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ELECTRONIC STRUCTURES AND ENDOR SPECTRA OF POLARONS IN POLY(*p*-PHENYLENE VINYLENE)

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Abstract Polaron states in electroluminescent conjugated polymer, poly(*p*-phenylene vinylene) (PPV) are studied theoretically. The Pariser-Parr-Pople model which includes a long range electron-electron interaction is applied to a π electron system on a PPV chain. Using the unrestricted Hartree-Fock method, we calculate the properties of polarons, such as the structures of spin and charge densities. Electron-nuclear double-resonance spectra calculated from the theoretical spin density of a polaron well explain corresponding experiments in undoped, oriented PPV.

INTRODUCTION

Electroluminescence (EL) is one of the current topics in the research field of novel organic materials, among which conjugated polymer, poly(*p*-phenylene vinylene) (PPV) and its derivatives have been much investigated because of their high efficiency of EL.[1,2] In conjugated polymers with non-degenerate ground state as in the case of PPV, charge carriers are expected to take the form of polarons or bipolarons owing to electron-lattice coupling and low dimensionality. Therefore, investigations on such non-linear excitations are significant in understanding the electronic processes of EL. In terms of the polaron picture, Brendel *et al.* analyzed electron-nuclear double-resonance (ENDOR) spectra of doped PPV oligomers.[3] Recently, Kuroda *et al.* suggested the presence of trapped polarons in undoped, oriented PPV by ENDOR measurements in a dark state.[4,5] As for theoretical works, the non-interacting model of the Su-Schrieffer-Heeger (SSH) [6] type is often applied to polarons and bipolarons in PPV.[7-9] The treatment of these states with taking account of the electron-electron (e-e) interaction is rare, in spite of much controversy on the role of the interaction.[2]

In the present paper, we adopt the Pariser-Parr-Pople (PPP) model which includes a long range e-e interaction and study theoretically the properties of polarons in a PPV chain. Furthermore, we compute ENDOR spectra of polarons based on their theoretical spin density (SD) and demonstrate that our model with the e-e interaction successfully explains the experiments.[4,5] A more detailed description is given in refs. 10 and 11.

MODEL

A π electron system on a PPV chain is described by the following PPP Hamiltonian,

$$H = -\sum_{<m,n>,\sigma} t_{m,n}(C^{\dagger}_{m,\sigma}C_{n,\sigma} + C^{\dagger}_{n,\sigma}C_{m,\sigma}) + \frac{K}{2}\sum_{<m,n>} y_{m,n}{}^2 + U\sum_{n}\rho_{n\uparrow}\rho_{n\downarrow} + \frac{1}{2}\sum_{m\neq n}\sum_{\sigma,\sigma'} V_{m,n}\,\rho_{m,\sigma}\rho_{n,\sigma'} \,. \quad (1)$$

Here, $C^{\dagger}_{n,\sigma}$ creates a π electron with spin σ at n-th carbon atom and $\rho_{n,\sigma} = C^{\dagger}_{n,\sigma}C_{n,\sigma}$ -1/2. The bond variable $y_{m,n}$ denotes the increase of the bond length between sites m and n from its mean value r_0 (= 1.4 Å). The transfer integral has a linear dependence on the bond variable with a coupling constant α as in the SSH model: $t_{m,n} = t - \alpha y_{m,n}$. The summation $<m,n>$ is taken over all the nearest neighbor pairs. K is the force constant for the elastic energy of the lattice. U denotes the strength of the on-site Coulomb repulsion. The long range part of the repulsion between sites m and n with distance $R_{m,n}$ is expressed by the Ohno formula,[12] $V_{m,n} = 1/\sqrt{(1/U)^2 + (R_{m,n}/Vr_0)^2}$.

The PPP Hamiltonian in eq. (1) is solved numerically by the unrestricted Hartree Fock (UHF) method under the periodic boundary condition. The electronic properties such as the SD and charge density (CD) of polarons are calculated from the UHF self-consistent solutions. The bond length is optimized so as to be consistent with the electronic structures using the Hellmann-Feynman force equilibrium condition within the adiabatic approximation. We assume intermediate e-e interaction, U= 2.5t and V = 1.3t, and a typical electron-lattice coupling constant $\lambda = 2\alpha^2/\pi tK$ = 0.16. In this paper, we present the results for the system of 128 sites (16 unit cells) with 127 electrons, which gives a cationic polaron.

The proton-ENDOR spectra of polarons are calculated from their theoretical SD in the following manner. Suppose that an applied magnetic field has the direction cosines p_i, (i=x,y,z) against the principal axis, x, y, and z, of the hyperfine coupling (hfc) tensor between a π radical and a proton in each CH unit. In Fig. 1, the coordinate system (x, y, z) is defined for the two uneqivalent CH directions in a PPV chain. The two branches of the ENDOR resonance frequency $\nu_{\pm}$ are expressed in terms of p_i and the principal value A_i of the hfc [13] as $\nu_{\pm} = \left[\sum_i (\nu_0 \pm A_i/2)^2 p_i^2\right]^{1/2}$. Here, ν_0 is the free NMR frequency of proton and is taken as 14.45 MHz in this paper. The hfc for a radical at site n is proportional to its SD s_n and is anisotropic due to the electron-nuclear dipole-dipole interaction as $A_x = -(1-a)s_nA_0$, $A_y = -(1+a)s_nA_0$, and $A_z = -s_nA_0$.[14] We use typical values of the McConnell's constant A_0 (= 70 MHz) and the relative magnitude of anisotropy a (= 0.5).[14,15]

Theoretical ENDOR spectra are obtained by superposing Lorentzian line shapes with their centers at $\nu_{\pm}$ over the carbon sites.[16] Note that sites without a bond to a hydrogen (A and D in Fig.1) do not contribute to the spectra. We take account of the distribution of chain orientations around the stretch direction of a PPV film. For simplicity, each ENDOR process is assumed to contribute to the spectrum with an equal weight regardless of its resonance frequency $\nu_{\pm}$. Instead, the sites with very small SD (< 0.002) are neglected in the calculations, since transition probability should be weaker for smaller SD. In practice, this cutoff affects the spectra in a narrow frequency range up to at most ± 0.21 MHz around ν_0.

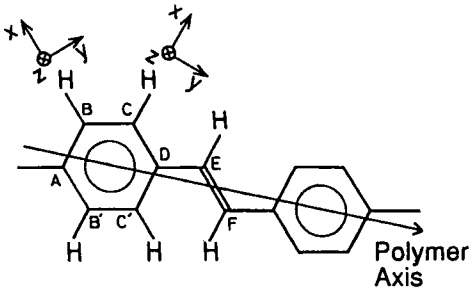

FIGURE 1 Molecular structure of poly(*p*-phenylene vinylene), (PPV). The principal axes (x , y , z) of the hyperfine coupling between a π electron and a proton are defined for two unequivalent orientations of CH bonds.

RESULTS

Figure 2 shows the structures of the SD, CD, and bond variable in a cationic polaron with up-spin. They are plotted according to the position of sites along the chain. The center of the polaron is located at a

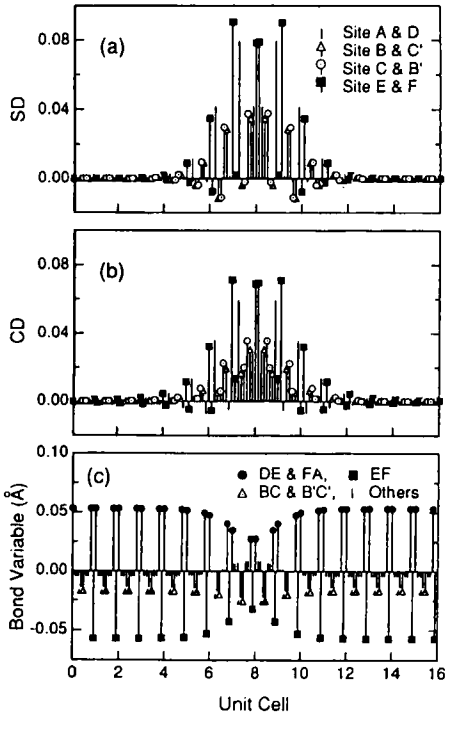

FIGURE 2 The spatial structure of a cationic polaron in a PPV chain. The spin density (SD), the charge density (CD), and the bond variable are presented in (a)-(c), respectively. Different kinds of sites and bonds are distinguished by marks. Sites A~F are defined in Fig. 1. In (a) and (b), SD and CD are arranged in the order of sites A, B, B', C, C', D, E and F in each unit cell. In (c), The bond variables are arranged in the order of bonds FA, AB, AB', BC, B'C', CD, C'D, DE, and EF in each unit cell.

vinylene bond (the bond EF in Fig. 1). The SD and CD extend over about four unit cells (~30 sites). The profile of SD and CD are similar to each other as a whole, although the magnitude of CD is somewhat smaller. They are more complicated than those in polyacetylene.[17] This is associated with the presence of different kinds of carbon sites in PPV which are distinguished by different marks in Fig 2. The e-e interaction enhances the alternation of SD and CD site by site and increases their maximum values.[17] Our model with the present parametrization gives the maximum values of the SD, s_{max}, 0.090 and that of CD 0.071. Their positions locate at vinylene sites in the next unit cell to the polaron center. s_{max} agrees with that estimated from the ENDOR measurements.[4,5] The enhanced alternation of the SD and CD due to the e-e interaction render the appearance of negative SD and CD. We can find several sites with small negative SD and CD in Fig. 2(a).

We note that the SD profile consists of three distinct groups of the magnitude of s_n: (i) large SD, $s_n = 0.09 \sim 0.08$, extending over two unit cells around the center; (ii) intermediate SD, $s_n \sim 0.04$, extending over four unit cells; (iii) much smaller SD, $|s_n| < 0.01$, extending over about six unit cells. This feature is specific to the case of the finite e-e interaction, whereas in the case of the SSH model we cannot group the SD clearly. The three groups in the SD distribution is directly reflected in the structure of ENDOR spectra, as will be shown below.

The polaron relax the bond variable over about two unit cells around its center as shown in Fig. 2(c). This width is narrower than those of the SD and CD distributions. The dimerization of the vinylene bond at the polaron center is weakened to about half of the undoped case. The polaron slightly enhances the quinoidal nature of phenyl rings, as pointed out in ref. 9, in the sense that the bonds BC and B'C' become shorter and the other four bonds become longer.

In Fig. 3, we compare the ENDOR spectra calculated from the SD in Fig. 2(a) with the experimental spectra of undoped, oriented PPV in a dark state.[3,4] In (a) and (b), the magnetic field is applied in the direction parallel ($H//$) and perpendicular ($H\perp$) to the stretch direction, respectively. Both of the calculated and observed spectra are almost symmetric around $\nu_0 = 14.45$ MHz. As shown in Fig. 3, the calculated spectra well reproduce the observed ones. In particular, our model can explain the following characteristic features in the observed spectra:

(i) *Maximum resonance frequency at about 19.4 MHz*
Since the hfc is proportional to the SD, the maximum SD 0.09 is responsible for the maximum resonance frequency.

(ii) *Anisotropy between the H// and H⊥ spectra*

The anisotropy arises from that in the hfc tensor. When the magnetic field is applied parallel to the *y* axis, the resonance frequency becomes largest. As shown in Fig. 1, the *y* axis is nearly parallel to the polymer axis at the sites B', C, E, and F, so that the resonance frequency is more likely to be larger for *H//* than for *H*⊥.

(iii) *Three kinds of structures in the H// spectrum (P1~P3 in the figure)*
The three distinct groups of the SD in Fig. 2(a) is relevant to the three structures. The three groups in the SD profile results in those in the hfc and, consequently, in the resonance frequencies, giving rise to the three structures in the spectra.

(iv) *Tails around 18-19.5 MHz and 9-10.5 MHz in the H// case*
In our model, the resonance in these frequency ranges originates from the two kinds of vinylene sites which belong to the group of large SD.

When the e-e interaction is neglected ($U = V = 0$), the reproduction of the observed spectra becomes worse.[10] In particular, the central peak around ν_0 is fairly broader. This is associated with the SD distribution not classified into the distinct groups clearly. Therefore, our results indicate the importance of the e-e interaction. Chandross *et al.* emphasized the essential contribution of the interaction to the optical properties of undoped PPV.[18] The optical absorption spectra and their polarization dependence of undoped PPV in our model are discussed in detail in ref. 11.

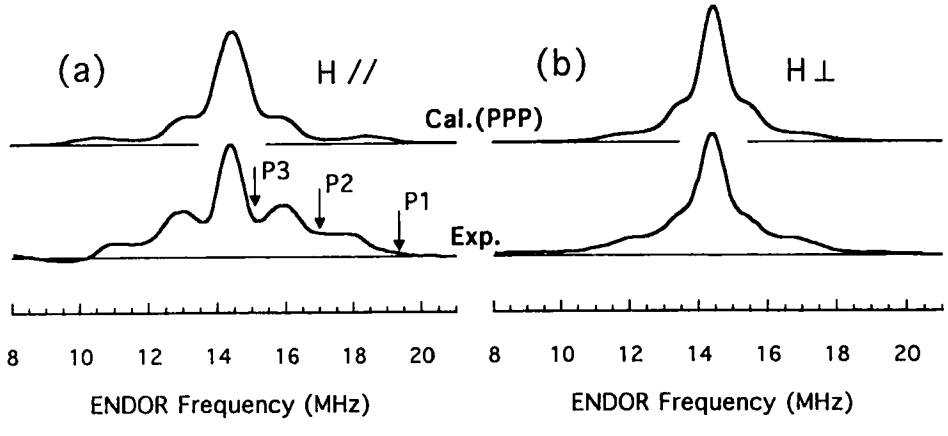

FIGURE 3 Theoretical (upper carves) and experimental (lower curves) proton ENDOR spectra. In (a) and (b), the external magnetic field is parallel (*H//*) and perpendicular (*H*⊥) to the stretch direction in a PPV film, respectively. The observed spectra is for stretched undoped PPV in a dark state (refs. 4 and 5).

CONCLUSION

Using the PPP-UHF method with the intermediate e-e interaction, we calculated the properties of a polaron in a PPV chain. The SD and CD of a polaron extend about four unit cells (~30 sites) but the relaxation of bond variable is somewhat narrow. The maximum spin density 0.09 at the vinylene sites is in good agreement with the value deduced from the observed ENDOR spectra. The characteristic feature in the SD distribution is the three distinct groups in its magnitude, which is directly reflected in the structure of the ENDOR spectra. Theoretical ENDOR spectra of polaron explain successfully the observed ones, supporting strongly that the observed π radicals are trapped polarons. The PPP model reproduces the observed spectra better than the SSH model, indicating the importance of the e-e interaction in the polaron state of PPV.

REFERENCES

1. J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burns, and A. B. Holmes, Nature, 347, 539 (1990).
2. For recent progress, see Proc. 2nd Int. Conf. on Optical Probes of Conjugated Polymers and Fullerenes, edited by Z. V. Vardeny and L. J. Rothberg (Salt Lake City, 1994) [Mol. Cryst. Liq. Cryst., 256 (1994)].
3. P. Brendel, A. Grupp, M. Mehring, R. Schenk, K. Müllen, and W. Huber, Synth. Met., 45, 49 (1991).
4. S. Kuroda, T. Noguchi, and T. Ohnishi, Phys. Rev. Lett., 72, 286 (1994).
5. S. Kuroda, K. Murata, T. Noguchi, and T. Ohnishi, J. Phys. Soc. Jpn., 64, 1363 (1995).
6. W. P. Su, J. R. Schrieffer, and A. J. Heeger, Phys. Rev. Lett., 42, 1698 (1979); Phys. Rev. B, 22, 2099 (1980).
7. H. Y. Choi and M. J. Rice, Phys. Rev. B, 44, 10521 (1991).
8. Z. Shuai, D. Beljonne, and J. L. Brédas, Solid State Commun., 78, 477 (1991).
9. H. A. Mizes and E. M. Conwell, Synth. Met., 68, 145 (1995).
10. Y. Shimoi, S. Abe, S. Kuroda, and K. Murata, Solid State Commum., 95, 137 (1995).
11. Y. Shimoi and S. Abe, submitted to Synth. Met.
12. K. Ohno, Theor. Chim. Acta, 2, 219 (1964).
13. H. Muto and M. Iwasaki, J. Chem. Phys., 59, 4821 (1973).
14. J. R. Morton, Chem. Rev., 64, 453 (1964).
15. J. E. Wertz and J. R. Bolton, Electron Spin Resonance (McGraw-Hill, New York, 1972), Chap. 6.
16. S. Kuroda, H. Bando, and H. Shirakawa, J. Phys. Soc. Jpn., 54, 3956 (1985).
17. H. Fukutome, J. Mol. Str. (Theochem), 188, 337 (1989).
18. M. Chandross, S. Mazumdar, S. Jeglinski, X. Wei, Z. V. Vardeny, E. W. Kwock, and T. M. Miller, Phys. Rev. B, 50, 14702 (1994).