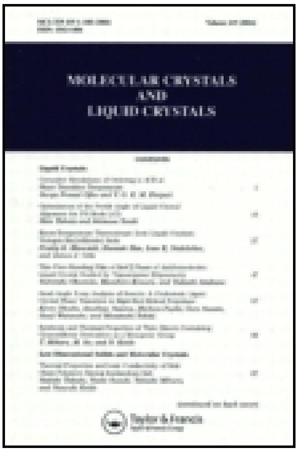

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Electroabsorption and Charged-Excitation Spectroscopy of II-Conjugated Polymers

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ELECTROABSORPTION AND CHARGED-EXCITATION SPECTROSCOPY OF Π-CONJUGATED POLYMERS

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Abstract Electroabsorption (EA) and photoinduced absorption excitation (PAE) spectra for charged excitations have been measured for luminescent [poly(phenylene acetylene), PPA] and nonluminescent (polydiethynyl silane, PDES) π-conjugated polymers at 80K, over the spectral range from 1.5 to 4 eV. Based on these measurements, a discussion of the locations of the singlet $1B_u$ and A_g states is presented, as well as an analysis of the first- and second-derivative nature of the EA lineshapes. It is argued that luminescence (or lack of) in these polymers depends on the location of an A_g state in close proximity to the $1B_u$ state.

INTRODUCTION

Electroabsorption (EA) spectra in conjugated polymers exhibit similar features. These include a large oscillation in $\Delta\alpha$ at the absorption edge associated with the Stark shift of the $1B_u$ exciton, and secondary higher-energy oscillations. And yet, in terms of EA, conjugated polymers seem to fall into two broad categories, following either the first derivative of absorption[1-7] or the second derivative of absorption.[1,2,8-12] A combination of the two is of course possible.[4] The features of EA spectra in these materials have been discussed in terms of lifetime broadening, the Stark effect, interband coupling, charge-transfer, Davydov splitting, and field-induced oscillator-strength transfer to forbidden states (see above references). Often seen is a high-energy feature (typically almost 1 eV higher) which does not correlate to anything in the absorption spectrum, although not all published studies show the extended EA spectra.

We assume that the general energy band scheme for conjugated polymers follows that suggested by a number of authors,[13-17] leading to a qualitative energy level diagram consisting of a ground state ($1A_g$), a singlet exciton state ($1B_u$), and other A_g and B_u states existing above the $1B_u$ exciton which eventually form a continuum band. Of particular importance may be an A_g state (mA_g) trapped between B_u states and strongly interacting with the $1B_u$ exciton, a B_u state just below a continuum band, and an A_g state ($2A_g$) in the vicinity of the $1B_u$ exciton. A triplet manifold also exists. Allowed and forbidden transitions between these energy states are easily predicted on the basis of symmetry.

EXPERIMENTAL PROCEDURE

For the EA experiments, polymer samples (about 1000 Å thick) were prepared and data acquired as described elsewhere.[10] The resulting $-\Delta T/T$ spectrum scaled linearly with intensity and quadratically with field strength, and was free of thermal modulation effects. The optical constants of these polymers are such that $-\Delta T/T = \Delta\alpha d$ to a good approximation.[2] For the PAE experiment, thick polymer samples with an optical density (OD) greater than 2 were solution-cast on sapphire substrates. $\Delta T/T$ at a single probe energy associated with the PA band for charged excitations (about 0.5 eV for PDES and about 0.8 eV for PPA) was measured as the sample was photoexcited with photon energies from below the HOMO-LUMO gap to ultraviolet energies. Quantum efficiencies (QE) were calculated by normalizing the excitation spectrum to the absorbed number of photons.

RESULTS

The EA and absorption first derivative spectra for PPA at 80K are shown in Fig. 1A. The EA and absorption second derivative spectra for PDES at 80K are shown in Fig. 1B. The EA spectra of both materials show important similarities, indicating that similar physical mechanisms contribute to their optical properties. Both EA spectra show strong induced absorption at low energies *(a)*, followed by weaker bleaching with superimposed oscillations. Each spectrum also shows a relatively weak induced absorption *(b)*, not obviously connected with any bleaching, at about 0.6 or 0.7 eV above the primary exciton transition. This induced absorption also has no analog in the absorption spectrum for either polymer.

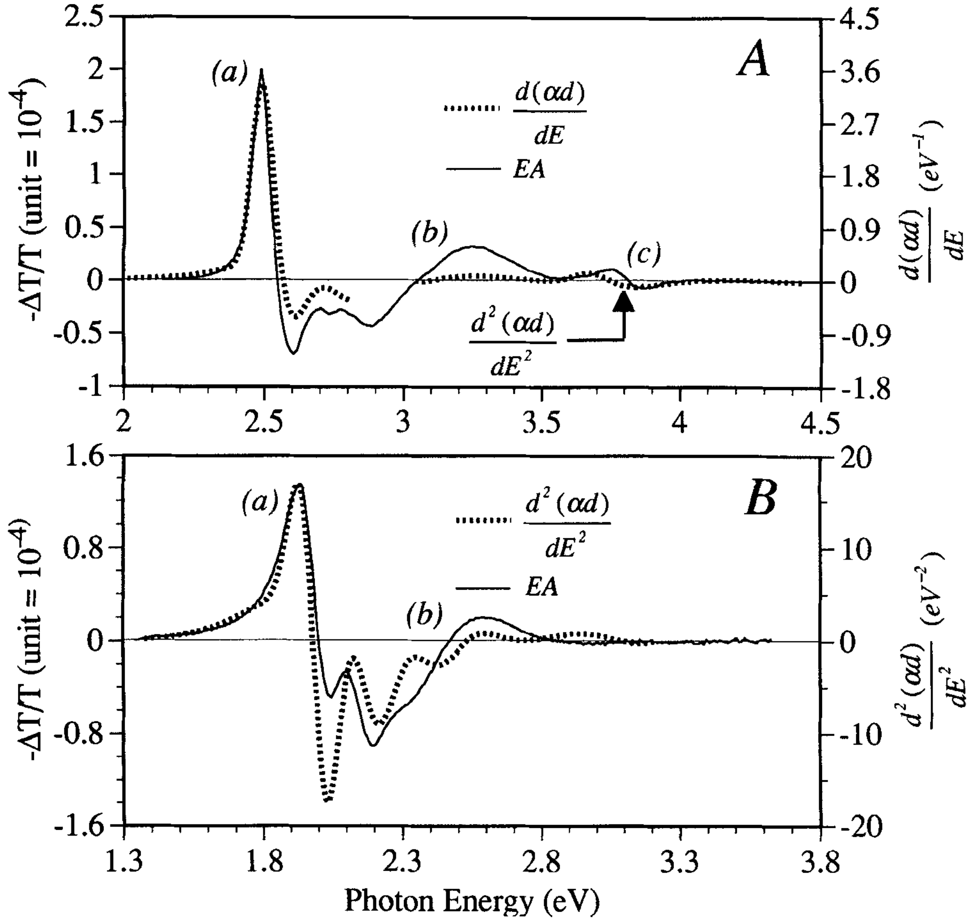

Figure 1. EA and Derivatives for PPA and PDES

On the other hand, there are important differences in the two EA spectra. Most obvious is that at low photon energies *(a)*, PPA follows an absorption first-derivative lineshape, whereas PDES seems to follow an absorption second derivative (Figs. 1A and 1B). We especially note that both quickly depart from any correlated derivative lineshape soon after the low-energy zero-crossing. In addition, neither shows a derivative structure that correlates with the high-energy induced absorption *(b)*. The PPA EA also shows a peculiar signature at about 3.8 eV *(c)*. Such a signature is also seen in MEH-PPV, although it is much weaker.[18] This feature can be seen in the derivatives but does not correlate well with either. Finally, region *(a)* in the EA spectrum in PDES has a broader low-energy tail than that seen in PPA or other polymers we have tested (*e.g.*, MEH-PPV[18]).

Figures 2A and 2B show the absorption and PAE QE spectra for PPA and PDES, respectively.

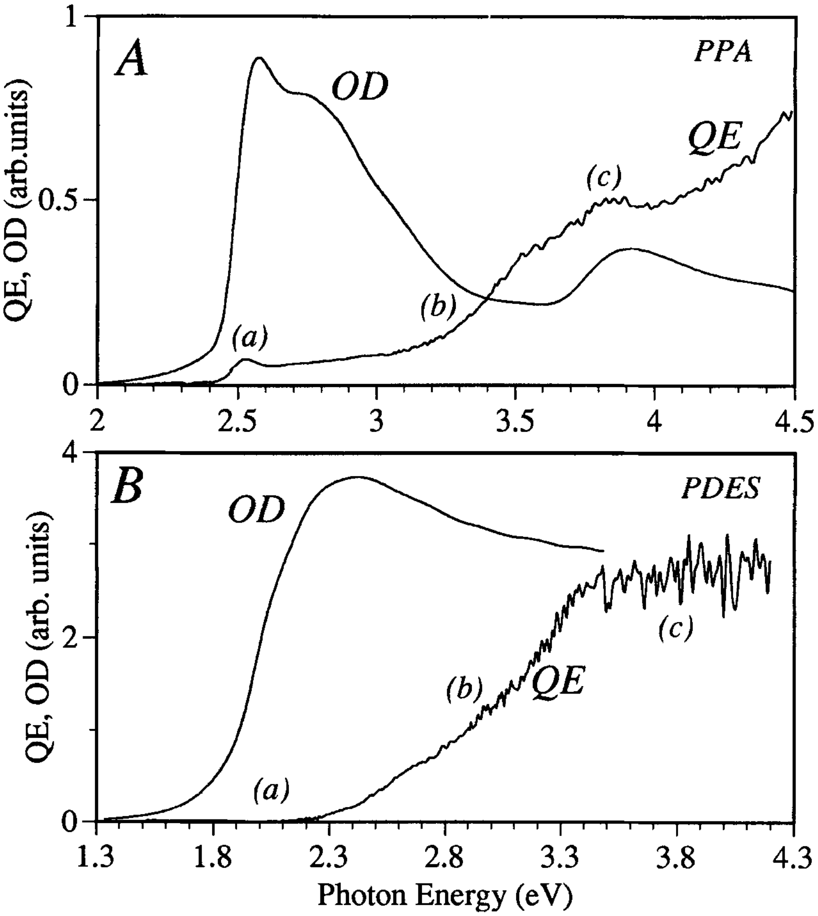

Figure 2. Optical Density and QE for PPA and PDES.

The PPA absorption has a relatively well-resolved peak at about 2.5 eV, a shoulder at about 2.8 eV, and another transition at about 3.8 eV (same location as the "peculiar" feature in EA in Fig. 1A). The absorption for PDES is noticeably different, with a very broad peak centered at about 2.4 eV, a weak shoulder at about 2 eV, a tail into the gap, and no discernible high energy features. Seen in the QE spectra are three distinct regions (Figs. 2A and 2B; *a*, *b*, and *c*). In PPA, region *(a)* shows a sharp onset correlated with the absorption at 2.5 eV, while region *(b)* shows an additional increase which clearly implies a higher-energy charge-generation channel. Region *(c)* would appear to be related to the 3.8 eV feature. On the other hand, the QE spectrum of PDES shows no feature correlated with the exciton absorption *(a)*, but does show the same sort of high-energy increase *(b)* as seen in PPA. The QE spectrum of PDES saturates above 3.4 eV *(c)*. Although not discussed here, a very similar comparison occurs for the PDES triplet-triplet QE and the PPA 1.7 eV transition QE spectra.

DISCUSSION

The quadratic Stark shift of an energy level is given by $\Delta E = -\frac{1}{2} pF^2$, where p is the polarizability of the energy state, and F is the field strength. This shift produces an EA spectrum that follows the first derivative of the absorption, which is clearly seen for PPA in Fig. 1A. A comprehensive derivation of the relationship in full tensor notation is given by Mathies;[19] simplification assuming electron mobility only in the direction of the chain yields a result similar to that given by Kepler:[5]

$$\Delta\alpha d = \frac{7}{60}\Delta p F^2 \frac{d(\alpha d)}{dE} \qquad (1)$$

where E is the photon energy, α is absorption coefficient, d is the sample thickness, and Δp is the difference between the polarizabilities of the ground and excited states. Applying this relationship to the data for PPA yields $\Delta p \approx 1500$ Å^3. This result is intermediate to that of DCHD PDA ($\Delta p \approx 8200$ Å^3; exciton binding energy of ≈ 0.5 eV[20]) and PMPS ($\Delta p \approx 180$ Å^3; exciton binding energy of ≈ 1.1 eV[5]), and implies a binding energy in PPA between 0.5 and 1.1 eV.

The second derivative nature of the PDES EA (Fig. 1B) precludes the obvious application of Eq. 1, and instead implies some sort of charge transfer mechanism, *e.g.*, a change in permanent dipole moment, or a charge transfer exciton. An approach not unlike that for Eq. 1 yields the result[19]

$$\Delta\alpha d = \frac{1}{10}(\Delta\mu)^2 F^2 \frac{d^2(\alpha d)}{dE^2} \qquad (2)$$

where $\Delta\mu$ represents the change in dipole moment. Application of this equation to the data for PDES yields $\Delta\mu \approx 5$ eÅ. This contrasts with reports of highly delocalized exciton states in other materials; in addition, this value is not consistent with a charge transfer exciton in PDES, whose unit cell is larger than 5 Å. Of greater concern in this analysis is the lack of a Stark shift mechanism. The EA spectra of PPA and PDES are not so dissimilar that one can easily invoke the Stark shift for one and neglect it for the other. An alternative explanation is that the coupling between allowed and forbidden states in an electric field produces a second-derivative-like lineshape in PDES. This effect has long been known for F-centers in alkali-halide crystals,[21] in which a field-induced shift in oscillator strength to a *nearby* forbidden transition creates the appearance of a second-derivative lineshape. This possibility for conjugated polymers may explain the second-derivative lineshape in PDES without resorting to charge-transfer arguments.

The Stark shift of the $1B_u$ exciton is accompanied by a loss of oscillator strength which can be transferred to forbidden states. One of these is the higher-energy mA_g state, which may be close to a nearby continuum band.[15,16,22] Another is an A_g state ($2A_g$), whose position sensitively depends on the chain length,[13] and can be very close to the $1B_u$ state. Our data for PDES suggest that the $2A_g$ state does exist below and in close proximity to the $1B_u$ state. This is already implied by the fact that PDES is not luminescent. An A_g state very close to and below the $1B_u$ exciton can provide an decay channel which rapidly depopulates the photoexcited $1B_u$ excitons. Pump and probe experiments at 2 eV show that the $1B_u$ exciton decays in less than 1 ps.[23] In addition, the QE spectrum (Fig. 2B) of PDES shows a complete absence of spectral feature at the $1B_u$ energy level *(a)*, in contrast to the spectrum for PPA (Fig. 2A). It has been argued that this $2A_g$ state will be difficult to observe in EA experiments[14,24] because of the weakness of the $\langle 2A_g|\mu|1B_u\rangle$ matrix element; however, the value of the matrix element as calculated may not be valid for disordered materials with a chain-length distribution, which would tend to make the $2A_g$ location ill-defined, perhaps splitting it into a band and complicating the mixing of states due to an electric field. In addition, the near-degeneracy of the $2A_g$ and $1B_u$ states could lead to effects not considered theoretically. The signature of such a $2A_g$ state as a field-induced forbidden transition below the $1B_u$ exciton is also implied by the uncharacteristic broadness of the EA spectrum at 1.9 eV, compared to PPA. Further evidence of the existence of this state and its close proximity to the $1B_u$ exciton is seen in strain-induced absorption measurements.[25]

In the spirit of Ref. 26, we have subtracted the absorption first-derivative lineshape for each polymer from the EA spectrum. The resulting difference should be related to the field-induced change in oscillator strength (Δf), if no other mechanisms are involved. As the PPA EA spectrum very closely coincides with the first-derivative at low energies, we retain the value $\Delta p = 1500$ Å^3. The result for PPA is shown in Fig. 3, and indicates a loss in oscillator strength at the $1B_u$ exciton *(a)*, with a gain at the location of the mA_g state *(b)*. Minor gain and loss is also seen at the unknown feature at 3.8 eV *(c)*. The integrated spectrum is close to zero, justifying the assumption for Δp.

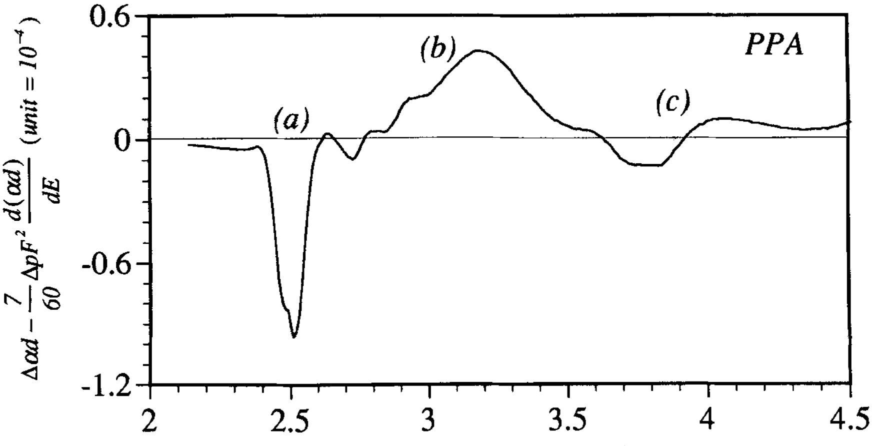

Figure 3. Difference between EA and First-Derivative for PPA

As a working assumption, we set Δp for PDES at 1500 Å^3 also, with the result shown in Fig. 4. One can clearly see an increase in oscillator strength not only at the mA_g location *(b)*, but also in close proximity *(d)* to the loss for the $1B_u$ exciton *(a)* (which also might appear to have a sideband). We suggest this as the source of second-derivative-like lineshapes in PDES. By assuming or otherwise knowing the locations and symmetries of other states, one can fit the EA lineshape closely with only the first-derivative of absorption and the Δf spectrum.

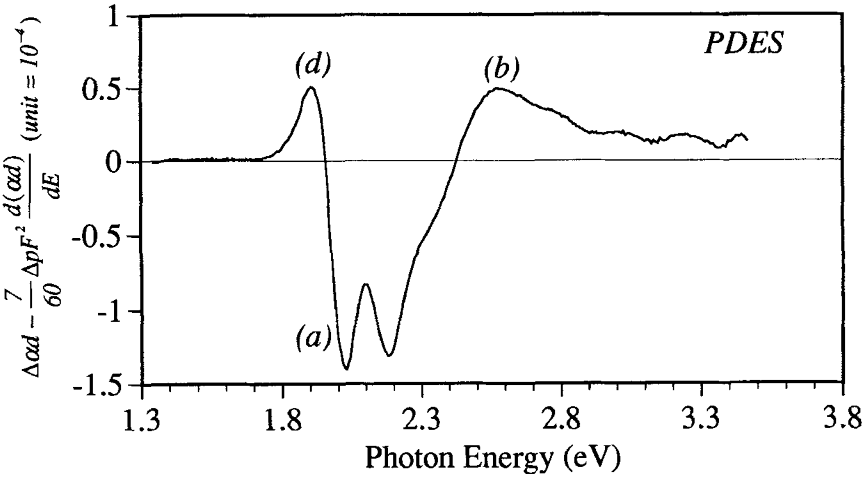

Figure 4. Difference between EA and First-Derivative for PDES

Questions of consistency arise in interpreting this difference. Since we are assuming no injection, the integral of Δf over all frequencies should be zero. This is only approximately obeyed in the spectral range measured (Figs. 3 and 4); however, a comprehensive treatment of Δf requires a knowledge of both the real and imaginary parts of the index of refraction and their field-induced changes. These can be determined by a Kramers-Kronig analysis and will be included in future work.

We interpret the high-energy feature in EA as the signature of the forbidden mA_g state. If we assume that current theories of polymer energy states are correct,[18,19] this forbidden state would also mark a lower limit to the location of a continuum band. To this end, the excitation data (Fig. 2) are suggestive. An extrapolation of the high-energy slope of the QE spectra as described in Ref. 5 suggests the beginning of a band in the region just above this high-energy EA feature for both polymers. For a well-ordered material, such a band-edge should be a step function, since the data are normalized to the absorbed number of photons; however, the effects of disorder (*e.g.*, chain-length distribution) tend to wash out an abrupt increase, therefore justifying the extrapolation.

Based on both theoretical predictions and the experimental EA and PAE spectra, we suggest that the binding energy of the $1B_u$ exciton (defined as the separation between the exciton and a continuum band) is about 0.9 eV for PDES and about 1 eV for PPA, and a $1B_u$-mA_g separation of about 0.6 eV and 0.7 eV for PDES and PPA, respectively.

SUMMARY

Electroabsorption, absorption, derivative, and PAE spectra for PPA and PDES have been presented. PPA displays an absorption first-derivative shape, consistent with a number of other polymers, whereas PDES displays a second-derivative shape, also consistent with other, nonluminescent, polymers. The latter result is not easy to interpret in terms of a Stark shift, and yet it is difficult to believe that these two polymers are so dissimilar. We have assumed that both polymers have similar values of Δp, and have shown that a simple theory in which the first-derivative $1B_u$ Stark shift lineshape is masked by shifts in oscillator strength to a lower ($2A_g$) state in close proximity to the $1B_u$ state (creating the illusion of a second-derivative), is consistent with the data. The PAE data and lack of luminescence also support the belief that $E(2A_g) < E(1B_u)$ in PDES. The EA spectra indicate the presence of a high-energy mA_g state, which is predicted by theory to be in close proximity to a continuum band. The QE spectra tend to reinforce this interpretation and suggest binding energies of about 0.9 and 1 eV in PDES and PPA, respectively. Future work will include EA and PAE spectroscopy of other luminescent and nonluminescent polymers, and detailed quantitative analysis of field-induced changes in oscillator strength.

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