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Magnetic Resonance Studies of Spin Dynamics in Trans-Polyacetylene

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MAGNETIC RESONANCE STUDIES OF SPIN DYNAMICS IN TRANS-POLYACETYLENE

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We present a study of the temperature dependence of the spin dynamics in trans-polyacetylene using dynamic nuclear polarisation, nuclear relaxation and EPR measurements.

There is still some controversy about the nature of the paramagnetic species which exist in pristine trans-polyacetylene with concentration of the order of one spin per one or two thousand CH units. While it has been proposed by Goldberg et al¹ that they are neutral solitons corresponding to the domain walls between the two equivalent configurations of the polymer chain, this proposal has been censured by Tomkiewicz et al². An important argument in favor of the soliton picture was provided by the dynamical properties of the spins as observed by room temperature dynamic nuclear polarisation (DNP) and nuclear relaxation time (T_1) measurements³. While the DNP yields 10^{11} rad/s as a lower limit for the motion rate, the analysis of the nuclear relaxation leads to a very fast and highly anisotropic spin motion. The on-chain spin diffusion coefficient is found to be $D \approx 10^{-3} \text{ cm}^2/\text{s}$ and the diffusion anisotropy larger than 10^5 . These results first appeared in contradiction with the values reported for the EPR linewidth

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($\Delta H \sim 1G$), which correspond to a much smaller degree of motional narrowing⁴. However it turned out that the EPR linewidth is not at all intrinsic and depends strongly on the oxygen contamination⁵. More recent values of the EPR linewidth ($\Delta H \sim 0.2G$)⁶ are now consistent with NMR data. In agreement with the fact that the spin susceptibility does not increase with oxygen contamination, the extra linewidth contribution can be interpreted as arising from a trapping of a part of the mobile spins by oxygen⁷. As a consequence, the EPR line in common samples mainly reflects the trapped spins, while the NMR relaxation is governed by the spins which remain mobile and visit most of the nuclear spin sites.

In this communication, we examine the temperature dependence of the spin dynamics in undoped trans-polyacetylene. Again an apparent contradiction arises between NMR and EPR data, which can be overcome by assuming a trapping of the spins as the temperature decreases. Fig. 1 exhibits the enhancement of the NMR signal intensity when the EPR

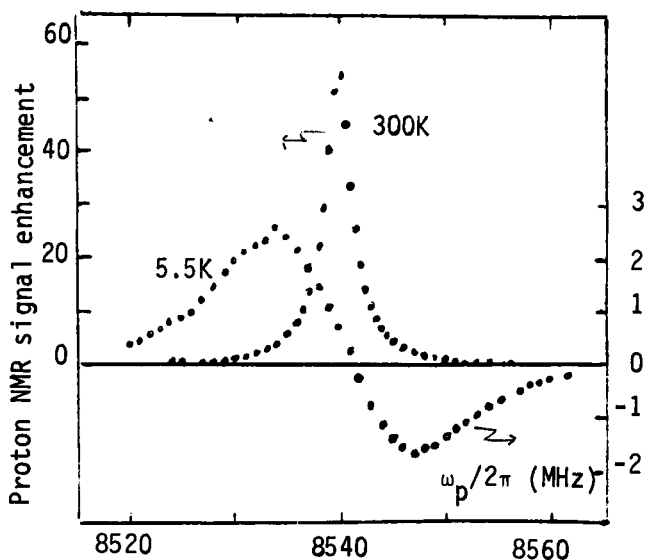


FIGURE 1 : Enhancement of the proton NMR amplitude as a function of the microwave pumping frequency $\omega_p/2\pi$

line is saturated at a pumping frequency ω_p near the electronic Larmor frequency⁸. By cooling down, the DNP enhancement is changed from a complete overhauser effect at room temperature to a dominant solid state effect at 5K. This proves that the high temperature mobile spins become mostly frozen at low temperature. In a similar way the broadening of the EPR linewidth as the temperature decreases (Fig.2) corresponds to a slowing down of the spin motion. An important point in Fig.2 is that the low temperature limiting value for the linewidth is the same for the "pure" and for the oxygen contaminated sample, which indicates some common mechanism for oxygen contamination and cooling down. Moreover spin echo experiments reported by Shiren et al⁹ show that the line becomes inhomogeneous at low temperature ($T < 130K$). In other words, below 130K, the spin-spin exchange is not fast enough to average the inhomogeneous local magnetic fields due to hyperfine interactions.

On the other hand, the nuclear relaxation rate has been shown to be dominated by a 1D spin diffusion both at 300K³ and 4.2K¹⁰ and can be accounted by the relation :

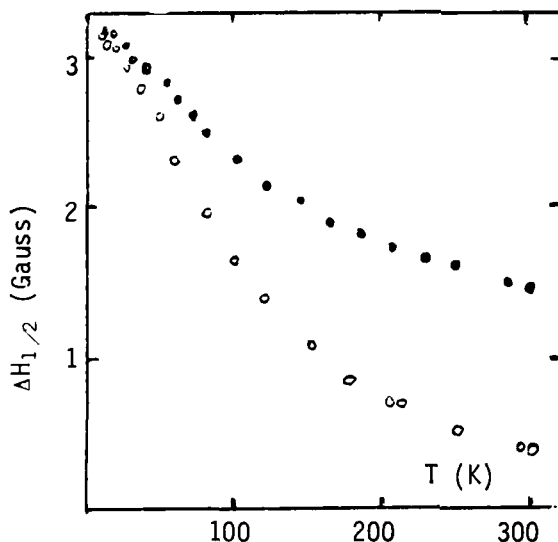


FIGURE 2 : Temperature dependence of the EPR linewidth of scaled under vacuum (o) and open to air (●) trans-(CH)_x

$$T_1^{-1} \sim nd(2\tilde{D}\omega)^{-1/2}$$

where nd is the number of diffusive spins, ω the Larmor frequency and \tilde{D} the diffusion rate $\tilde{D} = D/c^2$ (c is the intersite distance). If one assume a simple slowing down of the spins, i.e. a decrease of \tilde{D} , one should expect an increase of the relaxation rate when the temperature decreases. That we observe in Fig.3 is just the opposite : T_1^{-1} decreases with decreasing temperature. The simplest way to reconcile EPR and NMR data is to suppose that a part of the spins become trapped, as for the effect of oxygen. These trapped spins give rise to a broadening of the EPR line, while those spins which remain mobile are less numerous (nd decreases) and thus induce a slower nuclear relaxation. As a matter of fact, it is not necessary to assume two different kinds of spins : one may instead imagine that the same spin shares its time inside and outside the traps.

Based upon these simple idea, we have developed a model of the spin dynamics in trans-polyacetylene¹¹ whose main features are the following : the spins are neutral

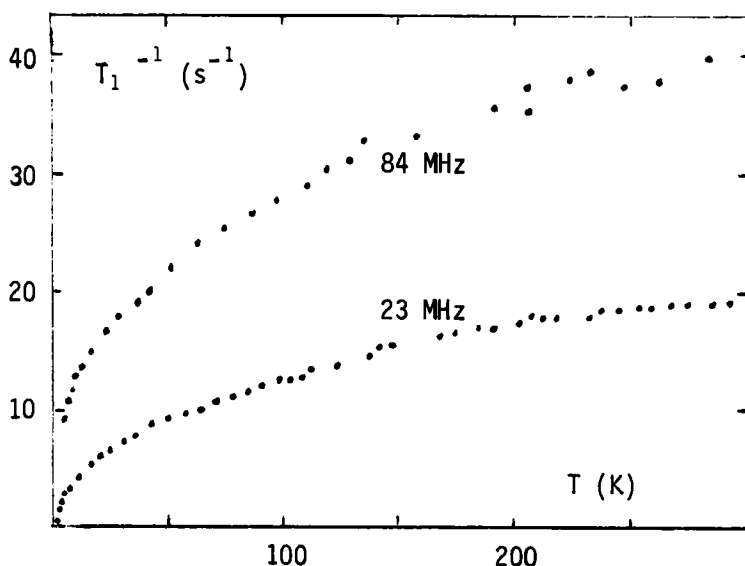


FIGURE 3 : Temperature dependence of the proton nuclear relaxation rate of trans-(CH)_x

solitons, whose mobility increases with increasing temperature as a result of the strong soliton-phonon coupling. Moreover solitons may be trapped by impurities¹². The trap concentration depends on the purity of the sample, in particular on its oxygen content and the mean trapping time (or the mean concentration of trapped solitons at a given time) is a function of the temperature via activated process. These two competing mechanisms-intrinsic temperature dependent mobility and extrinsic pinning- are necessary to account for the whole magnetic resonance data in trans-polyacetylene.

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