



NUCLEAR MAGNETIC RELAXATION IN POLYACETYLENE

J.-C. Scott, T. Clarke

► To cite this version:

J.-C. Scott, T. Clarke. NUCLEAR MAGNETIC RELAXATION IN POLYACETYLENE. Journal de Physique Colloques, 1983, 44 (C3), pp.C3-365-C3-368. 10.1051/jphyscol:1983374 . jpa-00223035

HAL Id: jpa-00223035

<https://hal.science/jpa-00223035>

Submitted on 4 Feb 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

NUCLEAR MAGNETIC RELAXATION IN POLYACETYLENE

J.C. Scott and T.C. Clarke

IBM Research Laboratory, K32/281, 5600 Cottle Road, San Jose, CA 95193, U.S.A.

Résumé - Les taux de relaxation nucléaire spin-réseau du proton et du carbone-13 dans le polyacétylène ne peuvent pas être expliqués ni par un modèle de diffusion des spins nucléaires vers un défaut statique paramagnétique, ni par une rapide diffusion unidimensionnelle du défaut lui-même. On présente un modèle dans lequel une petite partie seulement des chaînes moléculaires contient des défauts. Les noyaux sur ces chaînes relaxent rapidement, tandis que les autres atteignent l'équilibre par diffusion des spins nucléaires. Les variations des taux mesurés en fonction de la fréquence et de la concentration isotopique sont en bon accord avec les prédictions de ce modèle.

Abstract - Nuclear spin-lattice relaxation rates for ^1H and ^{13}C in polyacetylene cannot be adequately explained in terms of either nuclear spin diffusion to a static paramagnetic defect or rapid one-dimensional diffusion of the defect itself. We propose a model in which only a small fraction of the molecular chains contain defects. Nuclei on these chains are rapidly relaxed, while the remainder achieve equilibrium by nuclear spin diffusion. The dependences of the measured relaxation rates upon frequency and isotopic concentration are in agreement with the predictions of this model.

I. Introduction

The nature of the paramagnetic defect observed by electron spin resonance in *trans*-polyacetylene continues to be a subject of controversy. Since the original measurement /1/ of the proton spin lattice relaxation rate revealed an inverse square-root dependence on the Larmor frequency, the argument has focussed on whether this characteristic behaviour arises from one-dimensional diffusion of the paramagnetic centre itself /1/, or from nuclear spin diffusion to a static defect /2/. The most telling evidence supporting the view of a mobile defect is the observation of an Overhauser effect /1/: enhancement of the proton NMR signal in the presence of strong pumping irradiation at the electron Larmor frequency. In this picture the paramagnetic centre is viewed as a bond-alternation domain wall, or soliton, as described by the coupled electron-lattice Hamiltonian of Su, Schreiffer and Heeger /3/. However, some doubt has been cast upon this interpretation because of the relatively long relaxation times observed for carbon-13 /4,5,6/.

In this paper we describe preliminary measurements of the carbon-13 spin-lattice relaxation rate. In order to distinguish between the two relaxation mechanisms discussed above, particular emphasis has been placed on measuring the frequency and isotopic concentration dependences, and on comparing the proton relaxation rates in the same samples. Additional sample characterization was made by means of ESR linewidth and intensity studies.

We begin by presenting the predictions of the two different models of nuclear relaxation in $(\text{CH})_x$. For the case of a mobile soliton the relaxation rate /1/ depends on the density of defects (N_e) , the hyperfine coupling interaction (A_H) and the spectral density of fluctuations at the electron Larmor frequency (ω_e) due to one-dimensional diffusion of the defect, with diffusion constant $D_{\parallel e}$:

$$T_{1S}^{-1} = (N_e/N) A_H^2 (D_{\parallel e} \omega_e)^{-1/2} \quad (1)$$

(N is the density of monomer CH units). It is well known from previous work on π -radical defects /7/ in conjugated systems, and has been found by ENDOR studies /8/ in $(\text{CH})_x$, that the hyperfine coupling constants for protons and carbon-13 are similar in magnitude. Therefore it is expected that the relaxation rates of the two types of nuclei should not only have the same frequency dependence, but also, contrary to observation /4,5,6/, should have similar magnitudes.

The case of nuclear spin diffusion to a static paramagnetic centre has been clearly discussed in an article by Blumberg /9/. For the sake of clarity we summarize his description for the situation in which nuclear spin diffusion is the rate limiting process, for it is only then that the $\omega^{-1/2}$ dependence arises. At short times, fluctuations of the orientation of the electron moment causes spin flips of only nearby nuclei. Since the dipole interaction falls off as r^{-3} , the probability that a given nucleus at radius r from the electron has flipped increases with time (t) as t/r^6 . Hence there is a growing region of radius $r_0 \sim t^{1/6}$ which is relaxed by direct contact with the paramagnetic centre. Since the number of nuclei in this region is proportional to r_0^3 , the initial recovery of the magnetization has a $t^{1/2}$ behaviour. Magnetization flows into this "well-relaxed" sphere from the remainder of the sample by mutual nuclear flip-flops due to the nuclear dipole-dipole interaction. r_0 continues to grow until magnetization diffusion balances the rate at which the defect induces nuclear spin flips. The magnetization then recovers exponentially at a rate given by /9/

$$T_{1nd}^{-1} = 4\pi N_e C^{1/4} D_n^{3/4} \quad (2)$$

where C/r^6 is the transition probability at radius r :

$$C = \left(\frac{3}{10}\right) \frac{g^2 \mu_B^2 \gamma_n^2}{\omega_n^2 \tau} \quad (3)$$

Here $g\mu_B$ is the electronic moment, γ_n is the nuclear gyromagnetic ratio, ω_n is the nuclear Larmor frequency, and τ is the correlation time for fluctuations of the electronic moment, in this case equal to the transverse relaxation time $T_{2e}/10$. D_n is the nuclear spin diffusion constant which, in the case of an sample containing a single spin species, is given approximately by

$$D_n \cong (1/30) \hbar \gamma_n^2 / r_{nn} \quad (4)$$

where r_{nn} is the mean internuclear distance. Nuclear spin diffusion is complicated by the detuning effect of a second nuclear species and by anisotropy in the crystal structure; however in general, one finds

$$T_{1nd}^{-1} \sim N_e N_n^{1/4} \gamma_n^2 \omega_n^{-1/2} T_{2e}^{-1/4}. \quad (5)$$

It is crucial to identify carefully the conditions under which diffusion limited behaviour pertains. When two different types of nuclei are present in the sample, the dipolar field exerted by the larger moment upon the smaller reduces the nuclear flip-flop rate of the latter (by "detuning"), and consequently leads to a lower diffusion constant. Thus the observation of diffusion limited behaviour for the nucleus with the larger moment implies, in general, that the smaller nucleus should also be in the diffusion limited regime.

II. Experimental Results

The nuclear spin-lattice relaxation rates of ^1H and/or ^{13}C were measured in three sample of polyacetylene containing 100% ^1H and 98% ^{13}C , 2% ^1H and 90% ^{13}C , 2% ^1H and 20% ^{13}C , respectively. The spectrometer was a Bruker CXP-100 with a 22 kOe electromagnet allowing frequencies up to 90 MHz for protons and 23 MHz for carbon-13. Both inversion-recovery and saturation-recovery pulse sequences were used. The results obtained at room temperature are summarized in table 1.

Table 1. Nuclear spin-lattice relaxation rates in three samples of polyacetylene. For protons the magnetization recovery is accurately exponential. For carbon-13 there is systematic deviation from exponential behaviour; the rates quoted are obtained by fitting to an exponential law over the same time interval for each frequency.

Sample	¹ H conc. %	¹³ C conc. %	Frequency MHz.	¹ H relaxn. rate (sec ⁻¹)	¹³ C relaxn. rate (sec ⁻¹)
1-100-98	100	98	90	18±1	-
"	"	"	23	37±2	1.9±0.1
"	"	"	11.5	45±3	1.9±0.1
2-2-90	2	90	23	-	2.3±0.2
"	"	"	12	-	2.6±0.1
3-2-20	2	20	23	-	0.9±0.2
"	"	"	12	-	0.9±0.2

The salient features are the following:

- 1. In the sample rich in both magnetic nuclei the proton rate is more than an order of magnitude faster than the carbon-13 rate, and varies as $\omega_n^{-1/2}$ while the latter is frequency independent. This is immediately seen to be inconsistent with the soliton relaxation mechanism which predicts similar rates and frequency dependences of the two species. It is also inconsistent with the picture of nuclear spin diffusion to a static defect, since if the proton relaxation is diffusion limited then that of carbon-13 should also be diffusion limited and exhibit the same frequency dependence.
- 2. The sample in which the relaxation of ¹³C shows a variation with frequency (namely 90% ¹³C, 2% ¹H) is that in which nuclear spin diffusion limited behaviour is least likely since the concentration of carbon nuclei is high, and substitution of deuterium for protons drastically reduces the detuning effect of the heteronuclear dipole field.
- 3. The carbon relaxation rate, normalized to the number of paramagnetic defect present, decreases as the ¹³C concentration is reduced. This is contrary to the prediction of the soliton model in which the rate should be independent of nuclear spin concentration.
- 4. The non-exponential nature of the decay of ¹³C suggests an inequivalence among carbon nuclei in different regions of the sample. It is reminiscent of the initial $t^{1/2}$ recovery of magnetization in the nuclear spin diffusion model, but inconsistent with the idea that rapidly diffusing solitons visit every nuclear site.

Thus, in summary, it is clear that, even qualitatively, *the experimental data cannot be explained by either model.* A new description is required.

III. A New Model

The model of polyacetylene which we propose to explain the relaxation data recognizes the fact that solitons need not exist on every chain, and therefore do not visit every nucleus. Indeed, there is compelling experimental evidence that relatively few chains contain mobile defects: namely the observation by both NMR nutation studies /11/ and X-ray diffraction /12/ of two distinct C-C bond lengths, with no indication of averaging by the rapid diffusion of a bond-alternation domain wall along the chain.

We take the point of view that the Overhauser effect implies rapid motion of the paramagnetic centre, since a cross-over to a solid state effect at low temperature /13/ is consistent with trapping and cannot be explained on the basis of exchange among static spins. The nuclei which are on chain segments containing a soliton are relaxed by direct (contact) hyperfine interaction with the defect, and exhibit the $\omega^{-1/2}$ dependence characteristic of one-dimensional diffusive motion. The remainder achieve equilibrium by nuclear spin-diffusion to this well relaxed core. This situation is rather different from the case in which a static defect interacts via the long range dipole field with the nuclei around it: there is no longer any frequency dependence of the relaxation by nuclear spin

diffusion, since the directly relaxed region is the chain containing a soliton and not the spherical region centred on a dipole.

The observed ^1H relaxation rate of $20\text{--}50\text{ sec}^{-1}$ is slower, by the fraction, f , of soliton containing chains, than the rate which would apply if all chains contained solitons. ENDOR linewidths /8/ and resonance Raman profiles /14/ suggest a value $f \sim 1/30$. Thus we may estimate the on-chain relaxation rate to be of order 10^3 sec^{-1} . This is slow relative to the estimated ^1H flip-flop rate of 10^5 sec^{-1} . Hence the protons are in a fast diffusion regime, and relax with a common rate characterized by the frequency dependence of the soliton model, as observed. The on chain relaxation rate, T_{1S}^{-1} , is given by eq. 1, but multiplied by a factor $1/f$ to reflect the increased spin density caused by localizing the defect to a fraction of the nuclei in the sample. This cancels the factor of f mentioned above and hence, in the fast diffusion regime, eq. 1 still applies /15/. One may then evaluate the soliton diffusion coefficient $D_{\parallel e} \sim 3 \times 10^{13}\text{ sec}^{-1}$. Unfortunately this is in considerable disagreement with the value of 10^{11} sec^{-1} obtained by analysis of ESR data /8/.

The situation for carbon is different: ^{13}C at 100% abundance and in a deuterated sample has a flip-flop rate of order 10^3 sec^{-1} and therefore approaches diffusion limited behaviour. At lower isotopic concentration, and with the interference of the proton dipole field, the ^{13}C spin diffusion rate is even further reduced. The rate at which magnetization flows to the few chains containing solitons is frequency independent, in accord with experimental observation. The characteristic rate is given by $T_{1*}^{-1} \sim N_e^{2/3} D_n \sim 1\text{ sec}^{-1}$, since $N_e^{-1/3}$ is the mean distance between defects.

In summary: it has been shown that a model of more or less rapid nuclear spin diffusion to a few molecular chains which contain rapidly diffusing paramagnetic defects (solitons) accounts well for all features of the room temperature relaxation of ^1H and ^{13}C in $(\text{CH})_x$. Several quantitative aspects of the model remain to be addressed by further experiments and by theoretical consideration of the nature of spin diffusion in a geometry of interpenetrating line sources.

References.

- [1] NECHTSCHIEIN M., DEVREUX F., GREENE R. L., CLARKE T. C., and STREET G. B., Phys. Rev. Lett. **44** (1980) 356.
- [2] SHIREN N. S., TOMKIEWICZ Y., THOMANN H., DALTON L. R., and CLARKE T. C., in these conference proceedings.
- [3] SU W. P., SCHREIFFER J. R., and HEEGER A. J., Phys. Rev. B **22** (1980) 2099.
- [4] MAZIN F., GUSMAN G., and DELTOUR R., Solid State Commun. **39** (1981) 505.
- [5] CLARKE T. C., SCOTT J. C., and YANNONI C. S., Bull. Amer. Phys. Soc. **27** (1982) 241.
- [6] GARDNER J. A., (private communication).
- [7] CARRINGTON A., and MCLACHLAN A. D., *Introduction to Magnetic Resonance*. (Chapman and Hall, London, 1967).
- [8] THOMANN H., DALTON L. R., TOMKIEWICZ Y., SHIREN N. S., and CLARKE T. C. (private communication). See also TOMKIEWICZ Y., SHIREN N. S., CLARKE T. C., THOMANN H., KIM H., and DALTON L. R., in these conference proceedings.
- [9] BLUMBERG W. E., Phys. Rev. **119** (1960) 79.
- [10] We are grateful to Prof. W. G. Clark for discussions on this point.
- [11] CLARKE T. C., KENDRICK R., and YANNONI C. S., in these conference proceedings.
- [12] FINCHER C. R., CHEN C.-E., HEEGER A. J., MACDIARMID A. G., and HASTINGS J. B., Phys. Rev. Lett. **48** (1982) 100.
- [13] NECHTSCHIEIN M., DEVREUX F., GENOUD F., GUGLIELMI M., HOLCZER K., TRAVERS J. P., and BIDAN G., in these conference proceedings.
- [14] LICHTMANN L. S., SARHANGI A., and FITCHEN D. B., Chem. Scripta **17** (1981) 149.
- [15] We are grateful for discussions with Dr. M. Nechtschein which clarified this point.