

# Charge transfer in polypyrrole

Ephraim Buhks and Ian M. Hodge<sup>a)</sup>  
BF Goodrich R&D Center, Brecksville, Ohio 44141

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Experimental electrical conductivity and optical absorption data are presented for fully oxidized polypyrrole. A charge transfer theory is described which gives an excellent account of the temperature dependence, carrier density dependence, and magnitude of electrical conductivity. The reorganization energy calculated from the temperature dependence of conductivity, 0.23 eV, is in good agreement with the value obtained from the near IR dielectric loss spectrum,  $\sim 0.25$  eV. Self-consistent hopping distances of about 5–10 Å are obtained from the reorganization energy, conductivity preexponential factor, and carrier density. Hopping between localized sites associated with the counteranion is indicated.

## I. INTRODUCTION

Polypyrrole is a stable conducting polymer usually prepared by electrochemical oxidation of pyrrole in solution.<sup>1</sup> Its electrical conductivity typically lies in the range 10–100  $\Omega^{-1} \text{ cm}^{-1}$ . The conduction mechanism in polypyrrole has proven difficult to establish because of structural disorder<sup>2</sup> and because the electrical properties exhibit both metallic and semiconductor behavior.<sup>1,3,4</sup> In this paper we present experimental conductivity and optical data on oxidized polypyrrole, and describe a charge-transfer model which gives a self-consistent account of both.

As prepared electrochemically, about one third of the pyrrole rings are oxidized.<sup>1,3</sup> Recent data on poly(dimethylpyrrole) suggest a degree of polymerization of 100–1000.<sup>5</sup> Electron diffraction patterns have been observed in neutral polypyrrole, prepared by electrochemical reduction of the oxidized polymer.<sup>2</sup> These indicate a sheet structure similar to that of graphite. The ordered regions which produce the diffraction pattern are estimated to be about 20–50 Å in size.

There is good agreement in the literature on the optical spectra of oxidized polypyrrole. Kanazawa, Diaz, Krounbi, and Street<sup>6</sup> reported absorptivity peaks at 1.2 and 2.9 eV. Yakushi, Lauchlan, Clarke, and Street<sup>7</sup> reported absorptivity peaks at 1.0 and 2.7 eV and a shoulder at 3.6 eV. Kronig-Kramers transformation yielded broad peaks at 0.5 and 2.7 eV in the conductivity and 0.25 and 2.7 eV in the dielectric loss. The shift in the low energy band between the absorption and conductivity spectra is due to the dispersion in refractive index, and that between the conductivity and dielectric loss is due to the frequency factor relating them. These shifts are greater at lower frequencies. Arwin, Aspens, Bjorkland, and Lundstrom<sup>8</sup> obtained spectroscopic ellipsometry data which showed an absorption peak at about 3 eV and a rising absorption at the experimental low frequency limit of 1.5 eV, which they attributed to dc conductivity. However, the real part of the permittivity exhibited a positive frequency dependence at low energy, indicating a resonance absorption rather than a relaxation (dc conductivity) origin for the low frequency rise in absorptivity. This would then be consistent with the conductivity maxima (i.e., resonance absorption) at 1.0 and

1.2 eV observed by Yakushi *et al.* Sharp absorption peaks at energies below about 0.25 eV are observed in the Raman<sup>6</sup> and IR<sup>7</sup> spectra.

There is less agreement on the temperature dependence of the conductivity of oxidized polypyrrole. Kanazawa *et al.*<sup>6</sup> reported a maximum in the conductivity of polypyrrole tetrafluoroborate at about 420 K, with reversible behavior below the maximum and irreversible behavior above it. On the other hand, a reversible temperature dependence below 300 K has been reported by others<sup>1,4</sup> to follow the form

$$\sigma = \sigma_0 \exp[ -(T_0/T)^{1/4} ], \quad (1)$$

associated with variable range hopping between localized states in a semiconductor. The thermoelectric power<sup>1,4</sup> is positive, indicative of hole carriers, and numerically small with a linear temperature dependence below 300 K, characteristic of a metal.

Our conductivity data confirm the temperature dependence reported by Kanazawa *et al.*<sup>6</sup> We believe the conductivity leveling off at high temperature is a characteristic feature of the conductivity mechanism, and propose a charge transfer model which is consistent with this feature. The model also provides an estimate of hopping distance.

## II. EXPERIMENTAL

### A. Sample preparation

Films were deposited on tin oxide coated glass at room temperature by electropolymerization from propylene carbonate solutions 0.4 M in pyrrole and 0.1 M in tetrabutylammonium bisulfate or tetrafluoroborate. Current densities of about 2 mA  $\text{cm}^{-2}$  yielded 0.02–0.03 cm thick films in about 3 h; thicker films up to 0.06 cm thick were formed over corresponding longer times. Samples about 4 cm long and 0.5 cm wide were cut from these films, and washed with acetonitrile and dried at 390 K for 45 min in an air circulating oven. This preconditioning was important for good reproducibility. Bulk density of the films was 1.4 g  $\text{cm}^{-3}$ .

### B. Conductivity

Four terminal ac conductivities were measured with a GenRad Digibridge impedance bridge (model 1688) in the frequency range 250 Hz–20 kHz. Separate experiments established that the frequency independent ac conductivity at

<sup>a)</sup> Present address: Research Laboratories, Eastman Kodak Co., Rochester, NY 14650.

room temperature agreed with four terminal dc measurements. Films were mounted on a mica support strip and clamped between copper blocks with narrow (about 1 mm copper foil wrapped around the mica and film at two points between the blocks for the four terminal potential probes. The experimental jig was placed in a grounded aluminum cylinder heated by cartridge heaters in conjunction with an in-house temperature controller. For subambient temperatures the aluminum block was packed in dry ice and dry nitrogen passed through the sample compartment. Measurements were made under near isothermal conditions, from about 200 to 540 K. Temperature drift during conductivity measurements was less than  $0.1 \text{ K min}^{-1}$ . During heating between thermal equilibration points the sample was short circuited to minimize any long time ionic polarization developing from the thermo-emf. A two minute equilibration time following open circuit switching was programmed before conductivity data were collected. The entire experimental protocol was controlled by a Hewlett-Packard 85 computer.

### C. Optical spectra

Optical measurements were made on deposited films of estimated thickness (1000 Å), with tin oxide coated glass as reference. The UV-visible spectrum (12 500 to 30 000  $\text{cm}^{-1}$ ) was measured with a Hewlett-Packard 8450A diode array spectrophotometer, and the near IR with a Beckman 5270 dual beam spectrophotometer. The absorbances from each instrument were adjusted for best overlap to give a composite spectrum.

### III. THEORY

We describe a charge-transfer multiphonon hopping model which gives a good account of our conductivity data. This formalism was developed in a general form by Kubo and Toyazawa<sup>9</sup> and Holstein,<sup>10</sup> and has been successfully applied to polaron conductivity in semiconductors,<sup>11</sup> inorganic redox reactions in solution,<sup>12-16</sup> electron transfer in low temperature glasses,<sup>17</sup> electron exchange reactions in organo-metallic systems,<sup>18</sup> charge transfer in molecular doped polymers,<sup>19</sup> and electron transfer in biological systems.<sup>20-23</sup>

The transition probability  $W$  for charge carrier transfer between donor-acceptor ions (or localized states) can be expressed in the nonadiabatic approximation (weak electronic interaction) as the product of the square of the charge-exchange integral  $V$  and thermally averaged Franck-Condon (FC) factors  $F(\{\omega_n\}, \{S_n\}, T, \Delta E)$ :

$$W = (2\pi/\hbar) |V|^2 F. \quad (2)$$

The charge exchange interaction  $V$  decreases exponentially with distance  $R$  as<sup>11,18,20,22,23</sup>

$$V = V_0 \exp(-\alpha R), \quad (3)$$

where  $\alpha = 1 \text{ \AA}^{-1}$  and  $V_0 = 12.5 \text{ eV}$  are found from analysis of nearest-neighbor interactions between aromatic molecules such as naphthalene and anthracene.<sup>22</sup> It has recently been shown<sup>23</sup> that the electron transfer integral between redox sites connected by rigid polymer links is characterized by  $\alpha = 0.98 \text{ \AA}^{-1}$  (through the bonds) and  $\alpha = 1.3 \text{ \AA}^{-1}$

(through space). The FC factors depend on the electronic energy difference between donor-acceptor centers (redox potential,  $\Delta E$ ), the frequencies  $\{\omega_n\}$  of vibrational modes  $\{n\}$ , and the corresponding electron-phonon coupling factors  $\{S_n\}$ , and temperature  $T$ . As shown by several investigators, in the harmonic approximation the FC factors for electron transfer between isoenergetic states ( $\Delta E = 0$ ) assume the form<sup>10,13-15</sup>

$$F = [2\pi \sum S_n (\hbar\omega_n)^2 \text{cosech}(\hbar\omega_n/2kT)]^{-1/2} \times \exp\{-\sum S_n \tanh(\hbar\omega_n/4kT)\}. \quad (4)$$

In the high temperature limit  $\hbar\omega_n < kT$ <sup>10,12-15,18</sup> valid for polymer electronic transport,<sup>19</sup> where low frequency torsional/backbone modes are involved, Franck-Condon factors assume the form

$$F = (4\pi E_r kT)^{-1/2} \exp(-E_r/4kT), \quad (5)$$

where

$$E_r = \sum S_n (\hbar\omega_n). \quad (6)$$

$E_r$  is the reorganization energy which in the continuum approximation yields<sup>12-16</sup>

$$E_r = e^2(1/\epsilon_{op} - 1/\epsilon_{st})(1/a - 1/R), \quad (7a)$$

where  $\epsilon_{op} = n^2$  and  $\epsilon_{st}$  are the limiting high and low frequency relative permittivities, respectively (relative to the hopping frequency),  $a$  is the radius of a redox center, and  $R$  is the distance between the redox centers (elementary jump distance). For  $R = 2a$ , Eq. (7a) becomes

$$E_r = e^2(1/\epsilon_{op} - 1/\epsilon_{st})(1/R). \quad (7b)$$

The appearance of the relative permittivities in Eqs. (7) reflects the polaron nature of the hopping event.

The electrical conductivity  $\sigma$  of a  $p$ -type conductor is given in its simplest form by

$$\sigma = p e \mu, \quad (8)$$

where  $p$  is the hole concentration and  $\mu$  is the mobility related to the diffusion coefficient  $D$  through the Einstein relation

$$\mu = eD/kT. \quad (9)$$

The diffusion coefficient of the carrier is related to the transition probability  $W$  and hopping distance  $R$  by

$$D = R^2 W/6. \quad (10)$$

The metal-like behavior of the thermo-emf of fully oxidized polypyrrole indicates that the hole concentration is independent of temperature. Thus the temperature dependence of electrical conductivity is determined by the hole mobility. For charge transfer between localized states which are coupled to lattice vibrational modes, we obtain the relation

$$\sigma = (e^2/6)(2\pi/\hbar)pV_0^2 R^2 \exp(-2\alpha R)(16\pi E_a)^{-1/2} \times (kT)^{-3/2} \exp(-E_a/kT), \quad (11)$$

where  $p$  is the hole concentration and the activation energy

$$E_a = E_r/4. \quad (12)$$

Equation (11) predicts a maximum in conductivity vs temperature at  $T = 2E_a/3k$ .

The optical transition probability  $I(\Omega)$  which is photoassisted by a photon  $\hbar\Omega$  charge carrier transfer between local-

ized states is, in the case of weak electron exchange interactions,<sup>20,26</sup>

$$I(\Omega) = e^2 R^2 V^2 (\hbar\Omega)^{-2} (4\pi E_r kT)^{-1/2} \times \exp\{ - [(\hbar\Omega - E_r)^2 / 4E_r kT] \}. \quad (13)$$

The absorptivity  $\alpha(\Omega)$  is related to  $I(\Omega)$  by<sup>24</sup>

$$\alpha(\Omega) = \{ (n/\epsilon)(E_0/E) \} N (8\pi^3/3\hbar)(\hbar\Omega/c) I(\Omega), \quad (14)$$

where  $n$  is the optical index of refraction,  $\epsilon$  is the limiting low frequency relative permittivity,  $N$  is the concentration of absorbing centers [ $= p$  in Eq. (11) for polypyrrole], and  $E_0/E$  is the ratio of the average electric field at the redox center to its average value in the bulk polymer (this is usually put equal to unity, and is omitted henceforth). For the approximation

$$\epsilon = n^2, \quad (15)$$

Eq. (14) becomes

$$\alpha(\Omega) = p(8\pi^3/3\hbar)(\hbar\Omega/nc) I(\Omega). \quad (16)$$

Comparison of the phenomenological relation between  $\alpha$  and the dielectric loss  $\epsilon''$ ,

$$\alpha(\Omega) = [\Omega\epsilon''(\Omega)]/nc \quad (17)$$

with Eq. (16) reveals that  $I(\Omega)$  is directly proportional to  $\epsilon''$ . Thus

$$\epsilon''(\Omega) = p(8\pi^3/3) I(\Omega), \quad (18)$$

where  $p$  is the concentration of absorbing centers.

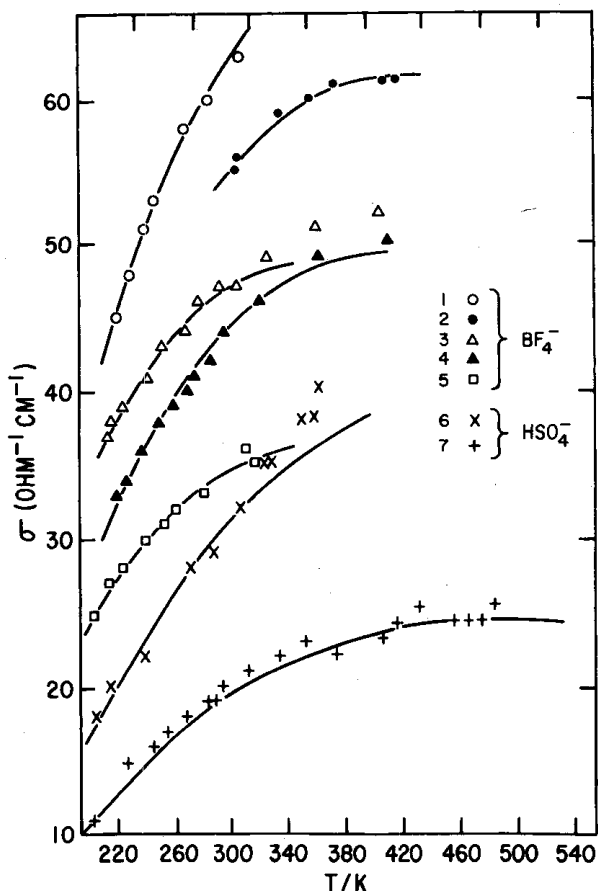


FIG. 1. Electrical conductivity data for eight samples of polypyrrole, as a function of temperature. Solid lines are best fits to Eq. (11).

TABLE I. Best fit parameters to  $\sigma = AT^{-3/2}\exp[-E_a/kT]$ .

Run # (Fig. 1)	$E_a$ (eV)	$\ln A$
1	0.0561	14.86
2	0.0598	14.81
3	0.0481	14.26
4	0.0550	14.47
5	0.0497	14.01
6	0.0625	13.94
7	0.0649	14.50
Average	0.0566	14.41

#### IV. EXPERIMENTAL RESULTS

Representative conductivity data for 30% oxidized polypyrrole films doped by bisulfate tetrafluoroborate ions are displayed in Fig. 1. Our findings are in general agreement with those reported by Kanazawa *et al.*<sup>6</sup>: a leveling off in conductivity near 420 K, with poorer reproducibility above that temperature. The data shown in Fig. 1 were least squares fitted to Eq. (11) in the form

$$\sigma = AT^{-3/2}\exp[-E_a/kT]. \quad (19)$$

The best fits are shown as solid lines in Fig. 1, and the best fit parameters are summarized in Table I. The average activation energy ( $\pm$  standard deviation) is  $(0.057 \pm 0.005)$  eV.

The optical spectrum, obtained from thin films of estimated thickness 1000 Å, is shown in Fig. 2. It agrees with literature data<sup>6,7</sup> with regard to the positions of absorption peaks (1.0 and  $2.8 \pm 0.1$  eV) and their relative magnitudes.

#### V. DISCUSSION

It is clear from Fig. 1 and Table I that Eq. (11) gives an accurate description of the conductivity data with best fit activation energies of about 0.057 eV and preexponential factors  $A$  of about  $2 \times 10^6 \text{ OHM}^{-1} \text{ CM}^{-1} \text{ K}^{3/2}$ . The hopping distance  $R$  can be estimated from these data using Eq. (11), once  $p$  is known. If a fraction  $1/f$  of the rings are oxidized and the true bulk density is assumed equal to the measured value of

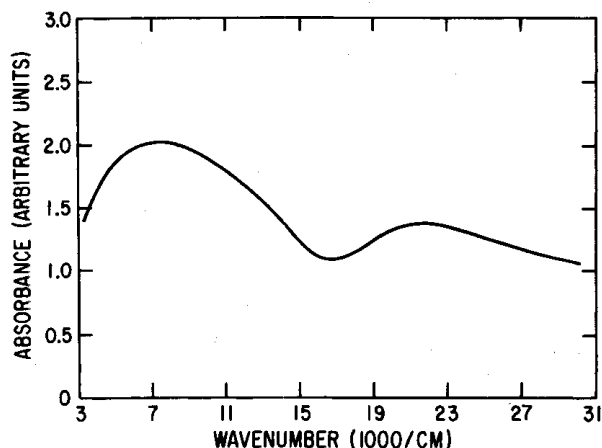


FIG. 2. Optical absorption spectrum of polypyrrole tetrafluoroborate.

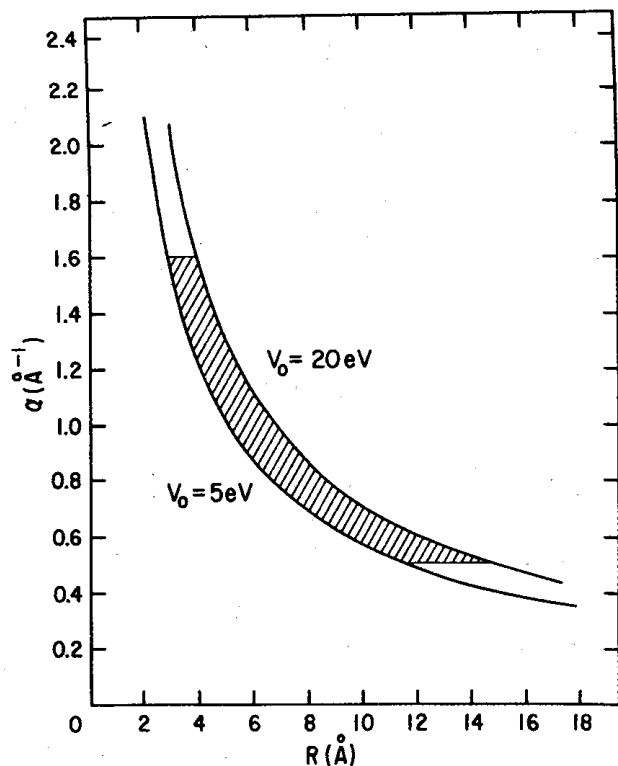


FIG. 3. Electron transfer parameter  $\alpha$  as a function of hopping distance  $R$ , calculated from the experimental values of the conductivity preexponential factor and activation energy in Eq. (11), for the indicated range in  $V_0$ . The shading corresponds to the area constrained by physically reasonable values of  $\alpha$  and  $V_0$  (see the text).

$1.4 \text{ g cm}^{-3}$ , and if  $p$  is equated to the anion concentration, then  $p$  is given by

$$p = (\rho N)/M. \quad (20)$$

In Eq. (20),  $\rho$  is the density,  $N$  is Avagadro's number, and  $M$  is the molecular weight of  $f$  pyrrole rings and the counteranion, given by

$$M = fM_p + M_a, \quad (21)$$

where  $M_p$  is the molecular weight of the pyrrole repeat unit and  $M_a$  is the formula weight of the anion. Equations (20) and (21) give

$$p = 1.3 \times 10^{22}/(f + m), \quad (22)$$

where  $m = M_a/M_p = 1.69$  and  $1.34$  for the bisulfate and tetrafluoroborate dopants, respectively. For as prepared films,  $f$  is about 3 and  $p$  is calculated to be about  $3 \times 10^{21} \text{ cm}^{-3}$  for both materials. This estimate of  $p$  is sufficiently accurate for our needs, since  $R$  is insensitive to  $p$ . As noted in the Introduction,  $\alpha$  typically lies in the range  $0.5$  to  $1.5 \text{ \AA}^{-1}$  and  $V_0$  is generally of the order 5 to 20 eV. Figure 3 shows the relationship between  $\alpha$  and  $R$  for values of  $V_0$  between 5 and 20 eV, obtained by inserting the experimental values of  $A$ ,  $E_a$ , and  $p$  into Eq. (11). For  $\alpha$  between  $0.5$  and  $1.5 \text{ \AA}^{-1}$ ,  $R$  is estimated to lie in the range 4–12  $\text{\AA}$ .

These estimated hopping distances are comparable with the average anion separation  $p^{-1/3} \approx 7 \text{ \AA}$  for oxidized pyrrole ( $f=3$ ), which suggests that hopping occurs between localized sites associated with the counteranion. Assuming this to be true, the carrier density dependence of conductivity

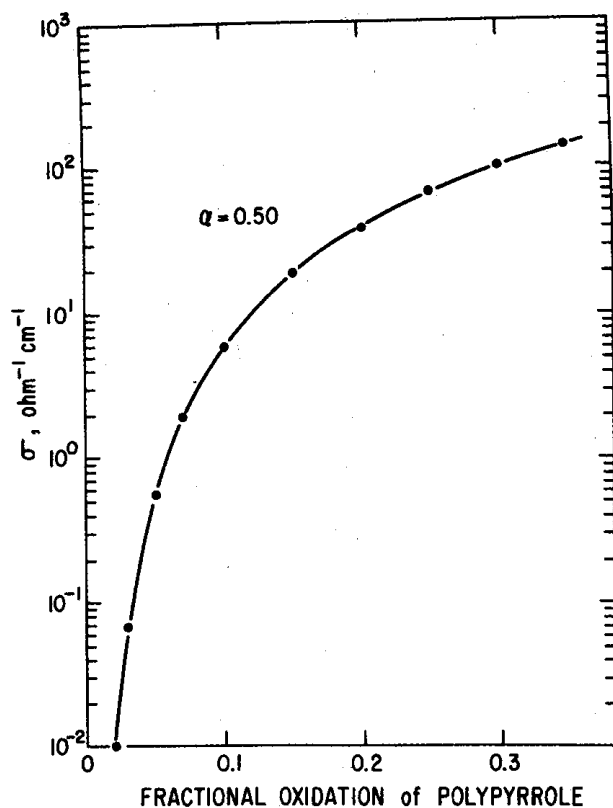


FIG. 4. Conductivity as a function of degree of oxidation according to Eq. (23) with  $\alpha = 0.5 \text{ \AA}^{-1}$ .

ity can be calculated in terms of the  $R$  dependence given by Eq. (11). Putting  $R = p^{-1/3}$  in Eq. (11) gives

$$\sigma \sim p^{1/6} \exp(-2ap^{-1/3}). \quad (23)$$

The functional dependence of  $\sigma$  on degree of oxidation ( $1/f$ ), calculated from Eqs. (22) and (23), is displayed in Fig. 4 for  $m = 1.4$  and  $\alpha = 0.5 \text{ \AA}^{-1}$ . A rapid increase in conductivity with  $p$  is seen at low  $1/f$ , with a leveling off at higher values of  $1/f$ . Similar behavior has been reported for  $\text{O}_2$  doped polypyrroles.<sup>27,28</sup>

As noted above the transition probability  $I(\Omega)$  is directly proportional to the dielectric loss [Eq. (18)]. It has been shown by Buhks<sup>26</sup> that the first moment of  $I(\Omega)$  is proportional to  $E_r$  with a proportionality constant close to unity. Since the first moment is numerically equal to the peak frequency for symmetric peaks, a dielectric loss peak is predicted to occur at about  $E_r = 4 \times E_a = 4 \times 0.057 = 0.23 \text{ eV}$ , in good agreement with the observed value of about  $0.25 \text{ eV}$ .<sup>7</sup> For  $E_r = 0.25 \text{ eV}$ ,  $n = 1.5$ <sup>8</sup> and estimated permittivity between 2.8 and 3.7,  $R$  is calculated to lie between 5 and 10  $\text{\AA}$ . This range is in good agreement with that calculated from the conductivity preexponential factor.

The physically reasonable and self-consistent estimates of hopping distance obtained from the activation energy and preexponential factor for conductivity lend strong support to our description of charge transfer in polypyrrole.

Equation (7b) predicts that the energy of maximum dielectric loss should red shift by a factor inversely proportional to the hopping distance. Published spectra<sup>7</sup> show a shift in absorptivity from 1 eV for an as-prepared sample to 0.7 eV

for a sample electrochemically reduced for 30 min at a potential of 2 V. If a degree of oxidation of 0.3 is assumed for the as-prepared film and the shift in absorptivity assumed to be the same as the dielectric loss, a degree of oxidation of 0.1 is calculated for the reduced film. The corresponding reduction in intensity of the absorption is calculated from Eqs. (13) and (16) to be of the order  $10^{-2}$  for  $\alpha = 1 \text{ \AA}^{-1}$ . This is consistent with the published qualitative spectra.

An absorption peak is also seen at about 1.4 eV for the most reduced films,<sup>7</sup> and a shoulder at the same energy appears in the spectrum of the most oxidized film. This energy corresponds to a hopping distance of about 3.6 Å, assuming that the permittivity and refractive index are the same as the oxidized polymer. It is speculated that this absorption reflects a localized ring to ring charge transfer process which significantly contributes to the conductivity only at the highest degrees of oxidation. At lower carrier densities this process would still take place but the long-range conductivity and associated charge transfer absorption would be determined by the less probable longer hops. Also, we note that the calculated hopping distances are comparable with the separation of closely packed chains. Since chain packing is expected to be sensitive to solvent type and other preparation details, interchain hopping may explain the extreme sensitivity of conductivity to solvent reported by Diaz and Hall.<sup>25</sup>

Charge mobilities of about  $10^{-1} \text{ cm}^2/\text{V s}$  are estimated from the experimental values of conductivity, assuming  $p = 3 \times 10^{21} \text{ cm}^{-3}$  for the fully oxidized polypyrrole. This value, although typical of inorganic semiconductors, is quite close to the upper mobility limit  $\sim 1 \text{ cm}^2/\text{V s}$  observed in molecular crystals and polymers.<sup>29-31</sup>

From the experimental value of the conductivity preexponential factor  $A$  and the estimated hopping distance of  $\sim 7 \text{ \AA}$ , the charge-exchange interaction  $V$  is estimated from Eq. (11) to be about  $10^{-2} \text{ eV}$ . This value is typical of similarly spaced donor-acceptor pairs in inorganic<sup>18</sup> and biological systems.<sup>20,22,23</sup>

It is of interest that the electron transfer rate,  $1/W$ , as calculated from Eq. (2) with  $V = 10^{-2} \text{ eV}$  and  $E_r = 0.25 \text{ eV}$ , is very fast (of the order  $10^{-11} \text{ s}$ ). Similarly, fast rates have been observed in biological systems and have been described in terms of activationless processes in which the redox potential of an exothermic electron transfer process is matched by the reorganization energy.<sup>32,33</sup> However, in the case of polypyrrole the reorganization energy  $E_r$  is smaller than in biological systems<sup>20-23</sup> (because of weaker electron-phonon interactions), and charge transfer occurs by activated hopping between isoenergetic sites.

If it is assumed that  $\alpha$  and  $V_0$  are similar for all conducting polymers, we predict maximum conductivities of  $10^2$  to  $10^3 \text{ } \Omega^{-1} \text{ cm}^{-1}$ . This is observed.

In a recent study of the magnetic properties of polypyrrole no correlation was observed between ESR signals and changes in conductivity with oxidation.<sup>27,28</sup> This has been interpreted as evidence for spinless charge carriers (bipolarons).<sup>27,28</sup> Since our model is quite general and does not depend on the nature of the charge carrier, bipolarons can be readily introduced into it.

## VI. SUMMARY

The charge transfer theory presented here accounts for the temperature dependence and magnitude of conductivity and the near IR optical spectrum of highly doped polypyrrole. The energy of maximum dielectric loss and the conductivity activation energy are shown to be determined by the reorganization energy for charge transfer between localized sites. The magnitude of the conductivity and the reorganization energy give self-consistent estimates of the hopping distance which correspond to the distance between anions. The dependence of conductivity on carrier density is qualitatively reproduced.

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