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^{13}C Hyperfine Interactions in t-(^{13}CH)x Studied by Electron Spin echoes

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^{13}C HYPERFINE INTERACTIONS IN t-(^{13}CH)x STUDIED BY ELECTRON SPIN ECHOES

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Abstract Electron Spin Echo (ESE) experiments have been performed on 99% ^{13}C-enriched trans-(CH)x. Strong modulation is observed in the envelope traced by the decay of the spin echoes. This modulation arises from the interaction of the paramagnetic defect with ^{13}C nuclei. The electron-nuclear hyperfine coupling may be determined by Fourier transformation of the time domain signal. At 6K we find a maximum hyperfine coupling of 1.75 Mhz.

INTRODUCTION

The spin density distribution of the radical defect in trans-(CH)x had been quantitatively predicted by the soliton model for the paramagnetic defect in polyacetylene[1]. Proton hyperfine couplings, obtained using SSH[1] spin densities, were used to simulate the EPR linewidth[2]. However, it is impossible to determine whether the simulation of an unresolved EPR absorption represents a unique fit. ENDOR spectroscopy[3,4] is a more direct method for measuring hyperfine couplings. However, the complications of electron-electron spin-exchange effects have limited detailed ENDOR studies to only the cis isomer. We report here the measurement of ^{13}C hyperfine couplings in 99% ^{13}C-enriched all trans polyacetylene.

EXPERIMENTAL RESULTS

Samples were prepared according to the Shirakawa procedure[5]. The echo experiment and instrumentation are described elsewhere[6]. The experimental echo envelope modulation (EEM) pattern observed at 6K is shown in Figure 1a. A pronounced modulation of the echo envelope is observed for ^{13}C-enriched trans polyacetylene which is not observed for the ^{12}C analogue[7]. The EEM phenomena[8] has been observed[9] in a number of electron-nuclear hyperfine coupled systems. It arises when the nuclei coupled to an electron spin are subjected to the sudden change in local dipolar magnetic field that occurs when the electronic spin is torqued by the strong resonance microwave pulses. This sudden reorientation of the electronic dipolar field causes the nuclei to branch into subsets of nuclei, one set which adiabiatically follows the new electronic dipolar field and one that does not. The ensuing modulation results from the quantum interference effects from these subsets of nuclei. Fourier transformation of the modulation pattern yields the hyperfine coupling frequencies[8,9].

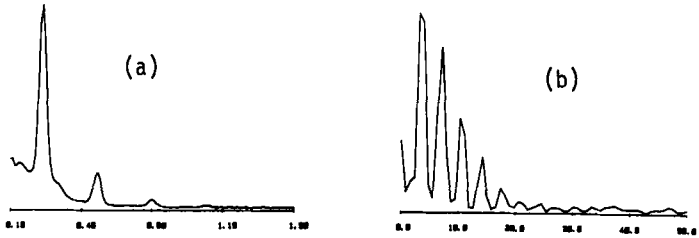

FIGURE 1: (a) Envelope obtained using a pi/2-pi pulse sequence
(b) FT spectrum of the 2 pulse echo envelope.

The Fourier transform of the echo envelope spectrum is shown in Figure 1b. The peak at 3.1 Mhz arises from weakly coupled ^{13}C nuclei. The width of this peak reflects the maximum hyperfine

coupling observed which is app. 1.75 Mhz. The peaks in the Fourier spectrum at higher harmonics of the fundamental peak do not arise from additional hyperfine couplings. A discussion of the origin of these peaks will be published elsewhere[10].

DISCUSSION

The magnitude of the observed ^{13}C couplings may be interpreted in terms of a static (time independent) spin distribution[3,11] or in a dynamic model[12] in which the SSH spin densities[1], modified to include electron correlations[13] are dynamically averaged to lower effective values. For the first order analysis in the present discussion, we assume that the effective hyperfine interaction arises from isotropic coupling only. Note that the calculation of the isotropic ^{13}C coupling from the carbon spin density must include electron correlation effects even to first order in the hyperfine interaction[14]. This is because spin polarization of the valence band electrons will introduce large contributions to the isotropic coupling on adjacent sites. The ^{13}C coupling at site i is[14] $a_C(i)=(S^C+\Sigma\, Q^C_{CX_i})\rho_i+\Sigma\, Q^C_{X_jC}\rho_j$ where S^C = -35.6 MHz; Q^C_{Ch} = 54.6 MHz, $Q^C_{CC'}$ = 40.3 MHz, and $Q^C_{C'C}$ = 38.9 MHz. The spin densities are obtained from the modified SSH theory[13] or from valence bond calculations[11]. Using the extrapolated valence bond results, $\rho_-/\rho_+ \sim -0.43$, or the experimental ENDOR results[3] for cis-(^{13}CH)x, $\rho_-/\rho_+ \sim -0.34$, with the above expression and the spin density normalization condition, we estimate N ~ 60 to 65 sites for a uniform static delocalization; which is in good agreement with previous estimates[3].

For the dynamic model[12], we can obtain an estimate of the diffusion coefficient, $D_\parallel$ (at 6K) required to dynamically average the largest (theoretical) hyperfine interaction to the observed effective value. The largest SSH spin densities are obtained for

$\rho(o)$ and $\rho(\pm 1)$. The calculated value of $a_c(o)$ depends on the value of the Hubbard U used in the Hartree-Fock (HF) model[13], since $U \neq o$ will scale the spin density ratio on alternate sites. Using the expression for $a_c(i)$ and the spin densities for U=3eV[13], we obtain $a_c(o)$ = 18.7 MHz. In order to average $a_c(o)$ from the HF limit $a_c(HF)$, obtained using $a_c(i)$ above, to the effective experimental value, $a_c(exp)$, requires hopping or diffusion over $N = a_c(HF)/a_c(exp)$ sites within the experimental observation time. A diffusion coefficient can be obtained for a site hopping model or for Brownian diffusion of the domain wall. For U in the range $0<U<3eV$ and for an experimental observation time of ω_n^{-1}, where ω_n is the nuclear Larmor frequency which equals $\omega_n/2\pi$, = 3.1 MHz, we obtained $D_{\parallel} \sim (1\text{-}2)\times 10^{-8}$ cm^2/sec for Brownian diffusion. For a simple two site hopping model, the hop rate $k = \frac{(18.7\ MHz)^2}{1.75\ MHz} = 2\times 10^8\ sec^{-1}$ so that $D_{\parallel} = b^2 k = 4\times 10^{-8}$ cm^2/sec, ($b = 1.4\times 10^{-8}$ cm). Note, that at this temperature, these values of $D_{\parallel}$ are 2 to 3 orders of magnitude less than previous estimates[15].

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