

Soliton Pinning in Polyacetylene Revealed by Multiple-Quantum Spin Coherences

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(Received 20 January 1987)

Multiple-quantum NMR coherences created from the coherent excitation of the soliton nuclear hyperfine interactions are generated and detected by electron-spin echoes in polyacetylene, $(\text{CH})_x$. The multiple-quantum spectra observed for both *trans*- and *cis*- $(\text{CH})_x$ are identical from 4 to 300 K, establishing that both the soliton spin-density distribution and on-chain mobility are identical in these isomers throughout this temperature range.

PACS numbers: 72.80.Le, 76.60.Lz

The central issues in the description of soliton spin and charge transport in $(\text{CH})_x$ are the 1D coherence length of the motion, and the magnitude and temperature dependence of the diffusion rate. The narrow EPR line observed for samples of *trans*- $(\text{CH})_x$ has usually been attributed to a high on-chain soliton mobility, while the much broader line found for *cis*- $(\text{CH})_x$ is taken as evidence for soliton trapping. These results agree with the Su-Schrieffer-Heeger theory developed for solitons in polyenes with degenerate ground-state electronic structures.¹ Solitons in conjugated polyenes are domain walls that separate two regions of opposite phase in the π -electron bond-order wave. The low effective mass ($\approx 6m_e$) of the domain wall is manifested by its rapid diffusion along the polyene chain.

Evidence for mobile neutral solitons has been obtained primarily from magnetic-resonance experiments. While some results can be interpreted by a model of highly mobile neutral solitons, this interpretation also leads to logical inconsistencies with other resonance experiments. From proton NMR T_{1n} measurements, it was concluded² that all solitons are mobile with $D_{\parallel} > \omega_e$ down to 4.2 K. The Overhauser enhancement (OE) observed in room-temperature dynamic nuclear polarization (DNP) experiments on *trans*- $(\text{CH})_x$ was interpreted as direct evidence for mobile solitons.³ But DNP experiments also required that some solitons be trapped at 200 K and that all be trapped below 20 K.⁴ Conflicting conclusions have also been reported for the temperature dependence of the diffusion rates determined by NMR experiments.⁵

In principle, EPR should be a more direct method for observing soliton motion. However, diffusion rates based on EPR linewidth,⁶ ENDOR,⁷ and electron-spin echo⁸ (ESE) experiments are 3–4 orders of magnitude lower than those obtained from NMR T_{1n} data.² It was suggested that this discrepancy could be reconciled by our taking into account the presence of trapped solitons that were proposed to dominate the EPR, ENDOR, and ESE

results.² In contradiction to this, the frequency⁹ and orientation¹⁰ dependence of the EPR linewidth were recently proposed to be *consistent* with the original NMR results. In addition, the trapping model is unable to resolve the contradiction derived from proton NMR T_{1n} (Ref. 2) and DNP (Ref. 4) data.

These results demonstrate the need for an unambiguous experiment to clarify the question of soliton mobility in $(\text{CH})_x$. To date, evidence for soliton motion has only been inferred from spin-relaxation measurements. Such experiments indirectly probe mobility by measuring the ability of local fluctuating magnetic fields associated with this motion to cause spin relaxation. Unfortunately, fluctuating local fields can also result from mechanisms other than soliton mobility. In this Letter we describe a new experiment, ESE-detected multiple-quantum NMR (ESE-MQNMR), in which the persistence of coherent interactions between the soliton and the nuclei on the polyene chain are detected. The detection of coherent interactions provides a method by which fluctuations caused by soliton mobility can be distinguished from other dynamic processes. Soliton diffusion will destroy MQ coherences; conversely, the persistence of MQ coherences suggests that spin relaxation must arise from other dynamic spin interaction mechanisms.

In NMR experiments, MQ transitions are generated and detected by the direct irradiation of nuclear magnetic dipole transitions with use of appropriate pulse sequences.¹¹ The most basic pulse sequence is $\pi/2$ - τ - $\pi/2$ - t_1 - $\pi/2$ - t_2 , which is divided into preparation (τ), evolution (t_1), and detection (t_2) periods. In the present experiments, the same resonant pulses are applied to the *paramagnetic electrons* rather than to the nuclear dipole transitions. Thus, in these experiments, MQNMR transitions are induced only in nuclei coupled to the solitons.

The MQ spectrum is determined by the multiple spin operators effective after the second pulse, which marks the end of the preparation period. These operators are

bilinear in the spin angular momentum. For an electron interacting with several nuclei the dominant operator is¹²

$$H_{en} = \sum_{i,j} S_{zi} (A_{ij} I_{zj} + B_{ij} I_{xj}). \quad (1)$$

The pseudodipolar operator ($S_z I_{\pm}$) governs the nuclear free-spin evolution when the magnitude of the hyperfine interaction is comparable to the primary Zeeman interaction. The pseudodipolar interaction assures that the pure nuclear-spin states defined by I_z are no longer good quantum numbers in the perturbed Zeeman field. This relaxes the single-quantum selection rule and obviates the need for a spectrometer frequency offset or TPPI technique to observe the higher-order NMR coherences.¹³ The present experiments differ from MQNMR experiments by the following. The applied pulses produce transverse coherence in the electron- rather than

nuclear-spin system. The pseudodipolar coupling replaces the homonuclear dipolar coupling as the dominant operator for generating MQ coherences. The time scale for the creation of these coherences is dictated by the magnitude of the hyperfine coupling rather than the nuclear dipolar coupling.

The ESE-MQNMR excitation spectra are the Fourier transform of the two-dimensional signal $S(t_1; \tau)$ for $\tau = t_2$. The ^{13}C MQNMR excitation spectra for 99% ^{13}C -enriched *trans*-(CH)_x and *cis*-(CH)_x with $\approx 20\%$ *trans* content are shown in Fig. 1. (CH)_x samples were prepared according to the standard procedure of Ito, Shirakawa, and Ikeda.¹⁴ Details of the pulsed EPR apparatus can be found elsewhere.¹⁵ Coherences of order 13 are observed at low temperatures, while an eleven-quantum coherence is observed at room temperature.

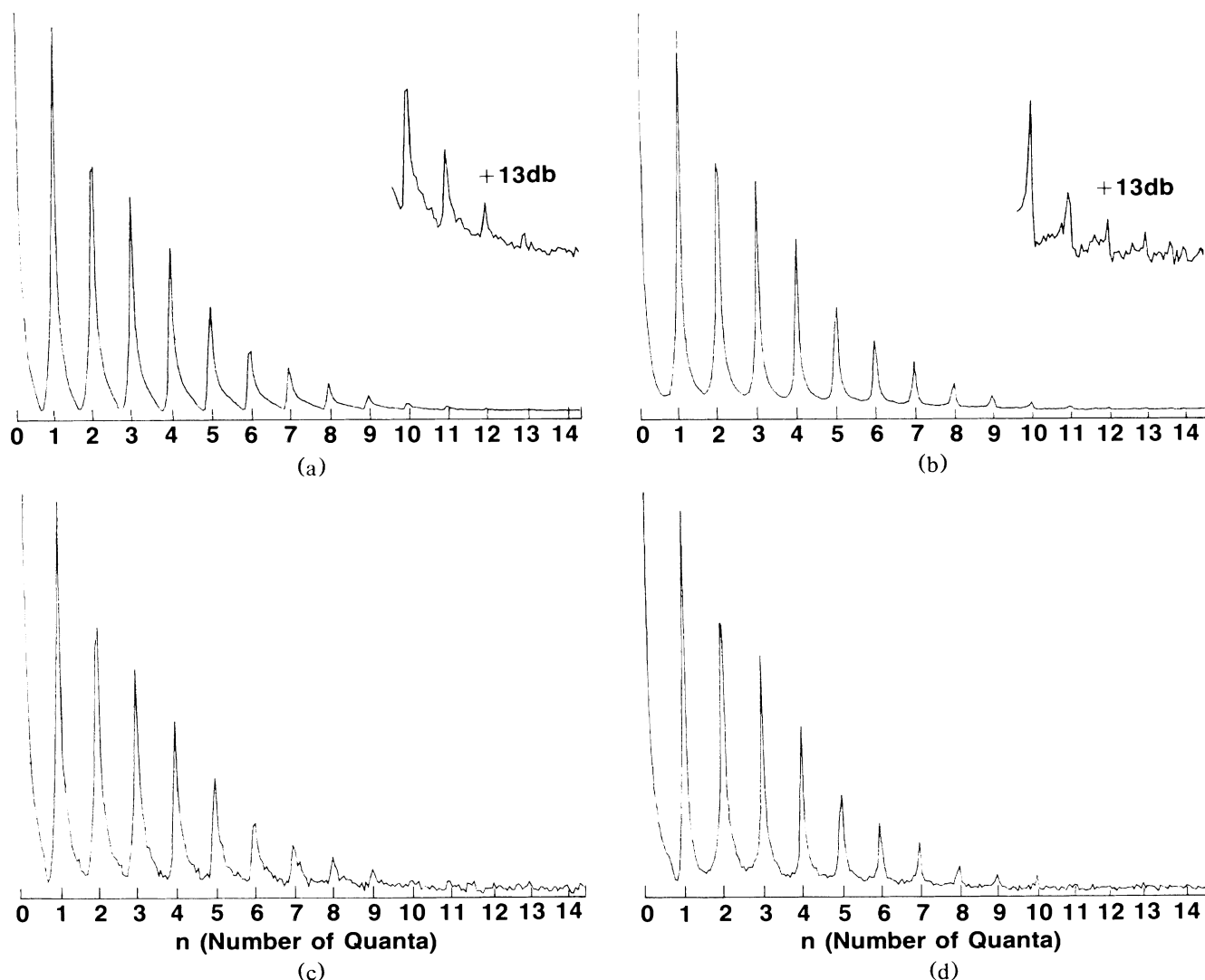


FIG. 1. ^{13}C multiple-quantum (MQ) NMR excitation spectra for 99% ^{13}C -enriched *trans*-(CH)_x at (a) 4 K and (c) 298 K, and for *cis*-(CH)_x composites at (b) 4 K and (d) 298 K.

Significantly, the multiple-quantum excitation profiles for *cis*- and *trans*-(CH)_x are almost identical at all temperatures. Multiple-quantum coherences can also be observed in the Fourier transform of the two-pulse ESE envelope. However, the three-pulse experiment is preferred because (1) the observation time is almost 3 orders of magnitude longer, (2) the spectra are not complicated by sum and difference frequencies,¹² and (3) hyperfine frequencies can be selectively enhanced or suppressed by the suitable selection of τ .¹²

The excitation profile and highest-order coherence observed will depend on the number of interacting nuclei,¹¹ the symmetry of the hyperfine interaction tensors,¹⁶ and the incoherent dephasing mechanisms operative during the creation and detection periods.¹⁷ In principle, the multiple-quantum spectrum can be used to count the number of nuclei coupled to the paramagnetic electron.¹⁸ In practice, this is only possible if the number of quanta observed is determined purely by the statistical probability distribution for transitions among spin levels¹⁸ and the density of states in the hyperfine spectrum and not by other intrinsic factors such as electron dephasing mechanisms or extrinsic factors such as a limited excitation-pulse-power bandwidth.¹⁷ At 4 K, the excitation spectra for the *cis* and *trans* isomer samples are identical but the numbers of quanta have not saturated under the present experimental conditions. Statistical arguments for counting the number of coupled nuclei may not be reliable under these conditions, but the fact that the spectra are identical establishes that the spin distribution is the same in both isomers.

Three explanations are possible for the persistence of MQ coherences at room temperature: All solitons are pinned and soliton diffusion rates are comparable to nuclear relaxation rates; all solitons are trapped in a potential well and are rapidly diffusing over a limited polyene chain segment; or the experiment is not observing the mobile solitons. Let us consider the last possibility. According to Mehring *et al.*,¹⁹ more than one type of spin is observed in time-resolved field-swept ESE experiments for samples prepared with the Luttinger catalyst. However, only one spin type is detected in these same experiments for *trans*-(CH)_x samples prepared by the Shirakawa procedure.²⁰ It has been shown that all spins, whether mobile or trapped, contribute to the observed ESR²¹ and ESE signals, and that all spins are coupled by electron dipolar interactions.²² For a system of coupled spins, the fastest relaxing spin dominates the relaxation spectrum. Because of these results it is not possible that mobile solitons are present but are not observed in the present experiments.

Three possibilities can be envisioned for deriving temperature-dependent spin dynamics from trapped solitons. In all cases, solitons are presumed to be trapped in a potential well whose length L is greater than the soliton width N_s . Temperature-dependent magnetic interactions can then arise from the overall diffusion of the confine-

ment region along the polyene chain, a temperature-dependent confinement length $L(T)$, or the temperature dependence of the soliton diffusion rate $D_{||}(T)$ within the confinement region. For diffusion of the confinement region to occur over distances greater than L , the bilinear nuclear dipolar coupling operator must propagate dipolar order along the (CH)_x chain to preserve the MQ coherences. The propagation of dipolar spin order is determined by the nuclear dipolar coupling, D_{ij} .¹¹ For MQ preparation times used in the present experiments, $\tau D_{ij} \ll 1$, and this mechanism is negligible indicating that the confinement region is quasistatic.

The second possibility within the trapping model is that the soliton rapidly diffuses over a limited polyene chain segment with $D_{||}(T)$. From previous data^{1,3,5,7,8} it was concluded that all solitons remain trapped in *cis*-(CH)_x indicating that $D_{||} < \omega_e$ for $T < 300$ K while in *trans*-(CH)_x, $D_{||} > \omega_e$ for $T > 200$ K. The present results demonstrate that the on-chain soliton mobilities for *both trans*- and *cis*-(CH)_x are, in fact, identical at 300 K as well as at 4 K. This rules out the possibility that the temperature dependence of the mobility for the soliton diffusing over a finite chain segment can account for the observed spin dynamics.

The third possibility within the trapping model is that $L(T)$ and L increase with T but $D_{||} > \omega_e$ and is nearly temperature independent. Exchange and dipolar interactions would therefore increase with temperature as the average distance between solitons decreases. This would imply that the number of hyperfine coupled nuclei, and therefore the maximum order of coherences observed, would increase with temperature. This is not consistent with the experimental results.

An alternative explanation for the present results is that all solitons are pinned even at room temperature, with $L \approx N_s$. Soliton-spin dynamics must then arise from solid-state spin-interaction mechanisms of pinned solitons. Electron Heisenberg spin-exchange interactions were recently shown to be important in (CH)_x.^{23,24} However, spin-exchange frequencies alone are too small to account fully for the observed relaxation rates.⁴ An additional mechanism for spin relaxation can be obtained from temperature-dependent spin-density fluctuations arising from phonon-driven internal modes of the soliton. Phonon-driven transitions between vibronic states of the soliton have recently been shown to account for the temperature dependence of the ESR linewidth without invocation of an impurity effect.²⁵ These vibronic excitations cause a time-dependent modulation of the soliton-spin-density distribution which modulates the many soliton-hyperfine, electron dipolar, and spin-exchange interactions. The frequency of these spin-density fluctuations will increase with temperature but the average spin density at a given nuclear position will be nearly temperature independent. In samples of *cis*-(CH)_x and *trans*-(CH)_x containing a lower density of solitons, where the magnitude of the exchange and electron dipo-

lar interactions are weak, the hyperfine frequencies are, in fact, observed to be nearly temperature independent.

Any model for soliton-spin dynamics must allow for a partial dynamic averaging of the on-chain electron nuclear dipolar hyperfine interactions since finite interactions are required to create the ESE/MQ-NMR coherences. Anisotropic averaging would be expected from the one-dimensional nature of the spin-density fluctuations arising from acoustic phonon excitations of pinned solitons. Both electron dipolar and electron-nuclear relaxation rates have, in fact, been observed to be anisotropic.^{9,10,16,17,22}

In summary, we have shown that the spin-density distributions and soliton mobilities are identical in *trans*- and *cis*-(CH)_x from 4 to 300 K. Since solitons are immobile in *cis*-(CH)_x, we are forced to conclude that they are pinned in *trans*-(CH)_x. The high-temperature spin dynamics previously attributed to soliton mobility must then arise from other mechanisms. Phonon-driven transitions between vibronic excitations of the soliton provide one possible spin dynamics mechanism. One possible pinning mechanism is the soliton confinement due to interchain coupling.²⁶

We would like to thank M. Mehring and W. G. Clark for stimulating discussions.

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