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MAGNETIC PROPERTIES II : ENDOR OF UNDOPED CIS-(CH)_x

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Résumé - Nous avons étudié la spectroscopie de double résonance électronique et nucléaire (ENDOR) du *cis*-polyacétylène enrichi à 99% en ¹³C à des températures entre 77 K et 300 K. Les spectres sont caractérisés par deux, et deux seulement, tenseurs hyperfins du ¹H et du ¹³C. Les amplitudes relatives et la symétrie des éléments du tenseur établissent que l'électron paramagnétique correspond à une orbitale délocalisée. Les résultats expérimentaux indiquent que l'électron délocalisé se déplace dans un puits de potentiel de ~ 100 Å de largeur.

Abstract - Pristine 99% ¹³C-enriched *cis*-polyacetylene has been investigated by electron-nuclear double-resonance (ENDOR) spectroscopy at temperatures between 77 and 300 K. Spectra are characterized by two and only two ¹H and ¹³C hyperfine tensors. The relative magnitudes and symmetry of the tensor elements establish that the paramagnetic electron resides in a delocalized orbital. Experimental results indicate that the delocalized electron is constrained to a potential well of approximately 100 Å in width.

A central feature of the soliton model of SSH¹ is a variation in bond alternation which is reflected in decreasing electron spin densities from the center of the defect on alternating sites and vanishing electron spin densities on the other sites. Several attempts have been made to analyze EPR spectra in terms of such a soliton wavefunction². However the frequency of an EPR transition is not simply related to the hyperfine interactions in terms of spin densities. Indeed, the resonance frequency of an EPR transition depends upon all electron Zeeman and hyperfine tensors that characterize the paramagnetic species, upon the relative orientation between these tensors, and upon the nuclear-spin quantum number associated with the particular transition. For an electron residing in a spatially anisotropic orbital such as a π -electron orbital of a polyene, analysis of conventional EPR spectra is clearly hopeless. ENDOR transition frequencies, on the other hand, are directly related to hyperfine interaction frequencies and hence to spin densities (Each ENDOR transition frequency depends only upon the hyperfine interaction giving rise to that transition and is independent of all other interactions. Indeed, for polyacetylene samples (*cis*-, *trans*-, and composite samples) ENDOR permits more than just measurement of general magnitudes of hyperfine interactions. Rather, transitions associated with different sites on the polyene backbone and with different orientations of the polyene backbone are clearly resolved, permitting determination of complete ¹³C and ¹H hyperfine tensors. The symmetry of such tensors defines the type of orbital, and the magnitudes of the tensor elements for various sites define the spatial extent of the wavefunction.

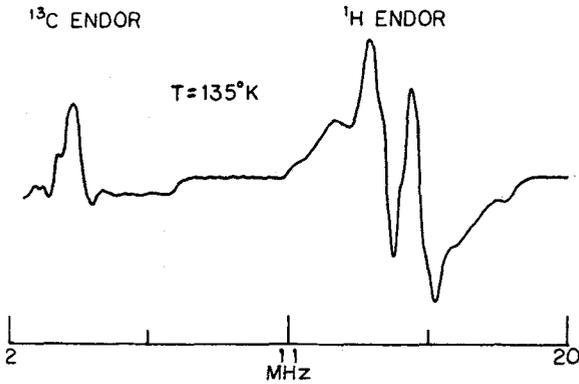


Fig. 1. The ENDOR spectrum of 99% ¹³C-enriched *cis*-rich (CH)_x recorded at 135 K is shown.

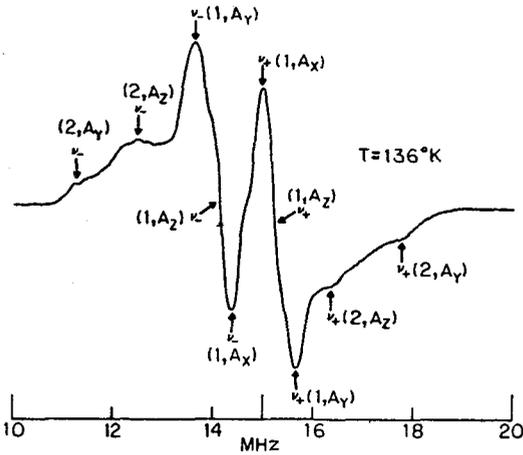


Fig. 2. The assignments of proton tensor elements to the turning points of the proton ENDOR spectrum recorded at 136 K are shown. Two distinct hyperfine tensors (sites) are identified and are denoted 1 and 2. The sense of ν_- is the ENDOR transition that occurs at higher frequency than the ν_+ transition.

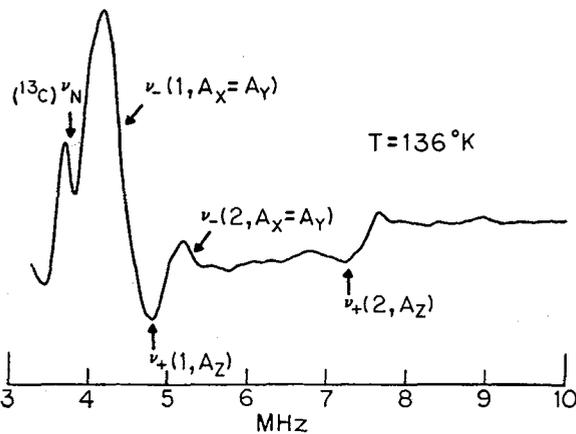


Fig. 3. The assignments of ¹³C tensor elements to the turning points of the ¹³C ENDOR spectrum recorded at 136 K are shown. Transitions at frequencies less than the ¹³C Larmor frequencies are not shown in this spectrum although these transition frequencies have been measured and employed to compute the ¹³C hyperfine tensors given in Table I. Note the weak distinct ENDOR signal.

In Figures 1-3 we show typical ENDOR spectra for a *cis*-rich sample of 99% ¹³C-enriched polyacetylene. The spectra shown were taken employing frequency modulation of the radiofrequency field (hence the derivative-like shape) and are independent of radiofrequency

TABLE I. PROTON AND ^{13}C TENSORS FOR CIS-RICH POLYACETYLENE MEASURED AT 136 K

	^1H Tensor	^{13}C Tensor
Site 1	$A_x = -0.5$ MHz $A_y = -2.1$ MHz $A_z = -1.1$ MHz	$A_x = -1.3$ MHz $A_y = -1.3$ MHz $A_z = +2.1$ MHz
Site 2	$A_x = -1.8$ MHz $A_y = -7.0$ MHz $A_z = -3.9$ MHz	$A_x = -3.1$ MHz $A_y = -3.1$ MHz $A_z = +7.0$ MHz

field intensity, microwave field intensity and modulation frequency. The spectra shown here as well as spectra for other polyacetylene samples have been quantitatively analyzed by density-matrix theory employing numerical methods. Such analysis yields insight into nuclear-spin-lattice and spin-spin relaxation times for various nuclei (^{13}C and ^1H along the polyene backbone) and into electron dynamics; however, as is shown in Figures 1-3, the principal elements of the ^{13}C and ^1H hyperfine tensors can be read directly from the spectra. The assignments shown in Figures 1-3 are consistent with ENDOR studies on partially aligned samples. Hyperfine tensors obtained from ENDOR spectra are summarized in Table I.

Note the axial symmetry of the nearly traceless ^{13}C hyperfine tensors. Such symmetry is consistent with the defect existing in a π -orbital. The absence of a significant isotropic ^{13}C hyperfine interaction rules out σ character. The symmetry and relative magnitudes of the principal elements of the ^1H hyperfine tensors are those expected for alpha protons. The hyperfine tensors thus unequivocally establish the defect as existing in a nearly pure π -orbital.

Spin densities can be calculated from the ^{13}C and ^1H tensors. Such calculations show that the ^{13}C and ^1H tensors can be pairwise associated and that the spectra are consistent with carbons containing two types of spin density characterized by $\rho_C = |0.06|$ and $\rho_C = |0.02|$. ENDOR-INDUCED-EPR experiments show that these spin densities are associated with the same paramagnetic electron or defect.

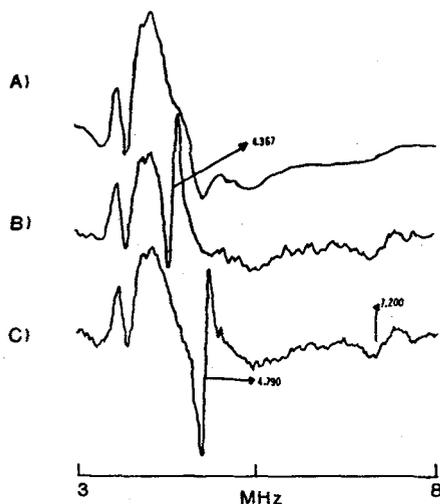


Fig. 4. The ENDOR (A) and Double-ENDOR (B,C) spectra of 99% ^{13}C -enriched, *cis*-rich polyacetylene recorded at 140 K. The arrows corresponding to the large intensities in B and C indicate the constant radiofrequency field used to saturate an NMR transition while sweeping the ENDOR spectrum. The NMR transition observed for the inequivalent ^{13}C nucleus is indicated at 7,200 MHz.

The results of selected general TRIPLE resonance experiments are shown in Figure 4. The observed ENDOR enhancements between sites 1 and 2 establish that the signs of the spin densities differ for these sites. A reduction would be observed for like signs. It should be noted that exhaustive general and special TRIPLE experiments have been conducted and analyzed. They quantitatively support the conclusions to this point, namely, $\rho_C = +0.06$ and $\rho_C = -0.02$. The signs and magnitudes of the spin densities at the carbons require an extensively delocalized π -orbital, namely, an orbital spread over about 100 Å. Our results are in clear disagreement with a static soliton model² which would predict weak hyperfine couplings (arising from small spin density associated with the tails of the soliton wave function) and therefore a resultant buildup of ENDOR spectral density near the uncoupled nuclear Larmor frequencies. Weak hyperfine interactions have been observed in virtually all investigated π -radical systems (radiation-damaged organic diacids, polymers, polyparaphenylene, graphite),³ where they are manifest by the expected spectral density near the nuclear Zeeman frequencies.

For a soliton model to explain the present experimental results for polyacetylene, it must have two features. First, the soliton must be free to move, either diffusively or coherently, in a deep potential well of width (~ 100 Å) to be consistent with the spin delocalization measured by ENDOR. Such a well might arise, for example, from end effects due to the *cis*-isomer regions that bound the *trans*-isomer segments where the spins are presumably localized in this predominantly *cis*-polyacetylene. Displacement of the soliton wave function within the well, i.e., translational motion, could average the hyperfine interactions to yield two tensor values. Second, some Coulomb correlations would have to be included, because in the simple SSH soliton model, the averaging process would result in two kinds of sites, one having a finite spin density, and the other having zero spin density. To be consistent with the present data, the Coulomb correlations would be required to provide finite spin density of the opposite sign at the "zero-spin" sites. It should be noted that the translational diffusion rate of the soliton within the potential well is constrained to lie within strict limits to be compatible with the known magnetic resonance data for *cis*-polyacetylene. The diffusion rate must be fast enough to effectively average the hyperfine interactions associated with a stationary soliton within one nuclear lifetime but slow on the hyperfine-interaction time scale.

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