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Nuclear spin-lattice relaxation in trans-polyacetylene (CH)_x. A confined soliton model including nuclear spin flip diffusion

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Résumé. — Un modèle de solitons confinés dans lequel les solitons se déplacent sur une petite partie de la chaîne a été développé. Les noyaux de la chaîne relaxent directement les interactions hyperfines de contact alors que les autres noyaux relaxent par une diffusion de l'aimantation des spins nucléaires. Les données sur la relaxation spin-réseau du proton peuvent être expliquées par un mouvement rapide et confiné de sauts à une dimension alors que celles relatives au ¹³C nécessitent en plus de tenir compte du mécanisme de diffusion de spin nucléaire.

Abstract. — A « confined soliton model » in which the solitons move over a small part of the chain is developed. The on-chain nuclei are relaxed directly by contact hyperfine interactions whilst the remainder nuclei relax via nuclear spin flip diffusion. It is found that the proton spin-lattice relaxation data can be rationalized in terms of the fast and confined one-dimensional hopping motion of the soliton whilst that for enriched ¹³C one requires in addition a much more dominating mechanism that of nuclear spin flip diffusion.

1. Introduction.

Trans-polyacetylene is known for quite some time to contain paramagnetic spins as a consequence of a bond alternating defect [1]. The interpretation and structural analysis of these defects in terms of topological kinks (solitons) by Su, Schrieffer and Heeger [2] has provided tremendous impetus to this field of research. In order to unravel the physical nature of these defects numerous experimental techniques have been applied. Here we restrict ourselves to taking a closer look at the proton NMR data and briefly carbon-13 data on enriched samples of polyacetylene obtained so far. Nechtschein *et al.* [3] were the first to observe an $\omega^{-1/2}$ dependence of the proton spin lattice relaxation rate T_1^{-1} in trans-(CH)_x, where ω is the Larmor frequency of the nuclear spins. The standard interpretation, once a frequency dependence of this sort is observed, is that of one-dimensional diffusion. Because of the slowly decaying correlation function of a 1D-diffusion process this typical frequency dependence of T_1^{-1} is observed, but only if the diffusion is highly one-dimensional.

On the other hand, $\omega^{-1/2}$ dependence of the relaxation rate T_1^{-1} has also been observed in the case of localized paramagnetic defects [4-6]. This typical frequency dependence comes about by what is usually called limited nuclear spin diffusion, not to be confused with the spin diffusion of the paramagnetic species. In order to avoid possible confusion we will use the term « nuclear spin flip diffusion » to describe the flow of nuclear spin temperature around a more or less localized paramagnetic defect, whereas the term « paramagnetic spin diffusion » will be reserved for the mobile paramagnetic species.

In other words, the observation of an $\omega^{-1/2}$ dependence of T_1^{-1} alone can not necessarily be interpreted as 1D-paramagnetic spin diffusion, but could well be caused by fixed paramagnetic spins in combination with limited nuclear spin flip diffusion. An analysis of the last kind was recently applied to T_1 measurements in trans-(CH)_x by Shiren *et al.* [7] who invalidated Nechtschein's interpretation on this basis. Clark *et al.* [8] have also given arguments, in combination with their results on deuterated polyacetylene, supporting this interpretation at low temperatures whilst at higher temperatures they allude to having a model which takes into account the paramagnetic spin diffusion. They have also reported the field-independence of the relaxation rate below $H \simeq 20$ Oe. Scott

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and Clarke [9] have analysed qualitatively the T_1 data at room temperature with the assertion that the on-chain nuclei, visited by the diffusing soliton, are directly relaxed whereas those on other chains relax by nuclear spin flip diffusion. One of their main findings is that the relaxation rate of ^{13}C enriched samples is frequency independent.

Different types of defects have also been investigated by time-resolved spin echo spectroscopy [10]. Three types of defects, namely mobile soliton defect, spatially extended static or pinned soliton defect and a highly localized point-like defect, were observed. The electron spin-lattice relaxation rates due to the mobile and pinned solitons were found to have a different temperature dependence above 50 K. Thus both the NMR and ESR results point out to the freezing (or immobilization) of the mobile soliton as the temperature is lowered. At larger temperatures, at least above 50 K, one can thus safely out Shiren *et al.*'s [7] interpretation whereby only nuclear spin diffusion to static paramagnetic centres gives rise to $\omega^{-1/2}$ behaviour in the proton relaxation rates.

The task of determining the populations of the moving and pinned solitons is non-trivial and this makes the theoretical treatment difficult. On the other hand, models like the trapping/diffusing one due to Nechtschein *et al.* [3], can be developed for the mobile soliton concentration as a function of temperature. Nutation NMR studies [11] on ^{13}C enriched samples of trans-polyacetylene show unambiguously that the solitons, if present, must be restricted to certain chain areas in the sample. Similar conclusions were also obtained earlier from ^{13}C NMR results [12, 13] and time-resolved ESR spectroscopy [10]. We therefore take the viewpoint that solitons are confined to move over a small part of the chain and do not visit all the nuclei on the chain. Baughman and Moss [14] and Baeriswyl and Maki [15] have also dealt with similar situations.

The purpose of the present paper is to develop a « confined soliton model » (discussed in section 2) in which the soliton having an average confinement length l relaxes directly the on-chain nuclei whilst the remainder nuclei achieve equilibrium through nuclear spin flip diffusion. The comparison between the experimental and the calculated results for pure trans-polyacetylene and ^{13}C enriched (^1H diluted) polyacetylene is made in section 3. Section 4 contains our conclusions.

2. The model of confined solitons

2.1 GENERAL. — Figure 1 presents a schematic summary of the findings [10] that polyacetylene contains at least three types of paramagnetic defects : (i) mobile solitons (m) which are confined to certain chain segments, (ii) pinned solitons (p) and (iii) catalyst residues (cat). All these paramagnetic defects may relax the nuclear spins in the sample and their different

Fig. 1. — Summary view of the different types of defects observed in polyacetylene.

contributions should be taken into account. The total spin-lattice relaxation rate T_1^{-1} is therefore given by

$$\frac{1}{T_1} = \frac{1}{T_{1m}} + \frac{1}{T_{1p}} + \frac{1}{T_{1cat}}. \quad (1)$$

It was found that T_{1cat}^{-1} can be neglected in Shirakawa type $(\text{CH})_x$ in contrast with Luttinger type $(\text{CH})_x$ where strong contributions from cobalt residues are present [10]. Since the experimental data we discuss here have been obtained on Shirakawa's material the last term in equation (1) will be ignored.

The relaxation is caused by : (i) direct (contact) hyperfine interactions between the mobile soliton and the on-chain nuclei, (ii) direct interactions between the mobile soliton and the nuclei on neighbouring chains (much smaller than (i)), (iii) hyperfine interactions due to spin flips of the mobile soliton, and (iv) hyperfine interactions due to static pinned solitons. In all these processes, the nuclear spin flip diffusion brings the system back to equilibrium. The interactions (i)-(iii), those corresponding to the mobile soliton, contribute to T_{1m} , whereas (iv) to T_{1p} . Although all these contributions can be treated quite rigorously we introduce certain simplifications in order to keep the whole analysis intelligible. We, therefore, ignore the orientation dependence and take powder averages and neglect the nuclear Larmor frequency ω_n w.r.t. the electronic Larmor frequency ω_e in the spectral density functions, i.e. $J(\omega_e + \omega_n) \simeq J(\omega_e)$.

The total nuclear magnetization of the sample is

$$M(t) = \int_V m(\mathbf{r}, t) d\tau, \quad (2)$$

where $M(\mathbf{r}, t)$ is the magnetic moment per unit volume.

The above expression, in the case of a 180° - 90° T_1 experiment, becomes

$$M(t) = \{ S(\infty) - S(t) \} / 2 S(\infty), \quad (3)$$

where $S(t)$ is the observed signal at time t and $S(\infty)$ is its equilibrium value.

2.2 CONFINED SOLITON MODEL. — The confined soliton model is schematically outlined in figure 2. Consider a cylinder of $(\text{CH})_x$ material of volume V which contains n_s mobile or pinned distributed defects (solitons) per cm^3 . The distribution length or

Fig. 2. — Schematic view of the confined soliton model as discussed in the text.

mobility range l defines the average length of each cylinder of volume V_s surrounding each confined soliton. With $V_s = 1/n_s$ the radius R_s of the cylinder is defined through

$$V_s = \pi R_s^2 l. \quad (4)$$

The soliton is placed in the middle of the cylinder. The relaxation of the nuclear spins in the volume V_s takes place either by direct relaxation within a cylinder of radius r_s or by nuclear spin flip diffusion for $r_s \leq r \leq R_s$.

For the situation where the soliton, which acts as a volume-like sink with strength density $\Gamma(\mathbf{r})$, moves only in an « active » volume v_a and the nuclei in the rest of the non active volume $V - v_a$ achieve equilibrium through spin flip diffusion, the governing equations can be written as

$$\nabla \cdot (\mathbf{D} \cdot \nabla m(\mathbf{r}, t)) - \Gamma(\mathbf{r}) m(\mathbf{r}, t) = \frac{\partial m(\mathbf{r}, t)}{\partial t}, \quad (5)$$

$$\hat{\mathbf{n}} \cdot \mathbf{D} \cdot \nabla m(\mathbf{r}, t) |_S = 0, \quad (6)$$

$$m(\mathbf{r}, 0) = M(0)/V, \quad (7)$$

where S denotes the bounding surface and $\mathbf{D}$ is the spin flip diffusion tensor.

Consider now that the soliton relaxes all nuclei in the tube with radius r_s (see Fig. 2) directly, whereas the

other nuclei are relaxed *via* spin flip diffusion up to a distance R_s . Effects near R_s due to neighbouring solitons are neglected. For simplicity we treat the spin flip diffusion problem one-dimensional. Let $m_1(r, t)$ ($0 \leq r \leq r_s$) and $m_2(r, t)$ ($r_s \leq r \leq R_s$) denote the linear magnetic moment densities in the two regions. By using the following boundary conditions

$$m_1(0, t) = m_1(r_s, t) = m_2(r_s, t), \quad (8)$$

$$\left. \frac{\partial m_2(r, t)}{\partial r} \right|_{r=R_s} = 0,$$

the diffusion problem can be formulated as

$$D \frac{\partial^2 m_2(r, t)}{\partial r^2} = \frac{\partial m_2(r, t)}{\partial t}, \quad (9)$$

with

$$r_s \Gamma m_2(r_s, t) = -r_s \frac{\partial m_2(r_s, t)}{\partial t} + D \left. \frac{\partial m_2(r, t)}{\partial r} \right|_{r=r_s} \quad (10)$$

Making the transformation $x = r - r_s$ and defining $m(x, t) = m_2(x, t)$ the above equations, along with their boundary conditions, yield

$$D \frac{\partial^2 m(x, t)}{\partial x^2} = \frac{\partial m(x, t)}{\partial t}, \quad (11)$$

$$r_s \Gamma m(0, t) = -r_s \frac{\partial m(0, t)}{\partial t} + D \frac{\partial m(0, t)}{\partial x}, \quad (12)$$

$$\left. \frac{\partial m(x, t)}{\partial x} \right|_{x=R_s} = 0, \quad (13)$$

$$m(x, 0) = M(0)/R_s. \quad (14)$$

The solution of the above problem is conveniently expressed as a sum of normal modes [16]

$$m(x, t) = \sum_{n=0}^{\infty} A_n X_n(x) G_n(t). \quad (15)$$

Here n refers to the mode number and A_n are the constants obtainable from the initial condition (14) and the orthogonality of the functions $X_n(x)$ as

$$A_n = \frac{M(0)}{R_s} \frac{\int X_n(x) dx}{\int X_n^2(x) dx}. \quad (16)$$

The functions $X_n(x)$ and $G_n(t)$ are obtained from equations (8) and (10) as

$$G_n(t) = \exp(-Dq_n^2 t), \quad (17)$$

$$X_n(x) = \cos \{ q_n(R_s - x) \}, \quad (18)$$

with

$$\begin{aligned} -q_n^2 &= \left\{ \frac{\partial G_n(t)}{\partial t} \right\} / DG_n(t) \\ &= \left\{ \frac{\partial^2 X_n(x)}{\partial x^2} \right\} / X_n(x). \end{aligned} \quad (19)$$

The boundary condition (12) yields the unknown q_n through the solution of the transcendental equation

$$\beta_n \tan \beta_n = -\beta_n^2 \frac{r_s}{R_s - r_s} + \frac{r_s(R_s - r_s) \Gamma}{D}, \quad (20)$$

where $\beta_n = (R_s - r_s) q_n$. The equation for the reduced magnetization (2) can therefore be written as

$$\begin{aligned} M(t) &= \int_0^{R_s - r_s} m(x, t) dx \\ &= M(0) \sum_{n=0}^{\infty} I_n \exp(-t/T_n), \end{aligned} \quad (21)$$

where

$$I_n = \frac{4 \sin^2(\beta_n)}{\beta_n \{ 2 \beta_n + \sin(2 \beta_n) \}}, \quad (22)$$

$$T_n = (R_s - r_s)^2 / D \beta_n^2, \quad (23)$$

with $\sum_n I_n = 1$. Note that T_n is, in fact, $(T_1)_n$ for spin-lattice relaxation, $(T_2)_n$ for spin-spin relaxation and so on. If spin flip diffusion plays a role, the magnetization recovery is according to equation (21) a sum of exponentials, i.e. non-exponential. The lowest mode is usually dominant in the « fast » and « intermediate » diffusion regimes. The different diffusion regimes are categorized according to the rate parameter

$$K = r_s(R_s - r_s) \Gamma / D :$$

fast if $K \ll 1$ and slow if it is much greater than unity. Thus for the lowest mode

$$T_{1m}^{-1} = \frac{D \beta^2}{(R_s - r_s)^2}, \quad (24)$$

where β is determined from $\beta \tan \beta = r_s R_s \Gamma / D$ ($r_s \ll R_s$).

For a radical coupled to a proton, the typical hyperfine tensor elements are [17] : $A_{11} = -11.5$ G, $A_{22} = -23$ G and $A_{33} = -34.5$ G. The isotropic part $A_i = \text{Tr} \{ A_{ii} \} / 3$ has indeed been observed (-23 G) in the case of polyacetylene [10]. We assume that under spin delocalization the hyperfine tensor is simply scaled by the spin density distribution ρ_j . In this situation, the equation for the sink strength density Γ can be obtained from reference [18] as

$$\begin{aligned} \Gamma &= \frac{a}{4l} \left[\frac{1}{10} \{ 3(A_{33} - A_i)^2 + (A_{11} - A_{22})^2 \} J(\omega_p) + \right. \\ &\quad \left. + 2 A_i^2 J(\omega_e) + \frac{7}{10} \{ (A_{33} - A_i)^2 + \right. \\ &\quad \left. + \frac{1}{3} (A_{11} - A_{22})^2 \} J(\omega_e) \right] \sum_j \rho_j^2. \end{aligned} \quad (25)$$

In the simple case of a rectangular spin density distribution function ($\rho_j = 1/L$ for $-L/2 \leq j \leq L/2$), $\sum_j \rho_j^2 = 1/L$. In the above formula, A_{ii} are the principal values of the hyperfine tensor. The anti-symmetric components have been neglected in writing equation (25). The expression for the spectral density function $J(\omega)$ for a hopping, confined and delocalized [19] spin $-1/2$ is obtained in the Appendix and reads as

$$\begin{aligned} J(\omega) &= \frac{\tau_{\parallel} L}{\pi} \int_0^{\pi} \left\{ \sum_{p=0}^m \alpha_p \sin^{2p}(q/2) \right\}^2 \times \\ &\quad \times \frac{\frac{\tau_{\parallel}}{\tau^*} + 2 \sin^2(q/2)}{\left\{ \frac{\tau_{\parallel}}{\tau^*} + 2 \sin^2(q/2) \right\}^2 + \omega^2 \tau_{\parallel}^2} dq \end{aligned} \quad (26)$$

with $\alpha_0 = 1$ and

$$\alpha_p = (-1)^p \frac{(L^2 - 1^2)(L^2 - 3^2) \dots \{ L^2 - (2p-1)^2 \}}{(2p+1)!}, \quad (27)$$

where $\tau_{\parallel}$ is the hopping time between two nearest sites and $1/\tau^* = 1/\tau' + 1/\tau_{2e}$. τ' is the correlation time of the confined motion which corresponds to the interruption (cut-off) in the 1-D motion of the soliton at the boundary of the mobile soliton domain and therefore can be straightforwardly determined from the relationship $\tau_{\parallel}/a^2 = \tau'/l^2$. The one-dimensional hopping can be interrupted either by an inter-chain transfer or by a trapping mechanism. The effect of the τ_{2e} term at the temperatures and frequencies of our interest is negligibly small.

Before we apply this model to physical situations, let us first study the behaviour of the transcendental equation which ultimately defines the dependence of the relaxation rate on frequency and concentration of the nuclear species under investigation. In figure 3, we plot β^2 as a function of K , the rate parameter from the solution of the equation $\beta \tan \beta = K$ (continuous line). To focus attention on the value of K from where the spin flip diffusion phenomenon starts contributing we have plotted (in dashed curve) $\beta^2 = K$ in the same figure. Three regions are immediately identifiable namely, $K < 0.1$, $0.1 < K < 100$ and $K > 100$. In the fast diffusion regime, $K \ll 1$ which implies that

Fig. 3. — β^2 as a function of K , the rate parameter, from the solution of the transcendental equation $\beta \tan \beta = K$ (continuous curve) and from $\beta^2 = K$ (dashed curve).

$\tan \beta \simeq \beta$. Thus, the relaxation rate is directly proportional to Γ and will exhibit the characteristic frequency dependence of the spectral density function. Moreover, in this regime, T_1^{-1} is independent of the nuclear spin flip rate D . In the slow diffusion regime, $K \gg 1$ and therefore $\tan \beta = \beta^\alpha$ where α can be any integral or fractional number greater than unity. This has the implication that the $\omega^{-1/2}$ dependence of the relaxation rate is suppressed appreciably, so much so that it becomes independent of frequency. In the intermediate diffusion regime, the behaviour of T_1^{-1} is much weaker than $\omega^{-1/2}$.

3. Results and discussion.

In the previous section, the contribution to the relaxation rate due to the mobile soliton was obtained using the confined soliton model. Since T_1^{-1} also includes the relaxation contribution from the pinned solitons we make their approximate estimates using the results of T_1 relaxation *via* paramagnetic centres as described by Lowe and Tse [5]. It is essential that the « radius of influence » of the paramagnetic centre (here pinned soliton) be larger than b_0 and, of course, b . b is the nuclear spin flip barrier radius whilst b_0 is the radius inside of which the nuclei have their resonance lines so much broadened that they are not measured in the experiment. Now $R = (3/4 \pi n_s)^{1/3}$ which, for $n = 1/2 \text{ 500}$, gives $R \simeq 16 a$. A rough estimate [20] of b is given by $b \sim (\gamma_e/z\gamma_n)^{1/3} d$ where z is a small integer and d is the internuclear distance. For protons with $z = 1, 2$ and 3 , b is equal to 16.5, 13 and 11.5 times a , respectively. Since $b_0 \simeq (b^4/3 d)^{1/3}$ (Ref. [5]), for $z = 3$, $b_0 = 14.5a$ using $d = 2.67 \times 10^{-10} \text{ m}$ [21]. Thus for z up to 3, $R \lesssim b_0$ and it can hence be concluded that the pinned solitons do not contribute much to the proton relaxation rate T_1^{-1} . Similarly, for carbon-13 nuclei $R < b_0$.

The results, to be described below, of the confined soliton model, similar to usual high field theories, can not be taken seriously at low fields and, at best, are only qualitative. Any analysis of the low frequency

cut-off behaviour must start with the appropriate Hamiltonian at low fields. The cut-off enters into our model through the dependence of $J(\omega_e)$ and $J(\omega_n)$ on l . As is clear, $J(\omega_e)$ is cut off at lower nuclear frequencies than $J(\omega_n)$ which depends on l through $\tau_{||}$.

3.1 APPLICATION TO PURE TRANS-POLYACETYLENE. —

Since $T_{1m} \propto \beta^2$ and $\beta \tan \beta = K$, it follows (see Eqs. (25) and (26)) that β must be much smaller than unity, that is in the « fast diffusion » regime, if $\omega^{-1/2}$ behaviour is to be observed. In the fast diffusion limit

$$T_{1m}^{-1} = \frac{r_s}{R_s} \Gamma \text{ or } T_{1m}^{-1} = \frac{r_s}{r_s + R_s} \Gamma \text{ if we do not make}$$

the assumption $r_s \ll R_s$. The ratio $r_s/(R_s + r_s)$ can be understood as the number of protons in the active and non active regions respectively. If the sink comprises of only the hyperfine interactions between the soliton and the on-chain protons, the expression for the relaxation rate can be written as

$$T_{1m}^{-1} = C_s l \Gamma / a, \quad (28)$$

where $C_s = n(1 - C)$, n is the concentration of free spins per -CH unit and C is the relative fixed spin concentration.

It is clear from equations (25)-(28) that the frequency dependence of the relaxation rate is contained in $J(\omega_e)$ and $J(\omega_p)$. The spectral density function $J(\omega)$ exhibits a cut-off at small frequencies which depends upon $\tau_{||}/\tau^*$ and ω^{-2} behaviour at large frequencies. The dependence of T_{1m}^{-1} on l arises through τ' only and the situation becomes identical to that proposed by Nechtschein *et al.* [3] except for the term τ^* . It may, however, be mentioned that the weights of the spectral density functions $J(\omega_e)$ and $J(\omega_p)$ are different from those of Nechtschein *et al.* because they treated the interactions in their analysis as purely dipolar.

Equation (28) does not predict the correct temperature dependence of the relaxation rates. From Overhauser and « Solid State Effect » experiments there is ample evidence of trapping or immobilization of the solitons with decrease in temperature [8]. A sample of polyacetylene always contains impurities, chain-end defects, etc. which may lead to trapping. The trapping mechanism may also be due to soliton-soliton interactions as discussed in reference [15]. We cannot distinguish between these different origins and therefore incorporate the temperature dependence of the trapping phenomenon by varying C .

The magnitude of the relaxation rate T_1^{-1} depends both on C and $\tau_{||}$. The $\omega^{-1/2}$ region increases with smaller values of $\tau_{||}$ but at the same time the magnitude of T_1^{-1} decreases. On the other hand, T_1^{-1} is directly proportional to C . It is clear that the effects of either increasing $\tau_{||}$ and decreasing C or decreasing $\tau_{||}$ and increasing C are non-compensating so far as the overall behaviour of T_1^{-1} is concerned. Thus only a unique set of values for l , $\tau_{||}$ and C give rise to the observed behaviour.

We first present our results at $T = 295$ K. The existence of mobile solitons with diffusion rate quite similar to that of Nechtschein *et al.* has also been experimentally demonstrated through ESR [22] at room temperature. In figure 4 we plot the results of

Fig. 4. — Proton spin-lattice relaxation rate T_1^{-1} as a function of proton frequency at $T = 295$ K : experiment (open circles) and calculated with (a) and without (b) delocalization effects due to the soliton extension. The broken line corresponds to the $\omega^{-1/2}$ behaviour.

our model calculation using equations (25)-(28). Curves (a) and (b) were obtained using $C = 0.07$, $\tau_{\parallel} = 2.0 \times 10^{-13}$ s and $l = 170 a$ with and without delocalization effects [19] of the soliton extension respectively. Although a rectangular instead of a realistic spin distribution has been used ($L = 15$), the results do show appreciable effects. The present choice of l gives a cut-off around $\nu = 0.04$ MHz but, as mentioned earlier, this value may not be taken seriously although it is fairly close to that found by Clark *et al.* [8]. The effect of changing l on the relaxation rate is shown in figure 5 for $l = 100$, 150 and 200 a (continuous, dashed and dashed-dot respectively). It is seen that l has to be in the range 150-200 a .

Fig. 5. — Proton spin-lattice relaxation rate T_1^{-1} as a function of frequency at $T = 295$ K for three values of l , namely (continuous) $l = 100 a$, (dashed) $l = 150 a$ and (dashed-dot) $l = 200 a$.

The results of the model calculation at 77 K are plotted in figure 6 using $C = 0.6$, $\tau_{\parallel} = 4.5 \times 10^{-13}$ s and $l = 170 a$. Again the agreement with the experiment is quite good and the calculated T_1^{-1} follow more or less $\omega^{-1/2}$ behaviour. It is interesting to note that no clear $\omega^{-1/2}$ behaviour is predicted either at $T = 295$ K or at $T = 77$ K. This is because both $J(\omega_e)$ and $J(\omega_p)$ contribute and each of which exhibits $\omega^{-1/2}$ behaviour in different regions.

Fig. 6. — Proton spin-lattice relaxation rate T_1^{-1} as a function of proton frequency at $T = 77$ K : experiment (open circles) and calculated with (a) and without (b) delocalization effects. The broken line corresponds to the $\omega^{-1/2}$ behaviour.

Figure 7 shows the results of our calculation at 4.2 K. The data at low frequencies has been taken from reference [8] at 7 K and renormalized around 8.5 MHz. Curves (a) and (b) correspond to $C = 0.964$, $\tau_{\parallel} = 4.0 \times 10^{-11}$ s and $l = 150 a$ with and without the inclusion of the delocalization effects. The overall agreement with the experiment is excellent. We find that, at this temperature, the so-called cut-off has its origin in $J(\omega_p)$ and not in $J(\omega_e)$.

Fig. 7. — Proton spin-lattice relaxation rate T_1^{-1} versus proton frequency at $T = 4.2$ K : experiment (open [3] and filled [8] circles) and calculated with (a) and without (b) delocalization effects. The broken line corresponds to $\omega^{-1/2}$ behaviour.

The values of C at $T = 295$ K, 77 K and 4.2 K which fit the data are 0.07, 0.6 and 0.964 respectively. The expression for C (Ref. [3]) is

$$C = \frac{p}{p + (1 - p) \exp(-E/kT)}, \quad (29)$$

where p is the concentration of traps and E is the trapping energy. In the model of Nechtschein *et al.* [3], the distribution function for the trapping energy has a constant value in the range $(0, E_0)$ and zero elsewhere. The averaging of equation (29) over E yields

$$C = \frac{kT}{E_0} \ln \{ 1 + p(e^{E_0/kT} - 1) \}. \quad (30)$$

This gives $C = 0.15$, 0.64 and 0.982 at the above three temperatures using $E_0/k = 650$ K and $p = 0.05$. On the other hand, if the distribution is assumed [8] to be in the range 175 K around $E_0/k = 100$ K, i.e. in the range (12.5 K, 187.5 K), equation (29), after averaging over E , gives $C = 0.07$, 0.18 and 0.986. We can only remark that our values are closer to those of Nechtschein *et al.* [3].

3.2 APPLICATION TO ^{13}C ENRICHED POLYACETYLENE. — Although we have demonstrated that spin flip diffusion is not limiting the relaxation process of protons in $(\text{CH})_x$ at frequencies above 1 MHz, the situation changes drastically in the diluted proton or ^{13}C enriched case. Equations (21)–(27) describe the expected non-exponential decay which has been observed for enriched ^{13}C and diluted protons in $(\text{CD}_x\text{CH}_{1-x})$ recently [9, 12, 24]. The expressions derived here allow to analyse these results quantitatively. At present we can put our hands only on rather limited data reported by Scott and Clarke [9] for various ^{13}C and ^1H concentrations and at two/three frequencies. We, in the following, apply our model to this data.

Let us first rewrite our expressions appropriate to this case. As asserted in the preceding section, $r_s = n(1 - C) l R_s/a$ with $R_s \ll r_s$, and from relation (4), using the unit cell parameters of reference [21], $R_s = \{ 6.95 a/(\pi \ln) \}^{1/2} a$. With $n = 1/2$ 500 $\beta \tan \beta = 2.2122(1 - C) \Gamma/D_f$ where $D_f = D/a^2$ is the spin flip rate in s^{-1} . The solution of this equation for β can then be substituted in equation (24) to compute the relaxation rate. For parameters C , l and $\tau_{\parallel}$ we use the same values as obtained in the case of pure polyacetylene at $T = 295$ K, i.e., $C = 0.07$, $l = 170 a$ and $\tau_{\parallel} = 2.0 \times 10^{-13}$ s. Since the hyperfine couplings for protons and ^{13}C are similar in magnitude [23], we use the same values as given in the earlier section. Thus the only remaining unknown is D_f which can be varied to reproduce the relaxation rates of reference [9]. The spin flip diffusion rate for ^{13}C cannot simply be derived from the second moment of the dipole-dipole interactions as in the case of protons

because it is strongly modified and partially quenched due to chemical shift anisotropy [10] and ^{13}C - ^1H dipole interactions. It is therefore expected that D_f would be rather small for ^{13}C in polyacetylene even in highly enriched samples.

Fig. 8. — ^{13}C spin-lattice relaxation rate T_1^{-1} versus frequency at room temperature : calculated and experimental results on $(\text{CH})_x$ having 20 % ^{13}C and 2 % ^1H concentration (a), 98 % ^{13}C and 100 % ^1H concentration (b) and 90 % ^{13}C and 2 % ^1H concentration (c); (d), (e) and (f) correspond to the model calculations using $D_f = 1.0 \times 10^2$, 1.0×10^3 and $1.0 \times 10^4 \text{ s}^{-1}$ respectively.

Figure 8 shows the results of our model-calculations along with the data of Scott and Clarke. Curve (a) is obtained with $D_f = 1.22 \times 10^1 \text{ s}^{-1}$ whilst curves (b) and (c) correspond respectively to $D_f = 2.65 \times 10^1 \text{ s}^{-1}$ and $D_f = 3.45 \times 10^1 \text{ s}^{-1}$. Curves (d), (e) and (f) have been calculated with D_f values of $1.0 \times 10^2 \text{ s}^{-1}$, $1.0 \times 10^3 \text{ s}^{-1}$ and $1.0 \times 10^4 \text{ s}^{-1}$ respectively. It is clear that the frequency dependence is progressively suppressed with decrease in the spin flip diffusion rate. The sample of results (a) contains 20 % ^{13}C and 2 % protons whereas that of results (c) contains 90 % ^{13}C and 2 % protons. It is therefore expected, and also found from our calculations, that the spin flip rate for (a) would be smaller than that for (c). The sample of results (b) contains 98 % ^{13}C and 100 % protons. The presence of protons in large concentration reduces the spin flip rate of ^{13}C as mentioned above and, that is why, D_f is smaller here than for (c). On the basis of the present calculations, we believe that the relaxation rate T_1^{-1} for ^{13}C in polyacetylene will not show $\omega^{-1/2}$ dependence. Some sort of weak frequency dependence will, of course, be observed at larger frequencies. In the absence of any information about the values for diffusion rates in these enriched materials, it is difficult to comment on their quantitiveness.

4. Conclusions.

We have developed a « confined soliton model » which includes the effects of nuclear spin flip diffusion.

In the case of protons, the spin flip diffusion rate is fast and the interpretation of the relaxation data is similar to that of Nechtschein *et al.* [3]. But in the ^{13}C enriched (and ^1H diluted) case the spin flip diffusion process is significantly dominant and suppresses the frequency dependence observed in the fully protonated case. The confinement length of the soliton over the investigated temperature range is around $170 a$. The hopping rate of the soliton is approximately within an order of magnitude to that extracted in reference [3]. The effects due to the finite extension of the soliton are appreciable and must be included.

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Appendix.

SPECTRAL DENSITY FUNCTION FOR A HOPPING, CONFINED AND DELOCALIZED SPIN. — Let $P(j, j', t)$ be the probability of finding a particle at site j' at time t when it was at position j at time $t = 0$ (j' runs from 1 to N). Owing to the hopping motion, the one-dimensional random walk equation of motion can be written as

$$\frac{d}{dt} P(j, j', t) = -\frac{1}{\tau_{\parallel}} \times \{ P(j, j' + 1, t) + P(j, j' - 1, t) - 2 P(j, j', t) \} \quad (\text{A.1})$$

where $\tau_{\parallel}$ is the hopping time between sites j' and $j' + 1$. Performing spatial transform in wave-vector space

$$P(j, j', t) = \frac{1}{N} \sum_q P(q, t) e^{iqa(j'-j)} \quad (\text{A.2})$$

the solution of (A.1) is

$$P(j, j', t) = \frac{2}{\pi} \text{Re} \int_0^{\pi} \cos \{ (j' - j) qa \} e^{-t/\tau_q} dq = g(j, j', t) \quad (\text{A.3})$$

where $1/\tau_q = 2(1 - \cos qa)/\tau_{\parallel}$. If τ' is the correlation time for the interruption in the 1-D motion of the particle, the correlation function (A.3) can be written phenomenologically as

$$g(j, j', t) = \frac{2}{\pi} \text{Re} \int_0^{\pi} \cos \{ (j' - j) qa \} e^{-t/\tau_q} e^{-t/\tau'} dq. \quad (\text{A.4})$$

In the case of the hopping unpaired spin-1/2, the relaxation effects due to τ_{2e} process can also be incorporated by replacing $1/\tau'$ by $1/\tau^* = 1/\tau' + 1/\tau_{2e}$. To obtain the auto-correlation function one puts $j' = j$ and in this case

$$g(t) = e^{-t/\tau'} e^{-t(2/\tau_{\parallel})} I_0(2t/\tau_{\parallel}) \quad (\text{A.5})$$

where $I_0(x)$ is the modified Bessel function. The corresponding spectral density function defined as

$$J(\omega) = \text{Re} \int_0^{\infty} dt g(t) e^{-i\omega t} \quad (\text{A.6})$$

is readily obtained as

$$J(\omega) = (\tau_{\parallel} \tau')^{1/2} \times \left\{ \frac{[(\Omega^2 + 1)(\Omega^2 \varepsilon^2 + (4 + \varepsilon)^2)]^{1/2} + 4 + \varepsilon - \Omega^2 \varepsilon}{2(\Omega^2 + 1)[\Omega^2 \varepsilon^2 + (4 + \varepsilon)^2]} \right\}^{1/2} \\ \varepsilon = \tau_{\parallel} / \tau' \\ \Omega = \omega \tau' \quad (\text{A.7})$$

In general, the frequency correlation function of equation (A.4), using (A.6), is given as

$$J(j, j', \omega) = \frac{\tau_{\parallel}}{\pi} \int_0^{\pi} dq \times \left\{ \frac{\tau_{\parallel}}{\tau^*} + 2 \sin^2(q/2) \right\} \cos \{ (j' - j) qa \} \\ \times \frac{1}{\left\{ \frac{\tau_{\parallel}}{\tau^*} + 2 \sin^2(q/2) \right\}^2 + \omega^2 \tau_{\parallel}^2}. \quad (\text{A.8})$$

The above spectral density function describes in Fourier space the correlation of a spin between sites j and j' at time t . Since the spin in question (soliton) has a finite extension L , one has to consider cross-correlations arising from various sites, at time t and 0, which belong to the common delocalized segment. The total spectral density function in this case, for a rectangular spin density distribution, can be written as [19]

$$J(\omega) = \frac{1}{L} \sum_{r=-2m}^{2m} \{ L - |r| \} J(r, \omega) \quad (\text{A.9})$$

where $r = (j' - j)$ and $m = (L - 1)/2$. Making use of (A.8) and (A.9) one gets equation (26).

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