 80K and α = 0.225 μsec^{-1}. Similar data (not shown) recorded at a microwave frequency of 16 GHz θ = 80K and α = 0.245 μsec^{-1}

and report $\bar{R}_1$ proportional to T^2. We use Eqs. 6,8,14 and 17 and the optimized values of α and θ and estimate b. The distance of closest approach ranges from 1.5 to 3.7 Å. Similarly $D_{\parallel}$ can be estimated to range from 0.4 to 8 cm^2/sec. The lower values agree well with other estimates.[11,12]

DISCUSSION

The analytical expression of Equation 14 assumed a simple Hückel hamiltonian and uniform bonds. More complicated models[13] may give similar results but will require numerical solutions. If the ENDOR results represent a dynamic averaging of soliton states[14] and the resultant wave function appears time independent only over a long time period, then these results apply to a limited frequency range. Frequencies of 20 GHz or lower at temperatures above 4K are consistent with the rapid dynamic averaging. This issue can be resolved by ENDOR data in the ultra low temperature region. The range of spin delocalization may be determined either by the intrinsic nature of the defect to self-localize or by externally imposed defects such as crossbridges or cisoid segments. The spin-spin interaction is modulated by diffusive motion which results from scattering by lattice phonons with no significant displacement of the mean of the defect. Such a model is consistent with ENDOR data, and explains the temperature, frequency and isotope dependence of the spin-lattice relaxation data.

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