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FREQUENCY AND TEMPERATURE DEPENDENCE OF $^1$H NMR OF TRANS-(CH)$_x$ (a)

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Abstract - We have carried out a study of the temperature (0.3K < T < 4.2K) and frequency (23MHz < f < 35MHz) dependence of the proton spin lattice relaxation time, $T_I$, of trans-(CH)$_x$. The data at 4.2K are in agreement with earlier measurements of Nechtschein et al. As the sample is cooled, $T_I$ continues to increase, with $T_I^{-1} = \alpha f^{-\frac{1}{2}} - \beta$, where $\alpha$ and $\beta$ are temperature dependent quantities. Alternately $T_I$ is expressed as an activated quantity, $T_I^{-1} = A \exp(-\Delta/T)$, with $\Delta =$ $\gamma$H (A and $\gamma$ are constants). The observed g factor of 3.3 for the activation energy suggests that we are in the low temperature limit for I-D nuclear spin diffusion as discussed by Clark et al.

Polyacetylene, (CH)$_x$, has been the subject of much recent work (1,2). Many of the studies have concentrated on the question of the existence of domain walls (solitons) in the trans-(CH)$_x$ chain. Earlier experiments that have attempted to measure the motion of the soliton and its coupling to the (CH)$_x$ chain have been in the temperature range from room temperature to 4.2K, where the magnetic spin energy is much less than the thermal energy, kT. We report here measurements that are at lower temperatures where the magnetic spin energy becomes comparable to or larger than kT.

Recent Nuclear Magnetic Resonance (NMR) and Dynamic Nuclear Polarization (DNP) measurements at room temperatures have demonstrated that solitons are mobile and diffuse freely in one dimension (I-D) along the chain. Nechtschein and coworkers (3) have found that

$$T_I^{-1} \propto \frac{1}{D_{II} \omega}$$

for the I-D diffusing soliton and that $D_{II}$, the diffusion constant along the chain, is $6 \times 10^{-13}$ cm$^2$/s at room temperature. Their observation of the Overhauser Effect (OE) in DNP experiments supports the I-D soliton diffusion model.

At low temperatures, 100K and below, the interpretation of the results is not as clear. The I-D diffusive behavior for $T_I^{-1}(T \propto \omega^0)$ is still observed (4), but the relaxation rate extrapolates to a negative value at infinite frequency.
DNP experiments show a Solid State Effect (SSE) indicating that the soliton is becoming localized. For a localized soliton nuclear relaxation will occur through diffusion of the nuclear magnetization, along the \((\text{CH})_x\) chain, to the fixed soliton.

### $^1$H Nuclear Relaxation

When the electron and nuclear Zeeman energies, \(\omega_e\) and \(\omega_n\) respectively, are much smaller than \(kT\) the nuclear relaxation rate is given by /5/

\[
\tau_1 = \frac{\pi}{6} \left[ 6 \langle A^2 \rangle \phi^2(\omega_n) + (7 \langle D^2 \rangle + 5 \langle A^2 \rangle) \phi^+(\omega_e) \right]
\]

(2)

where \(\langle A^2 \rangle\) and \(\langle D^2 \rangle\) are the mean square of the scalar and dipolar parts of the hyperfine coupling and \(\phi^+\) and \(\phi^\star\) are the Fourier transforms of spin correlation functions. At high temperatures in the isotropic paramagnetic region one has \(2 \phi^2(\phi^\star)\). For a soliton moving with I-D diffusive behavior the spectral density is given by

\[
\phi(\omega) = \frac{C}{2\pi} (2 D_{II} \omega)^{-1/2}
\]

(3)

where \(C\) is a normalization constant. This leads to the I-D diffusive result given by Equation 1.

At low temperatures the Zeeman energy of the electron spin becomes comparable to the thermal energy and Equation 2 is no longer valid since \(\phi^\star\) will no longer be effective in relaxing the nuclear spins. If the soliton remains freely diffusing at low temperatures then we would observe the behavior predicted by Equation 1 with a different proportionality constant than the high temperature value.

The DNP experiments at low temperatures indicate that the soliton is becoming localized. In this case we expect that the nuclear relaxation will proceed via I-D diffusion of the nuclear magnetization along the chain to the fixed soliton i.e. nuclear spin diffusion. In this case the relaxation rate is given by /6/

\[
\tau_1^{-1} = \frac{4\pi}{3} C (\mu B / Y_n)^{1/2} D^{3/4} \omega^{-1/2} \zeta^{-1/4}
\]

(4)

where \(C\) is the soliton concentration, \(D\) is the nuclear spin diffusion constant, and \(\zeta\) is the electron relaxation time. Because the Zeeman energy for the soliton is on the order of the thermal energy \(\zeta\) could show a thermally activated behavior of the form

\[
\zeta = \zeta_0 e^{-\Delta / kT}
\]

(5)

where \(\zeta_0\) is a constant and \(\Delta\) is the activation energy. The magnetic energy of the soliton will determine \(\Delta\) and we would therefore expect \(\Delta\) to depend on the magnetic field.

### Experimental Results

We have measured the temperature \((0.3K < T < 4.2K)\) and frequency \((23MHz < f < 35 MHz)\) dependence of the $^1$H nuclear relaxation rate. At the highest temperatures studied in this work our measurements overlap with previous measurements /4/ and our results are in good agreement with them. We find a relaxation time that increases monotonically as the sample is cooled. Also, at constant temperature the relaxation time increases with increasing magnetic field. We will present the data in terms of both the I-D soliton diffusion model and the nuclear spin diffusion model.

Figure 1 presents the data in a form that shows the I-D soliton diffusion character of the results. Equation 1 predicts that a straight line passing through the origin should represent the data. We find that the data is represented by a straight line, but that it does not pass through the origin. The data is best represented by the form

\[
\tau_1^{-1} = \frac{\alpha}{T} - \beta
\]

(6)
where $\alpha$ and $\beta$ are temperature dependent. A diffusion constant can be obtained from $\alpha$ and we find that this diffusion constant increases with decreasing temperature. Below 1K the diffusion constant can be fit to the thermally activated form

$$D_{II} = D_0 e^{-EF \kappa / T}$$

where $D_0$ is a constant. Only relative values of $D_{II}$ can be obtained so no value for $D_0$ is quoted.

Figure 2 presents the data in a form that shows the 1-D nuclear spin diffusion behavior. The lines are fits to the thermally activated form

$$T_1 = A e^{-\Delta / T}$$

where $A$ is a constant and $\Delta$ is the activation energy. The measured activation energy, shown in Figure 3, depends on the magnetic field applied to the sample. The field dependence is given by

$$\Delta = 218 \left( K / K_\gamma \right) H$$

which has been constrained to pass through zero. Thus we can express our results, in terms of the composite variable $H/T$, in the simple form

$$T_1 = A e^{-218 H / T}$$

DISCUSSION

Using the 1-D soliton diffusion model we find that the predicted form (Equation I)
does not fit the data without the addition of a temperature dependent negative intercept. It has been proposed /7/ that if the soliton diffusion rate is slow enough effects due to the finite extent of the soliton need to be considered. In this case the intercept will decrease as the diffusion constant increases, in agreement with our measurements.

The diffusion constant obtained from these measurements increases in a thermally activated manner as the temperature decreases. This type of behavior has been predicted by Maki /8/ using a model in which the solitons propagate ballistically at low temperatures. The activation energy Maki predicts, approximately 10K, is much larger than the experimentally observed activation energy. This model is also in disagreement with the observed SSE at low temperatures.

Alternately, we have presented the data using the I-D nuclear spin diffusion model. Observation of the SSE at low temperatures in DNP experiments indicates the solitons are localized and that nuclear relaxation should be due to nuclear spin diffusion. The observation of thermally activated behavior for the nuclear relaxation time implies that the electron spin relaxation time is also thermally activated. The field dependence of the activation energy gives an observed g factor of 3.3, assuming $\Delta g = \mu N$. Clark /9/ has proposed that in the high field low temperature limit (g$\approx$$\mu$N) the observed g factor should be 2g$\approx$$\mu$N in rough agreement with our results.

In conclusion, we find that both the I-D soliton diffusion model and the I-D nuclear spin diffusion model fit the experimental results, within the limitations discussed in the text. In view of the DNP experiments and experiments on (CD)$_2$ /2/ it is most likely that relaxation proceeds via nuclear spin diffusion to a fixed soliton. In this case the measurements indicate an electron relaxation time that is thermally activated and depends on the composite variable H/T.

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![Activation Energy as a function of magnetic field or frequency.](image)