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DISTRIBUTION OF SPIN DENSITY IN UNDOPED $(CH)_x$

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Résumé - Nous avons simulé les spectres de RPE de solitons immobiles dans le polyacétylène en utilisant les densités de spins théoriques et l'interaction hyperfine anisotrope des électrons π . Les résultats sont consistants avec les spectres observés sur les échantillons riches en cis quand les densités de spins sont dérivées pour des énergies de Coulomb finies sur les sites.

Abstract - ESR spectra of immobile solitons in undoped polyacetylene were computer simulated using theoretical spin densities and the anisotropic hyperfine interaction of π -electron. Simulated results were consistent with observed spectra of *cis*-rich sample when the spin densities derived for finite on-site Coulomb energy were used.

As for the microscopic origin of the ESR center in undoped $(CH)_x$, the soliton model /1-3/ has been the only one proposed so far. Its validity is still the subject of debate. Due to the model the ESR center should be a π -electron which has a delocalized spin density around the kink (Fig. 1). The form of the spin density distribution is one of the important quantities predicted by the model. The π -electron character of the ESR center has been recently confirmed by the study of the anisotropy of ESR and ENDOR spectra in stretch oriented samples /4-6/. This justifies the use of the theory of π -electron in the analysis of magnetic resonance spectra.

For the given form of the spin density, it is possible to simulate the ESR spectrum of immobile solitons. The immobile ESR center in *cis*-rich sample is known to arise from the *trans* portion of the sample /2/. Thus the comparison of the spectrum of *cis*-rich sample with simulated one tests the theory, provided that the ESR center in *cis*-rich sample has the same origin as that of *trans* sample but is immobile in small length of *trans* polymer locked in by regions of *cis* polymer.

Such a simulation was originally studied by Weinberger et al. /2/, however, their calculation ignored the anisotropic part of hyperfine coupling and is not quantitatively correct. Our present purpose is to make the calculation using correct anisotropic hyperfine tensor of π -electron /7/. Also the modified spin density derived for the finite on-site Coulomb energy /8/ is studied by spectrum simulation.

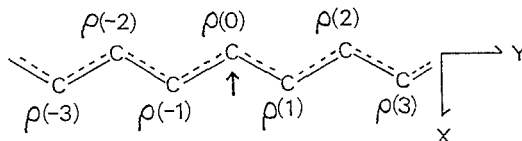


Fig. 1 - Spin density distribution in the bond alternation kink in *trans* polymer. $\rho(n)$ is the spin density at the n -th monomer unit away from the center of the kink. Coordinate axes used are also shown. z-axis is normal to the paper and y-axis is parallel to the polymer axis.

1 - ESR SPECTRUM SIMULATION OF IMMOBILE SOLITONS

The spin density at the n -th monomer unit from the center of the soliton, $\rho(n)$, is given as follows /3/,

$$\rho(n) = (1/N)\text{sech}^2(n/N)\cos^2[(\pi/2a)na]. \quad (1)$$

N is the soliton half width in lattice constant a . The ESR spectrum of randomly oriented immobile solitons is calculated in the following manner. For the soliton at the particular orientation to the external magnetic field, which is denoted by the polar angles of θ and ϕ , the hyperfine splitting from the proton of n -th monomer becomes $\rho(n)A(\theta, \phi)$. Here

$$A^2(\theta, \phi) = A_{xx}^2 \sin^2\theta \cos^2\phi + A_{yy}^2 \sin^2\theta \sin^2\phi + A_{zz}^2 \cos^2\theta. \quad (2)$$

A_{xx} etc. are hyperfine tensor components that are diagonal in the axes given in figure 1 /7/. They are approximately given as: $A_{xx} = -(1-\alpha)A$, $A_{yy} = -(1+\alpha)A$, $A_{zz} = -A$. A represents the magnitude of isotropic coupling and takes a value between 20 and 30 gauss. α is introduced here to represent the relative magnitude of the anisotropic coupling. Its value is usually 0.5 to 0.6 in actual π -electron radicals. Then the summation over n and angles (θ, ϕ) gives the spectrum of randomly oriented solitons.

Figure 2 shows the effect of anisotropic term on the simulated lineshape for soliton half width of five lattice constants ($N = 5$). 30.0 gauss and 0.5 are assumed for A and α respectively. The natural width is taken to be 0.8 gauss to illustrate the effect of anisotropic term. Figure 2(a) shows the results for the isotropic coupling only. This is quite consistent with figure 5 of reference 2. Introduction of the anisotropic term tends to wash out the structure as in figure 2(b).

Figure 3 shows the dependence of the simulated linewidth on the soliton half width N for $A = 30.0$ gauss and $\alpha = 0.5$. The natural width is assumed to be 2.0 gauss which will be explained later. Upper closed circles are results for $(\text{CH})_x$ whereas lower closed circles are those for $(\text{CD})_x$. The simulation of the spectra in $(\text{CD})_x$ can be performed in the similar way as in $(\text{CH})_x$ considering the gyromagnetic ratio and spin quantum number of deuteron.

Upper solid line represents observed peak to peak linewidth for *cis*-rich $(\text{CH})_x$ at 4.2 K (10.4 gauss) and lower one is that for *cis*-rich $(\text{CD})_x$ (3.7 gauss). Even when the largest possible value of 30.0 gauss is used for A and fairly large natural width of 2.0 gauss is assumed, spin density for predicted soliton half width ($N = 7$) gives smaller linewidth than observation. Observed linewidths are close to those for $N = 5$. However, the lineshape is deviated from observation as is known by comparing figure 2(b) and observed curve in figure 4. Thus it is concluded that the



Fig. 2 - Effect of anisotropic term of hyperfine coupling on simulated ESR spectra of randomly oriented immobile solitons. Curve (a) is the result for the isotropic coupling only. Curve (b) is that including anisotropy. Anisotropic term tends to wash out the structure of the curve (a). Parameter values for A and α are 30 gauss and 0.5 respectively. Natural width of 0.8 gauss is assumed.

theoretical spin density of equation (1) does not reproduce the observed result quantitatively.

Strictly speaking, there is another effect which must be included in the calculation. This is the so called second order effect in the hyperfine structure which brings the appearance of so called *forbidden transition* /9/. Our present calculation also include this effect though its contribution is relatively minor.

Above discrepancy between the theory and the observation is possibly removed by using the modified spin density /8/. Subbaswamy and Grabowski calculated the effect of finite on-site Coulomb energy U which was neglected in the original calculation by Su et al. For finite values of U they showed that negative spin density appears on odd sites ($n = \pm 1, \pm 3 \dots$) where the original spin density was zero as in equation (1). To cancel those excess negative spin densities, positive densities at even sites also grow and the net spin density remains unity. This effect apparently increases the simulated linewidth because only the absolute spin density affects the hyperfine splitting. For odd sites x - and z -components of hyperfine tensor are approximately interchanged compared with even sites due to the effect of larger positive densities of adjacent even sites /9/.

The simulated widths are also shown in figure 3 by open circles for $U = 0.5$ eV and open squares for $U = 3.0$ eV for the same parameter values used in the calculation by equation (1). It is plotted for $N = 6$ because the predicted soliton half width is nearly this values in this case. It is seen that the simulated results for $U = .5$ eV agree with observed results quite well. This is why the natural width was assumed to be 2.0 gauss. In principle similar agreement is expected for $U = 3.0$ eV with smaller value of A . However, it was then difficult to find the simultaneous agreement for $(CH)_x$ and $(CD)_x$ for adequate natural width.

The comparison between simulated and observed lineshapes is shown in figure 4. Thick solid line is the observed result of *cis*-rich $(CH)_x$ at 4.2 K. Thin solid line is simulated result for $U = 0.5$ eV by the spin density of reference 8 and dotted line is that for $N = 7$ of equation (1). It is seen that the simulated lineshape for

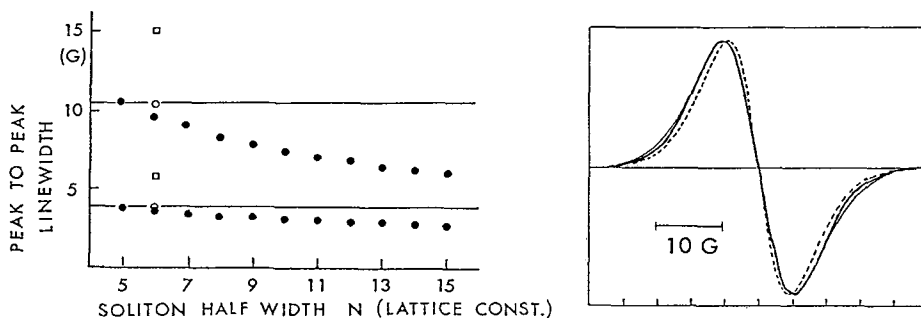


Fig. 3 (left) - Dependence of simulated peak to peak linewidth on the soliton half width N . Closed circles are results obtained by theoretical spin density of equation (1). Upper circles are for $(CH)_x$ and lower ones are for $(CD)_x$. Two solid lines are observed width in undoped *cis*-rich sample at 4.2 K for $(CH)_x$ (upper line) and for $(CD)_x$ (lower line). Open circles are simulated results of spin density derived in reference 8 for $U = 0.5$ eV. Open squares are those for $U = 3.0$ eV. For all calculations, 30.0 gauss, 2.0 gauss and 0.5 were assumed for A , natural width, and α respectively.

Fig. 4 (right) - Comparison between the observed first-derivative ESR spectrum of an unoriented *cis*-rich sample at 4.2 K with simulated results. Thick solid line shows the observed curve. Thin solid line is a simulated result by the spin density of reference 8 for $U = .5$ eV. Dotted line is a result using spin density of the soliton theory ($N = 7$). Parameter values are similar as those of Fig. 3.

$U = .5$ eV is fairly consistent with observation. On the other hand original spin density of $N = 7$ gives somewhat smaller linewidths. Parameter values are similar as in figure 3.

2 - DISCUSSION

Since there are ambiguities in parameter values for A and U , it is difficult to determine the spin density from ESR study alone. Natural width may be mainly dipolar width but the detailed discussion is beyond the scope of this work. It should be pointed out also that even more delocalized spin densities with more excess negative densities may give similar simulated result.

In solids, especially in single crystals, detailed determination of spin density distribution is usually achieved by ENDOR /10/. In the case of $(CH)_x$, the ENDOR determination is more difficult than the single crystal case because powder spectra from a spatially delocalized spin system should be analyzed. In actual ENDOR spectra in unoriented *cis*-rich sample the spin density larger than 0.1 is not observed clearly /5,11/. On the other hand if the theoretical spin density is correct, the central spin density $\rho(0)$ well exceeds 0.1.

There are two possibilities for this discrepancy. One possibility is that theoretical spin density is actually correct but larger spin densities than 0.1 are not observed in ENDOR presumably due to weaker intensity from larger anisotropy and shorter spin lattice relaxation times. The other possibility is that spin is actually more delocalized than theoretical prediction which gives smaller $\rho(0)$. It is known that diagonal components of the hyperfine tensor can be determined from the turning points of powder spectra /12/.

On this point measurements in stretch oriented samples may serve to the unique assignment of such peaks. It should be emphasized that once the spin density is determined by ENDOR, it must reproduce the observed ESR spectra. The spin density in undoped *cis*-rich polyacetylene will be completely determined by those studies.

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