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PHOTOGENERATION OF CONFINED SOLITON PAIRS (BIPOLARONS)  
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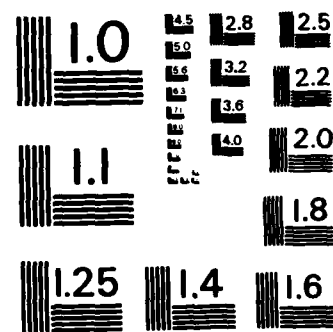
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Contract N00014-85-K-0098

Technical Report No. 1

Photogeneration of Confined Soliton Pairs (Bipolarons) in Polythiophene

Prepared for Publication in Physical Review Letters

by

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## REPORT DOCUMENTATION PAGE

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| 1a. REPORT SECURITY CLASSIFICATION<br>NONE                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |                                          | 1b. RESTRICTIVE MARKINGS<br>NONE                                                      |                       |
| 2a. SECURITY CLASSIFICATION AUTHORITY<br>NONE                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |                                          | 3. DISTRIBUTION/AVAILABILITY OF REPORT<br><br>Unlimited                               |                       |
| 2b. DECLASSIFICATION/DOWNGRADING SCHEDULE<br>NONE                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |                                          |                                                                                       |                       |
| 4. PERFORMING ORGANIZATION REPORT NUMBER(S)<br>IPOS - ONR # 1                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |                                          | 5. MONITORING ORGANIZATION REPORT NUMBER(S)<br>ONR N00014-85-K-0098                   |                       |
| 6a. NAME OF PERFORMING ORGANIZATION<br>University of California,<br>Santa Barbara                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    | 6b. OFFICE SYMBOL<br>(If applicable)     | 7a. NAME OF MONITORING ORGANIZATION<br>Office of Naval Research                       |                       |
| 8a. ADDRESS (City, State and ZIP Code)<br>Santa Barbara, CA 93106                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |                                          | 7b. ADDRESS (City, State and ZIP Code)<br>800 N. Quincy Avenue<br>Arlington, VA 22217 |                       |
| 9a. NAME OF FUNDING/SPONSORING ORGANIZATION<br>Office of Naval Research                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              | 9b. OFFICE SYMBOL<br>(If applicable)     | 9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER                                       |                       |
| 10a. ADDRESS (City, State and ZIP Code)<br>800 N. Quincy Avenue<br>Arlington, VA 22217                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                                          | 10. SOURCE OF FUNDING NOS.                                                            |                       |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |                                          | PROGRAM<br>ELEMENT NO.<br>-                                                           | PROJECT<br>NO.<br>-   |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |                                          | TASK<br>NO.<br>-                                                                      | WORK UNIT<br>NO.<br>- |
| 11. TITLE (Include Security Classification)<br>"Photogeneration of Confined Soliton Pairs (Bipolarons) in Polythiophene"                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |                                          |                                                                                       |                       |
| 12. PERSONAL AUTHOR(S)<br>Z. Vardeny, E. Ehrenfreund, O. Brafman, M. Nowak, H. Schaffer, A. J. Heeger and F. Wudl                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |                                          |                                                                                       |                       |
| 13a. TYPE OF REPORT<br>Technical                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     | 13b. TIME COVERED<br>FROM _____ TO _____ | 14. DATE OF REPORT (Yr., Mo., Day)<br>10/1/85                                         | 15. PAGE COUNT        |
| 16. SUPPLEMENTARY NOTATION<br>None                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |                                          |                                                                                       |                       |
| 17. COSATI CODES<br>FIELD GROUP SUB GR                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                                          | 18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)     |                       |
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| 19. ABSTRACT (Continue on reverse if necessary and identify by block number)<br><p>From photoinduced absorption and light induced electron spin resonance, we demonstrate that the dominant photocarriers generated in polythiophene with excitation above the energy gap (<math>E_g</math>) are charged bipolarons (spin zero). The observation of bipolarons (<math>B^{2\pm}</math>) rather than polarons (<math>P^\pm</math>) as the dominant photoexcitations demonstrates that the Coulomb contribution to the bipolaron energy (<math>U_B</math>) is sufficiently small that <math>P^\pm + P^\pm \rightarrow B^{2\pm}</math>. From the analysis of the spectra, we find <math>(U_B/E_g) \approx 0.12</math>.</p> <p><i>Handwritten:</i> <math>P^\pm</math> superscript + or - <math>B^{2\pm}</math> superscript + 2 + or - <math>U_B/E_g</math> <math>B^{2\pm}</math> superscript + or - 2</p> |                                          |                                                                                       |                       |
| 20. DISTRIBUTION/AVAILABILITY OF ABSTRACT<br>UNCLASSIFIED/UNLIMITED <input checked="" type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS <input type="checkbox"/>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |                                          | 21. ABSTRACT SECURITY CLASSIFICATION<br>Unlimited                                     |                       |
| 22a. NAME OF RESPONSIBLE INDIVIDUAL<br>A. J. Heeger                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |                                          | 22b. TELEPHONE NUMBER<br>(Include Area Code)<br>(805) 961-3184                        | 22c. OFFICE SYMBOL    |

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Photogeneration of Confined Soliton Pairs  
(Bipolarons) in Polythiophene

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ABSTRACT

From photoinduced absorption and light induced electron spin resonance, we demonstrate that the dominant photocarriers generated in polythiophene with excitation above the energy gap ( $E_g$ ) are charged bipolarons (spin zero). The observation of bipolarons ( $B^{2+}$ ) rather than polarons ( $P^+$ ) as the dominant photoexcitations demonstrates that the Coulomb contribution to the bipolaron energy ( $U_B$ ) is sufficiently small that  $P^+ + P^+ \rightarrow B^{2+}$ . From the analysis of the spectra, we find  $(U_B/E_g) \approx 0.12$ .

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The possibility that the dominant charged excitations for a non-degenerate ground state polymer are confined soliton pairs (bipolarons) with charge  $\pm 2|e|$ , rather than polarons is a fascinating new idea<sup>1-4</sup> in the field of conducting polymers. The existence of stable bipolaron excitations would prove that when two like charges are injected onto a polymer chain, there is an indirect attractive interaction due to the presence of a self-consistently generated local structural distortion. Moreover, Brazovskii et al. have shown<sup>5</sup> that such spinless bipolarons could exhibit Bose condensation to a novel charged superfluid state. Thus, the identification of the dominant charged excitations in conjugated polymers with a non-degenerate ground state is of special importance.

Most of the previous experiments<sup>6-10</sup> on non-degenerate ground state conducting polymers have used charge transfer doping to study the charge storage configuration. Although there is considerable evidence that upon doping, charge is stored in bipolarons,<sup>6-9</sup> the interaction of the electronic charges with the dopant ions could significantly change the energy. Moreover, in some cases the evidence from doping studies is controversial.<sup>6,10</sup> Therefore, the question of whether bipolarons are intrinsically the lowest energy charged configurations in such polymers remains open.

As a representative of the class of polymers with a non-degenerate ground state, polythiophene (PT) is an ideal candidate. It is highly crystalline<sup>11</sup> with a simple backbone geometry (Fig. 1) similar to that of cis-(CH)<sub>x</sub> but stabilized in that structure by the sulfur. Since there is detailed evidence<sup>7,12,13</sup> that the sulfur interacts only weakly with the  $\pi$ -electrons of the backbone, PT may be thought of as a pseudo-polyene.

Using steady-state photoinduced absorption spectroscopy<sup>14,15</sup> and light induced electron spin resonance,<sup>16</sup> we show in this paper that charged bipolarons are photo-generated in neutral polythiophene. Although we find specific evidence of the repulsive Coulomb contribution ( $U_B$ ) to the bipolaron energy, the existence of bipolarons (rather than polarons) as the dominant long-lived charged photoexcitations demonstrates that  $U_B$  is relatively small.

The photoinduced absorption spectrum of PT at 20K is shown in Fig. 1. These data were obtained using a chopped laser ( $\hbar\omega_L = 2.7$  eV) with  $I_L = 20$  mW cm<sup>-2</sup> for the modulated pump beam and an incandescent light source dispersed by a monochromator as the probe beam. The PT samples were pressed KBr pellets containing approximately 0.25 wt % PT powder (obtained by condensation polymerization<sup>17</sup> of 2,5-diiodothiophene) with an optical density corresponding to an effective thickness of about 1000 Å. The transmission (T) and the photomodulation ( $\Delta T$ ) were measured with appropriate detectors and a lock-in amplifier. The system response

was accounted for by taking the ratio  $\Delta T/T$  which is proportional to the change ( $\Delta\alpha$ ) in the sample absorption coefficient. The photoinduced absorption spectrum consists of four main<sup>12</sup> infrared active vibrational (IRAV) lines below 0.2 eV and two asymmetric electronic bands with  $\Delta\alpha > 0$ . The low energy band peaks at 0.45 eV and the high energy band peaks at 1.25 eV. The photoinduced absorption bands derive their strengths from states above 2 eV where  $\Delta\alpha$  changes sign and turns into induced bleaching ( $\Delta\alpha < 0$ ). The oscillations seen in the bleaching part of the spectrum are similar to those observed in the photoinduced spectrum of trans-(CH)<sub>x</sub><sup>18</sup> and may be due to electroabsorption from the photocarriers or phonon overtones of a discrete defect level.

For the first time, the full photoinduced spectrum, including IRAV lines, and the two electronic bands are observed together and compared quantitatively under the same experimental conditions. We verified that all of the features in Fig. 1 have a common origin by measuring their dependences on the excitation intensity  $I_L$ , temperature, and chopping frequency, and by measuring the individual excitation profiles. We found that all the spectral features show the same behavior. At low  $I_L$ , they all increase as  $I_L^{1/2}$  followed by saturation at high  $I_L$ , similar to the photoinduced soliton absorption in trans-(CH)<sub>x</sub>.<sup>15,19</sup> They all monotonically decrease in intensity by an order of magnitude when temperature is changed from 20 to 300 K, and they all give signals which lag

in phase by  $\approx 40^\circ$  from the laser illumination chopped at 140 Hz (implying a photocarrier lifetime of  $\sim 5$  ns).

The IRAV excitation profile is shown in Fig. 2. The absolute value of the number of photogenerated charges ( $N_{ch}$ ) was estimated by comparing the strength of the lower energy electronic band with the corresponding band in samples of known doping concentration;<sup>7</sup> the two independent data sets were thus normalized to  $N_{ch} = 2 \times 10^{-4}$  per thiophene ring at  $\hbar\omega_L = 2.5$  eV. Consistent data (with minor quantitative deviations) were obtained with the modulation technique<sup>14</sup> and with the FTIR method,<sup>15</sup> using a dye laser as the pump beam in the former and a high intensity Xe lamp with a series of narrow band pass filters in the latter. The excitation profile consists of a relatively narrow peak at 1.95 eV followed by a steep increase for  $\hbar\omega_L > 2.2$  eV. The two electronic bands show the same excitation profiles. The steep increase for  $\hbar\omega_L$  higher than the energy gap<sup>7,17</sup> indicates that free carrier absorption is involved as an intermediate step, similarly<sup>19</sup> to trans-(CH)<sub>x</sub>. We identify the 1.95 eV peak as due to an exciton. Since a bound electron-hole (e-h) pair on a single polymer chain would rapidly recombine, the exciton is probably a bound state of an e-h pair on neighboring chains. A specific defect level in the gap is ruled out, because the induced bleaching begins above 2 eV (Fig. 1). The proximity of the 1.95 eV peak to the peak in the luminescence spectrum<sup>9</sup> may indicate that the luminescence is due to interchain exciton

recombination.

Light induced electron spin resonance measurements were carried out<sup>18</sup> at 20 K and 100 K on similar samples (~ 1 wt% PT powder in KBr pellet); the excitation profile for photogenerated spins ( $N_S$ ) is shown in Fig. 2. The absolute value of ( $N_S$ ) was estimated from the relative strengths of the photoinduced and dark signals (the latter is known<sup>13,17</sup> to be about  $260 \times 10^{-6}$  per thiophene monomer). Although a photoinduced ESR signal was observed (indicative of photo-generation of polarons<sup>16</sup>), the excitation profile for photogenerated spins is completely different from the excitation profile for photogenerated charges. Moreover, after improving the structural order by annealing the PT at elevated temperature,<sup>11</sup> the number of photogenerated spins drops below the detectable limit whereas the photoinduced absorption signal remains. Thus, the dominant charged photoexcitations in PT are spinless. A relatively small number of spin-1/2 excitations are photogenerated in the lower crystallinity (as-synthesized) samples as reported earlier.<sup>16</sup> Since the spin-1/2 excitation profile peaks deep in the gap (~ 1.5 eV), and since the annealed samples show no photoinduced ESR, polaron excitation occurs via defect states deep in the gap resulting from structural imperfection. The lifetime for the photogenerated spins is ~ 1 sec (much greater than that of the photogenerated charges) consistent with deep trapping on a defect.

We conclude that the photoinduced absorption spectrum shown in Fig. 1 defines a single charged photoexcitation with electronic levels self-consistently localized in the gap. We propose that it results from charged, spinless bipolarons, and we identify the 0.45 eV and 1.25 eV bands as transitions  $\omega_1$  and  $\omega_3$ , respectively, as shown in Fig. 1 (inset). The identification is based on the following: a) The IRAV show that a structural distortion is involved and that the excitation is charged.<sup>21</sup> b) The 0.45 eV and 1.25 eV bands are asymmetric indicating that transitions from (to) continuum states are involved, in agreement with predictions<sup>4</sup> for bipolaron transitions (Fig. 1, inset). c) The photoinduced absorption spectrum is similar to the  $\Delta\epsilon$  spectra obtained for PT at dilute doping concentrations. These doping-induced spectral changes also show two asymmetric bands, at 0.65 eV and 1.45 eV, identified with bipolaron transitions.<sup>7</sup> Moreover, the difference  $\omega_3 - \omega_1 \approx 2\epsilon_0$ , is the same (0.8 eV) for photoinduced and doping induced<sup>7</sup>  $\Delta\epsilon$  spectra. If bipolarons are produced in both cases, the splitting between the two gap states should be the same and not depend on the generation process, since  $2\epsilon_0$  is due to confinement.<sup>4</sup>

Since the relation  $\omega_1^0 + \omega_3^0 = E_g$  would hold in absence of Coulomb repulsion, the transition energies are shifted;

$$\omega_1 + \omega_3 = E_g - 2U_B \quad (1)$$

where  $U_B$  is the difference in Coulomb energy between initial state (double charge) and final state (single charge) with fixed lattice coordinates. From Fig. 1,  $\omega_1 + \omega_3 = 1.7$  eV, while  $E_g \approx 2.1 - 2.2$  eV was inferred from the absorption spectrum.<sup>7,16</sup> A more accurate value for  $E_g^{1d}$  has been obtained<sup>22</sup> from analysis of the IRAV and resonance Raman data using the amplitude modes formalism;<sup>23,24</sup>  $E_g^{1d} = 2.2$  eV. From eqn. 1, we find  $U_B = 0.25$  eV or  $(U_B/E_g) = 0.12$ . This small value for is consistent with the existence of bipolarons rather than polarons as the dominant charged excitation. Since the polaron is a bound state of a neutral and a charged soliton<sup>4</sup> whereas the bipolaron is a confined pair of charged solitons, a large  $U_B$  would favor polaron formation. For doping induced bipolarons, the shift of each transition by  $U_B$  is compensated by the Coulomb binding to the dopant ion ( $E_B$ ) so that  $\omega_1 + \omega_3 = E_g - 2(U_B - E_B)$ . Since  $U_B$  and  $E_B$  depend primarily on the spatial extent of the bipolaron, the two contributions approximately cancel.<sup>7</sup> Since there is no splitting of either the 0.45 eV or the 1.25 eV bands, charge conjugation symmetry<sup>25</sup> holds for PT, and therefore eqn. 1 describes negative or positive bipolarons.

The finite positive value found for  $U_B$  demonstrates that the underlying mechanism for bipolaron formation in PT is quite different from the negative-U centers in 3d semiconductors introduced by Anderson<sup>26</sup> and carried over to defect pairs in the chalcogenide glasses<sup>27</sup> and to impurities and vacancies in silicon.<sup>28</sup>

In PT (and presumably more generally in conducting polymers), the bipolarons result from the confinement of charged solitons pairs.

The existence of long-lived charged bipolarons requires pairs of like charges on PT chains. Although intrachain absorption processes are expected to dominate, the resulting electron-hole pairs evidently rapidly recombine (neutral bipolarons should be unstable with a short lifetime). Photoexcitation of electron-hole pairs on neighboring chains is expected to occur because of the finite interchain bandwidth. Such interchain pairs form polarons and/or weakly bound excitons, and they play a transient role in the formation of the charged bipolarons which are observed at long times. As these polarons diffuse, they will form bipolarons when two polarons with the same charge appear in a single chain. A similar mechanism was proposed<sup>29</sup> for the photoexcitation of charged solitons in trans-(CH)<sub>x</sub>. The excitation profile (Fig. 2) suggests that pumping interchain excitons is a particularly efficient means of generating bipolarons in PT; the detailed mechanism by which this occurs is, however, not understood.

Our work does not exclude the importance of charge states different from bipolarons under different circumstances: Polarons were identified<sup>8,9</sup> in electrochemically prepared samples at dilute doping concentrations (< 1%). This may indicate slow kinetics of the reaction  $P^+ + P^+ \rightarrow B^{+2}$  for disordered samples with relatively low crystallinity. A small number of polarons are observed<sup>18</sup> as

photoexcitations in as-synthesized PT, as described above. Measurements with  $\hbar\omega_L = 1.95$  eV (which is the peak in the IRAV excitation profile below the gap) yield an IRAV spectrum identical to that in Fig. 1, but the intensity of the 1.25 eV band is reduced by a factor of two and the lower energy band peaks at 0.35 eV. This, and the observation that the excitation profile for photogeneration of spins peaks at  $\sim 1.5$  eV, suggest that different charge states contribute for excitation at  $\hbar\omega_L < E_g$ .

In conclusion, we have shown that the dominant charge states in PT generated with  $\hbar\omega_L > E_g$  are bipolarons. The observation of bipolarons, rather than polarons, as the long lived charged excitations demonstrates that the Coulomb contribution to the bipolaron energy is relatively small; from analysis of the spectra, we find  $(U_B/E_g) \approx 0.12$ . Since  $U_B > 0$ , stable bipolarons result from the confinement of charged soliton pairs. The existence of bipolarons during photoexcitation or after doping thus implies an indirect attractive interaction between two like charges due to a self-consistently generated local structural distortion.

### Acknowledgment

We thank Dr. F. Moraes and Dr. Y.-W. Park for help and advice on the photoinduced ESR experiments. The work at Technion was supported by the US-Israel BSF; the work at UCSB was supported by the Office of Naval Research (photo-induced absorption) and by the National Science Foundation DMR82-12800 (ESR).



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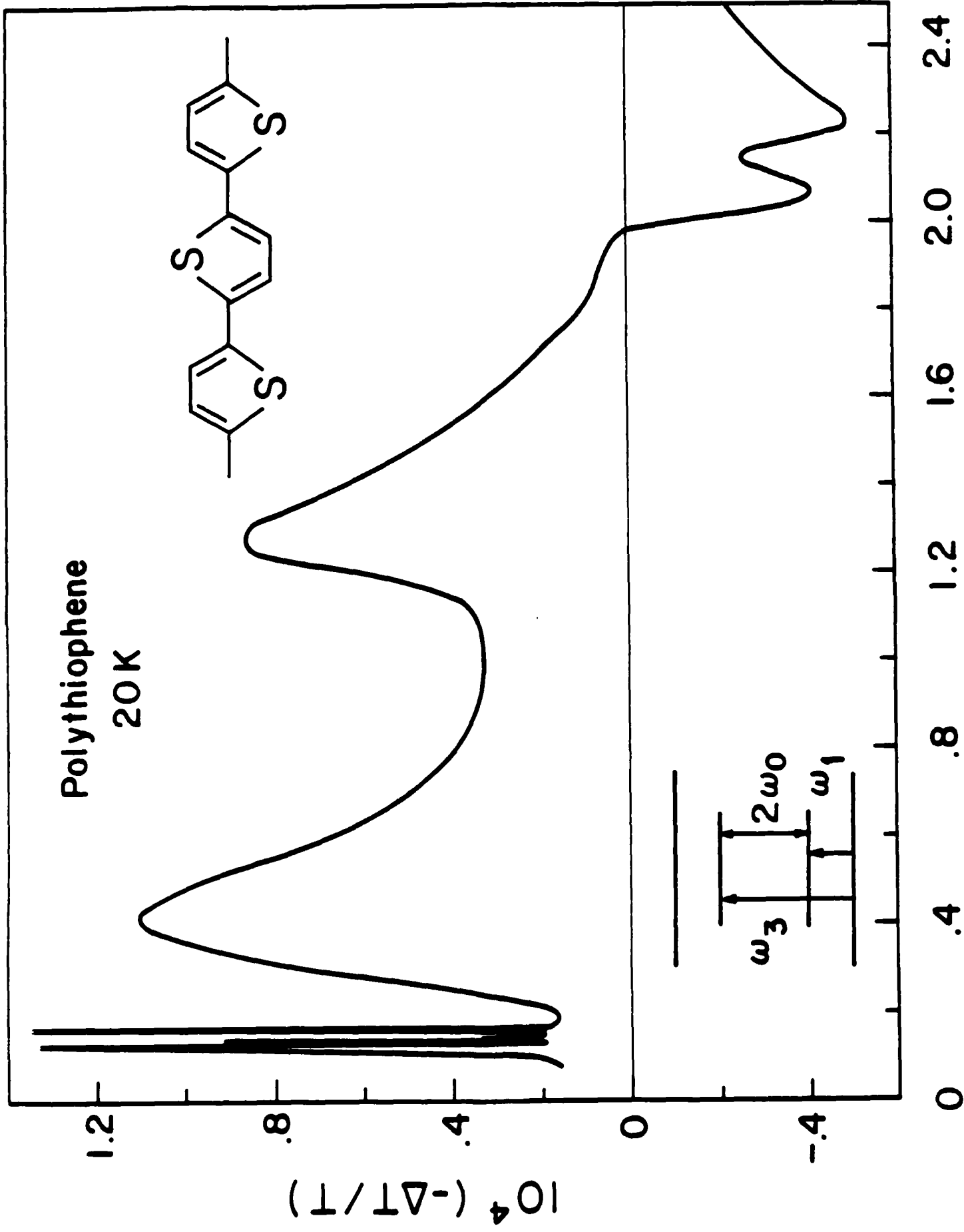
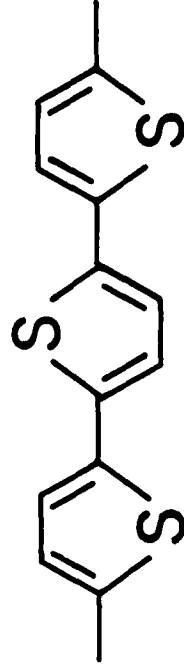
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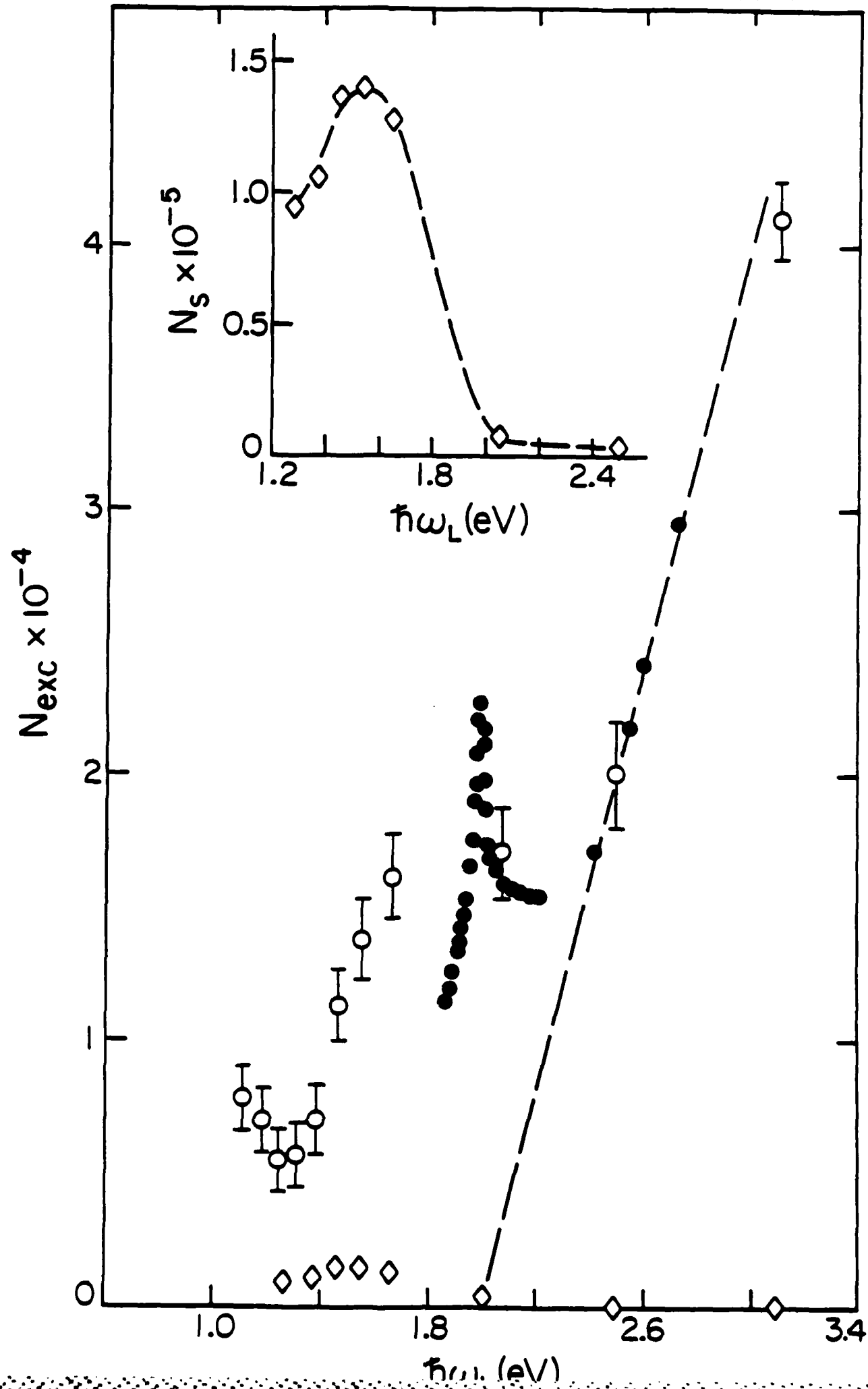
## Figure Captions

1. Photoinduced absorption of PT at 20 K obtained with  $I_L = 10 \text{ mW cm}^{-2}$  at  $\omega_L = 2.7 \text{ eV}$ . The insets show a chemical structure diagram of PT (upper) and the energy levels and allowed transitions for  $B^{2+}$  (lower).
2. Excitation profile of PT;  $N_{Ch}$  (ooo and ooo) and  $N_S$  (xxx) are plotted as a function of pump energy ( $\omega_L$ ). The dots were obtained with the modulation technique (20 K), open circles with FTIR ( $\sim 100 \text{ K}$ ). Both  $N_{Ch}$  and  $N_S$  were normalized (by  $I_L^{1/2}$ ) to an equivalent pump power of  $10 \text{ mW cm}^{-2}$ . The dashed line extrapolates to the observed energy gap ( $\sim 2 \text{ eV}$ ). The inset shows  $N_S$  vs.  $\omega_L$  on an expanded scale.

Polythiophene

20K





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