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Excitons in poly(*para*-phenylenevinylene)

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We show that one-electron band theory fails to describe optical absorption in PPV and the absorption spectrum can be described only within a Coulomb-correlated model. The lowest optical state is an exciton, whose binding energy is estimated theoretically to be 0.90±0.15 eV. Measurements of the photoconductivity quantum efficiency in poly[2-methoxy,5-(2′-ethyl-hexyloxy)-1,4 phenylenevinylene] reveal a binding energy in good agreement with the theoretical value.

The role of electron correlations in π-conjugated polymers has been a topic of continuing debate for more than a decade.[1,2] Current interest in π-conjugated polymers stems from the recent demonstration of electroluminescence in poly(p-phenylenevinylene) (Ref. 3) (PPV) (see Fig. 1) and poly[2-methoxy,5-(2′-ethyl-hexyloxy)-1,4 phenylenevinylene] (Ref. 4) (MEH-PPV). The nature of the primary photoexcitations in PPV derivatives is presently highly controversial.[5] Indirect evidence for the excitonic nature of the lowest photoexcitation, implying moderate to strong Coulomb interactions,[2] is found in a number of experiments,[6–9] but estimates of the exciton binding energy E_b vary widely, from 0.4 (Ref. 10) to 1.1 eV.[8] In contrast, the observation of photoconductivity (PC) at the absorption threshold has been interpreted as an indication of delocalized electrons and holes in the lowest excitation,[11] and therefore of weak Coulomb interaction.[1]

We present here direct theoretical *and* experimental demonstrations of the excitonic nature of the lowest excitations of PPV. Theoretically, we give a convincing proof that the optical absorption in PPV and its derivatives cannot be explained within one-electron theories, and estimate E_b in PPV as 0.90±0.15 eV. From measurements of the PC quantum efficiency in MEH-PPV we then determine experimentally $E_b=0.95\pm0.15$ eV.

Our theoretical model is similar to the Pariser-Parr-Pople (PPP) model for π-conjugated systems,

$$H=U\sum_i n_{i,\uparrow}n_{i,\downarrow}+\tfrac{1}{2}\sum_{i,j} V_{ij}(n_i-1)(n_j-1) - \sum_{\langle ij\rangle,\sigma} t_{ij}[c^\dagger_{i,\sigma}c_{j,\sigma}+c^\dagger_{j,\sigma}c_{i,\sigma}]. \quad (1)$$

Here $c^\dagger_{i,\sigma}$ creates a π electron of spin σ on carbon atom i, $n_{i,\sigma}=c^\dagger_{i,\sigma}c_{i,\sigma}$, $n_i=\Sigma_\sigma n_{i,\sigma}$, and t_{ij} is the one-electron hopping integral ($\langle\,\rangle$ implies nearest neighbors). We consider standard $t_{ij}=t=2.4$ eV for the phenyl bonds. In order to have the lowest optical state at comparable energies, we choose $t_{ij}=t_1$ (t_2)=1.9 (2.9) eV for the single (double) bonds of the vinylene units for noninteracting electrons, and 2.2 (2.6) eV for interacting electrons. Our conclusions are independent of the magnitudes of t_{ij}. U and V_{ij} are the on-site and long-range Coulomb interactions, respectively. V_{ij} are assumed to have the Ohno[12] form,

$$V_{ij}=U/(1+0.6117R^2_{ij})^{1/2}, \quad (2)$$

where R_{ij} is the distance, in Å, between carbon atoms i and j. We have verified that the results obtained with other forms of V_{ij} are identical. Unlike the standard PPP model, we consider the entire range of interactions from the Hückel model ($U=0$) to the full PPP potential ($U=4.64t$).

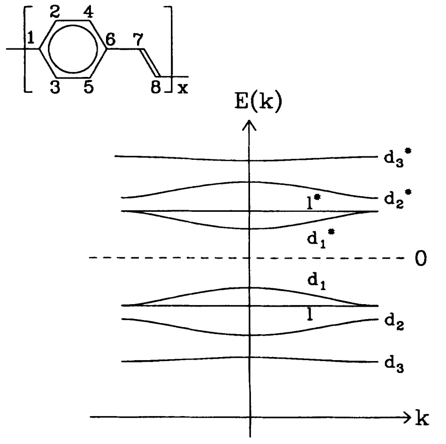

FIG. 1. Band structure of PPV with the unit cell shown as an inset.

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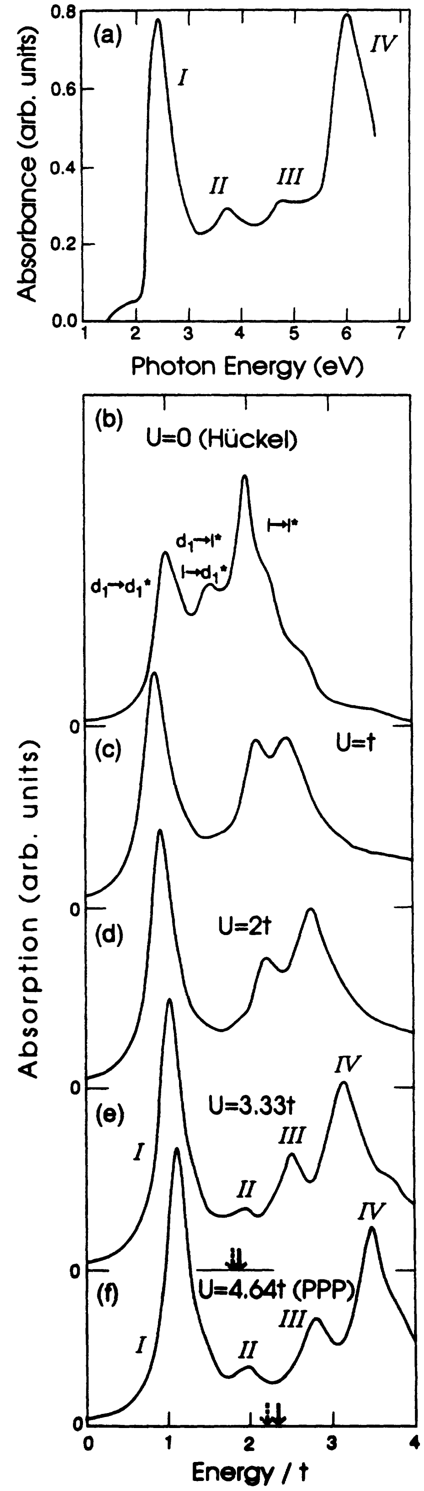

FIG. 2. (a) Experimental absorption spectrum of a thin film of MEH-PPV. (b) Calculated linear absorption for a 12-unit PPV oligomer with a linewidth parameter $\Gamma = 0.3$ eV. (c)–(f) calculated linear absorption for an 8-unit oligomer for $U = 2.4$, 4.8, 8, and 11.13 eV, respectively, with $\Gamma = 0.4$ eV. The solid and dashed arrows on the x axes in (e) and (f) indicate the HF band threshold and the nB_u, respectively.

For $U = 0$ the band description is valid. The band structure of PPV is shown in Fig. 1. Electrons in the d_i and d_i^* bands are delocalized over all carbon atoms, while the localized l and l^* bands have electron densities only on carbon atoms 2, 3, 4, and 5 (Fig. 1, inset).

The experimental absorption spectrum of a MEH-PPV thin film [see Fig. 2(a)] has a low-energy band that peaks at 2.4 eV (peak I), two additional small peaks at 3.7 and 4.7 eV (peaks II and III, respectively), and a strong broad band centered at 5.9 eV (peak IV). Very similar absorptions are observed in other PPV derivatives,[13] while in PPV itself the 3.7-eV peak appears as a distinct shoulder[14] on a broad peak I. We therefore consider the spectrum of Fig. 2(a) as characteristic of the π-conjugation network of PPV, with the side-groups affecting the absorption spectrum weakly. Consequently, our theoretical work is for PPV only.

The calculated $U = 0$ absorption spectrum for a 12-unit capped PPV oligomer finds a *single* central peak in between two strong transitions [see Fig. 2(b)]. The strong absorption at low energy corresponds to $d_1 \rightarrow d_1^*$ transitions. The high density of states of the l and l^* bands lead to the second strong absorption at high energy, while the weak central peak is predominantly due to the degenerate $d_1 \rightarrow l^*$ and $l \rightarrow d_1^*$ transitions. All optical transitions involving the d_2, d_3, d_2^*, and d_3^* bands are weak. The occurrence of a single central peak is associated with the accidental degeneracies peculiar to the Hückel model.[15]

The origin of four, instead of three, peaks in the absorption spectrum must be attributed to electron correlations. For $U > 0$, we include configuration interaction (CI) with all single excitations (hereafter SCI).[14,16] The limitations of the SCI approximation are understood from comparisons of recent SCI (Ref. 16) and exact finite-chain calculations[17] of the third-order optical nonlinearity of the polydiacetylenes. SCI misses the covalent even-parity A_g states,[18] but both SCI and finite-chain calculations find that optical nonlinearity is determined almost entirely by the optically allowed odd-parity $1B_u$ exciton, a dominant A_g exciton (the mA_g) above the $1B_u$, and the threshold of the conduction band (the nB_u). Thus SCI captures the essential *qualitative* physics of the energy region of interest here. Our estimates for the exciton binding energy are based on such qualitative considerations and not quantitative comparisons, as SCI is known to overestimate the band gap.

In Figs. 2(c)–2(f) we show the calculated absorption spectra for an eight-unit capped PPV oligomer for $U/t = 1.0$, 2.0, 3.33, and 4.64, respectively. At $U/t = 1$, the central peak of the $U = 0$ spectrum has weakened, while the intense high-energy peak has split into two peaks of comparable intensities. With further increase in U/t to 2.0 a distinct absorption appears in the region of peak III, but the overall absorption is still different form the experimental spectrum. Only for $U/t = 3.33$ and 4.64 do the calculated spectra resemble the experimental spectrum.

The evolution of the spectra in Figs. 2(c)–2(f) can be understood from analysis of the CI wave functions.[19] At the smallest U, the CI and Hartree-Fock (HF) results are nearly the same. HF induces mixing of Hückel ground-state and excited configurations, thus reducing the intensities of all absorptions. The central peak, weak to begin with, thus dis-

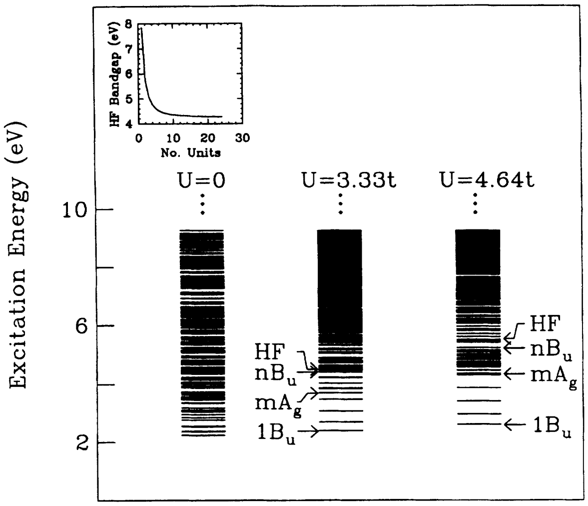

FIG. 3. Excitation energy spectra of a 12-unit PPV oligomer for $U=0$ and an 8-unit PPV oligomer for $U=3.33t$ and $4.64t$, respectively. The $1B_u$, mA_g, nB_u, and the HF band threshold are indicated. The inset shows the HF band threshold for $U=3.33t$ against the number of PPV units.

appears. CI between the $l \rightarrow l^*$ and the $d_1 \rightarrow l^*$ and $l \rightarrow d_1^*$ leads to the splitting of the high-energy peak in Fig. 2(c). At still larger U, CI is stronger, and peaks II, III, and IV in Figs. 2(e) and 2(f) arise from transitions to states that are strong admixtures of configurations involving the l and l^* levels. The appearance of a larger number of absorptions, upon including CI, is well known in molecular quantum chemistry.[15]

In Fig. 3 we show the excitation energies for $U/t=0$, 3.33, and 4.64. The conduction-band edge for $U>0$ in SCI is the HF gap,[16] above which the states are seen to be continuumlike and more closely spaced than the $U=0$ band levels. The band edge was also calculated separately according to the prescription of Ref. 17, viz., the mA_g state is first identified as the unique A_g state with exceptionally large dipole coupling with the $1B_u$; the band threshold nB_u state is then identified from its large dipole coupling with the mA_g. As seen in Fig. 3, the two estimates of the conduction-band threshold are close. *The nB_u is weakly dipole coupled to the ground state and is not visible in absorption.*[17] As shown in the inset of Fig. 3, the HF band threshold does not change significantly beyond eight units. Thus the only difference in a long chain would be the appearance of a true continuum above the band threshold. Peak I in Figs. 2(e) and 2(f) is due to transition to the $1B_u$. The discrete nature of the energy spectrum in this region for nonzero U indicates that the $1B_u$, and several other low-lying states, are excitons. The dense levels immediately below the continuum edge for $U/t=4.64$ are linear combinations of the $d_1 \rightarrow l^*$, $l \rightarrow d_1^*$, and $l \rightarrow l^*$ configurations. These levels occur above the band threshold for $U=3.33t$. Transitions to these levels give rise to peak II in Figs. 2(e) and 2(f). Our measurement of the PC quantum efficiency (see below) shows that the conduction-band threshold is below peak II, indicating that the full PPP potential is too large. We therefore do not discuss $U=4.64t$ any further.

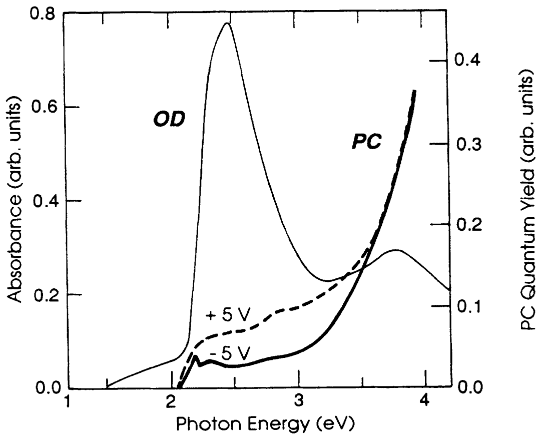

FIG. 4. PC quantum efficiency of an ITO/MEH-PPV/Al photodiode, with the ITO being biased at +5 and −5 V, respectively. The absorption spectrum of a thin film of MEH-PPV is also shown.

The experimental peak at 3.7 eV [Fig. 2(a)] corresponds to peak II in Fig. 2(e). Although the energies of peak II and the band threshold are too high within SCI, the remarkable similarity between the experimental and the calculated spectra allows us to correctly estimate the continuum threshold in PPV. We use two independent approaches to estimate this threshold. The first approach is based on the comparison of calculated and experimental linear absorption. The second is based on a similar comparison involving *nonlinear* spectroscopy.[8,20]

The arrows on the x axis of Fig. 2(e) give the locations of the nB_u and the HF band threshold. Scaling the calculated energy levels above the $1B_u$ such that the calculated peak II will occur at 3.7 eV, we find the continuum threshold at ~3.4 eV. Since the exciton in PPV is at ~2.4 eV, an upper limit of $E_b \sim 1.0$ eV is thus obtained.

An independent estimate of the *lower limit* for E_b is obtained from the relative location of the mA_g, which has been found to occur 0.5–0.6 eV above the $1B_u$ exciton in both two-photon absorption[20] and electroabsorption.[8] From comparison of previous SCI (Ref. 16) and exact finite-chain calculations[17] for the polydiacetylenes, it is known that SCI predicts an upper limit for $\Delta E_m / E_b$, where ΔE_m is the energy difference between the mA_g exciton and the $1B_u$ exciton. This is *expected*, as higher-order CI lowers the energies of the A_g states more than the B_u states. From our calculated $\Delta E_m / E_b = 0.68$ for $U=3.33t$ and the experimental ΔE_m of 0.5 eV, we predict a *lower limit* of 0.75 eV for E_b. *Note that our approaches involving comparisons to experiments bypass the problems associated with "gas-phase" calculations.* Our theoretical estimate of E_b in PPV is thus 0.90 ± 0.15 eV.

We have determined E_b in MEH-PPV experimentally by measuring the PC quantum efficiency $\eta(\omega)$, as a function of the photon excitation energy from 1.5 to 4 eV (see Fig. 4). PC was measured in a MEH-PPV photodiode,[21] constructed in a sandwich configuration of a semitransparent indium-tin-oxide (ITO) bottom electrode, an ~1000-Å MEH-PPV layer, and an aluminum (Al) top electrode. The measurements were at room temperature in vacuum, and the modulated illumination was provided from a premonochromatized 300-W xenon lamp through the ITO electrode, biased at +5 and −5 V, respectively. The PC spectrum was then divided by the spectral response of the system and the number density of the absorbed photons to give the spectrum of $\eta(\omega)$. As seen in Fig. 4, both η curves have two onsets: one at the exciton energy near 2.2 eV and the other at ~3.1 eV, where η starts to show a much steeper increase, *even though there is no corresponding features in the absorption spectrum* (note that the absorbance of MEH-PPV varies only slightly at ~3.1 eV and the increase in η cannot be caused by changes of the photon penetration depth around this energy[22]). Our PC quantum yield in MEH-PPV is in agreement with the photocurrent measurements in PPV (Ref. 22) up to 2.9 eV for biases from -2 to $+2$ V. The bias voltages of ± 5 V, much larger than those used previously,[22] and 10 times larger than the built-in potential of 0.5 V caused by the work-function difference between the two electrodes,[23] apply an external field of $\sim \pm 5 \times 10^5$ V/cm, thus compensating for the inhomogeneity of the internal electric field. The PC spectra from the first onset to below the second onset probably result from exciton dissociation or ionization.[13] Their relative magnitudes at 2.54 eV are in agreement with the photoinduced I-V characteristics of MEH-PPV light-emitting diodes.[23] The more important second onset clearly shows a different process being turned on at ~3.1 eV and the most natural explanation is that it arises from the continuum threshold, since at this high electric field direct-carrier photogeneration gives a much higher signal than carriers produced by exciton dissociation. The photogenerated carriers might also aid the dissociation of localized excitons by impact ionization. Linear extrapolation[24] of $\eta(\omega)$ gives the location of the continuum threshold at 3.1 ± 0.1 eV. Since the $1B_u$ exciton in MEH-PPV is located at 2.15 ± 0.05 eV, our experimental estimate of E_b is 0.95 ± 0.15 eV. Nearly the same binding energy is obtained from our measurements of PC quantum efficiencies in other PPV derivatives, as well as with calcium as the top electrode. These results will be reported elsewhere. In photoluminescence-detected magnetic-resonance (PLDMR) measurements, visible excitation yields a PL-enhancing polaron resonance in PPV's as well as in other π-conjugated polymers.[25] Recent measurements with UV excitation has found PL-quenching polaron PLDMR in MEH-PPV above a threshold energy that is very close to the continuum threshold found in this paper.[26] If the PL-quenching resonance is due to itinerant-band polarons, it would be entirely consistent with our estimate of E_b.

In conclusion, explicit inclusion of electron correlation is essential for a theoretical description of PPV and its derivatives. Comparisons of theoretical calculations and experimental linear and nonlinear optical spectra predict an exciton binding energy of 0.95 ± 0.15 eV, in excellent agreement with the binding energy extracted from measurements of PC quantum efficiency. Our conclusion has important implications for the entire class of π-conjugated polymers.

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