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Electromodulated Photoinduced Absorption; A new spectroscopy in π -conjugated polymer/ C_{60} -blends

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ABSTRACT

We have applied the electromodulated photoinduced absorption (EPA) technique to a variety of C_{60} -doped and pristine luminescent conducting polymer films. EPA measures the electric field-related change of the absorption in the sample as a result of above-gap illumination. An electric field leads to two major effects. One is a possible Stark shift of photoexcitation (polarons, polaron pairs, or C_{60}^-) energy levels, and the other is a change in the photoexcitation decay kinetics, which leads to reduction or enhancement of PA features. This can be due to an electric field enhanced dissociation of the 1Bu exciton or due to a lifetime reduction of polaron pairs. The EPA technique helps to elucidate the photoinduced absorption (PA) bands of the charge transfer complex $C_{60}^- P^+$, where P^+ is a positively charged polaron on the polymer chain. The following thin films were studied by EPA: MEH-PPV/ C_{60} , pristine MEH-PPV, PPP/ C_{60} , P3OT/ C_{60} , PTSi/ C_{60} , and pristine PTSi. We found for the two PA bands of polarons (LE and HE respectively) that $E(\text{LE}) + E(\text{HE}) = E_g (= E_{1B_u})$. We also found that the polarizability of polaron pairs (PP) is three orders of magnitude bigger than the polarizability of the 1B_u exciton.

Keywords: electromodulated photoinduced absorption (EPA), C_{60} doping, luminescence, electromodulated photoluminescence (EPL), polaron pair polarizability

INTRODUCTION

Recently it has been shown that application of a strong electric field modulates the photoinduced absorption (PA) of many π -conjugated polymer films, in particular of luminescent π -conjugated polymer/ C_{60} blends. Transient photocurrent measurements on MEH-PPV/ C_{60} show that EPA is not necessarily related to mobile charge carriers. Transient PA measurements under the influence of various electric field strengths showed that the EPA signal in MEH-PPV/ C_{60} is caused

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by the modulation of the polaron pair (PP) lifetime [1]. It can be easily shown, that the applied electric field modulates the tunneling probability for the electrons in a PP excitations and consequently this leads to a reduction in the lifetime of the PP's [4]. This effect is helpful to determine the energy levels of PP's and isolate their specific absorption bands in the PA spectrum.

Not for all material is the lifetime modulation of PP's the dominant effect. In PPP/C₆₀ the most dominant effect is the Stark shift of the PP energy levels. This leads to an EPA spectrum which resembles the derivative of the PA spectrum and allows for the calculation of the PP polarizability.

A third effect dominates the EPA of silicon bridged polythiophene (PTSi). In PTSi the number of polarons and PPs increases due to an electric field, which is the opposite result that occurs in PPV/C₆₀ or P3OT/C₆₀. Electromodulated photoluminescence (EPL) measurements showed that an electric field in this material enhances the nonluminescent decay of 1B_u, while EPA detects a larger number of polarons and PPs. Thus an electric field dissociates the 1B_u excitons in PTSi, leading to an increased number of polarons and polaron pairs ("photoexcitations"). In this work we give examples for each of these three dominant effects. We derive the PP polarizability from the spectrum of C₆₀ doped PPP and information about the photoexcitation energy levels from the spectra of the other polymer materials.

EXPERIMENTAL SETUP

The EPA spectrometer is schematically described in Figure 1. Light from a tungsten lamp is focused on a sample, which is simultaneously excited by an Ar⁺ laser beam. An electric field modulated the optical transmission of the sample. The light is then focused on a monochromator and detected with a silicon, germanium or indium/antimonite photodiode for visible, near IR and mid IR, respectively. Lockin amplification, referenced at twice the electric field frequency, leads to a signal which is proportional to the change in transmission due to an electric field in arbitrary directions. This spectrum is then normalized by the transmission spectrum.

The materials involved in this study are C₆₀ doped MEH 2,5-substituted poly(phenylene-vinylene) (MEH-PPV), silicon bridged Polythiophene (PTSi), poly(3-ocetyl thiophene) (P3OT) and pristine PTSi. The novel low bandgap polymer PTSi is described elsewhere in this volume [2]. The materials were cast from solution on sapphire substrates with an array of interpenetrating Au-electrodes that allow the application of an electric field in the order of 10⁵ V/cm.

STARK SHIFT OF PHOTOEXCITATIONS

Most EPA spectra do not show spectral features related to a shift of the excitation absorption spectrum caused by the electric field (Stark shift). In general the modulation of the number of photoexcitations by the electric field is a much stronger effect and overrides derivative like features which are a result of Stark shifts. In only one case in this study, namely in C₆₀ doped

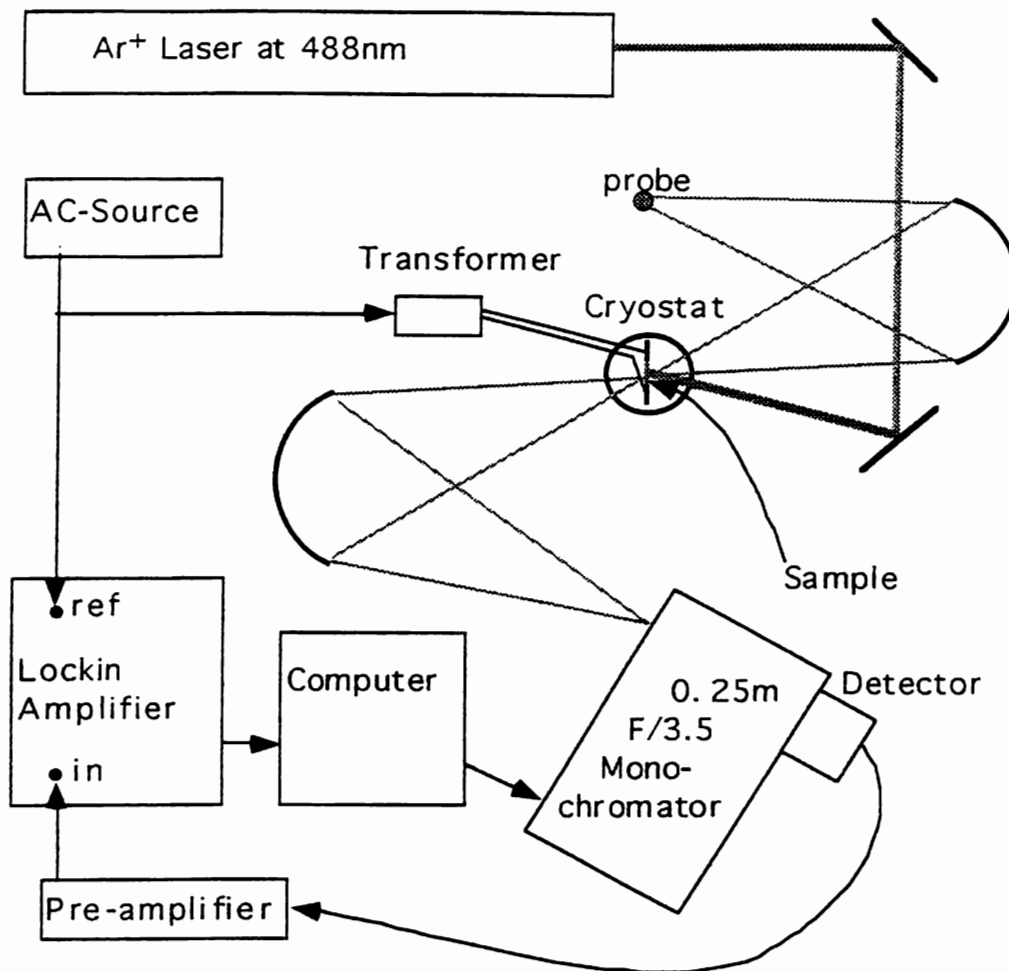


Figure 1: The EPA spectrometer

PPP, a Stark shift of the PP-like charge transfer complexes was observed. The exciton polarizability can be calculated using the ratio of the first derivative of the OD-spectrum and the electroabsorption spectrum [3]. If the EPA spectrum shows a Stark shift of a PA feature, then the polarizability of the corresponding excitation can be calculated from the ratio of the first derivative of the PA spectrum and the EPA spectrum in a similar fashion. In order to ensure the same number of photoexcitations during the PA and EPA measurement for both spectra, the same film and the same illumination intensity must be used. For the PA measurement, the chopping frequency must be low compared to the reciprocal lifetime of the photoexcitations so that the PA signal reflects the actual number of photoexcitations. Then the number of photoexcitations, detected using the PA measurement is equal to the number of photoexcitations which are present during the EPA measurement. A detailed derivation of the photoexcitation polarizability is given in [4]. The change in absorbance of the film $\delta\alpha d$ is:

$$\delta\alpha_d = -\frac{\Delta T_{EPA}}{T} = \frac{7}{60} p F^2 \frac{d\alpha_{dPA}}{dE} \quad (1)$$

Where p is the polarizability of the excitation. F is the electric field strength, ΔT_{EPA} is the change in transmission due to the applied electric field, T is the Transmission and $\Delta\alpha_{dPA}$ is the PA amplitude. As can be seen in Figure 2 a, the PA of C_{60} doped PPP shows distinct features at 1.1 eV, 1.7 eV and 2.4 eV, respectively. The EPA signal shows spectral features that resemble the PA derivative. The dotted line in Figure 2 c is to provide a zero line for the derivative interpretation. Since the features in the EPA spectrum are shifted in energy below the respective features of the PA signal, we conjecture that the longer conjugation lengths of the material dominate the EPA spectrum. The PA band at 2.4 eV can be assigned to the absorption of the positively charged polymer in a complex polaron formed with C_{60}^- ($P^+ C_{60}^-$). The polarizability of PPs involving a C_{60}^- ion was calculated using the equation (1). The ratio

$$\frac{A_{EPA}}{\frac{\partial A_{PA}}{\partial E}} = 0.025 \quad (2)$$

leads to a value of the polarizability of $3 \times 10^7 \text{ \AA}^3$. This is approximately 3 orders of magnitude bigger than the $1B_u$ exciton polarizability in most luminescent conducting polymers. This supports the interpretation of fast photocurrent in PPV as displacement current of excitons. Upon C_{60} -doping, the fast photocurrent response increases dramatically. This can be explained by the fact that C_{60} helps to dissociate the $1B_u$ excitons into PP-like charge-transfer complexes which then possess a higher polarizability.

FIELD-INDUCED MODULATION OF PP LIFETIME

MEH-PPV/ C_{60}

The detailed analysis of EPA in MEH-PPV/ C_{60} has been published elsewhere [1]. It has been shown that the EPA bands at 0.3 eV and 1.65 eV especially are due to the low energy transition (PP_1) and the high energy transition (PP_2) of PPs. We want to stress that $2E(PP_1) + E(PP_2) = E(1B_u) + 0.05 \text{ eV}$. We assign this additional energy to the sum of the relaxation energies of the two energy levels in PPs. An energy level diagram based on our EPA data is shown in Figure 3.

P3OT/ C_{60}

PA and EPA spectra were measured in C_{60} doped P3OT. Superficially analyzed, the EPA spectrum does not reveal anything more than has already been seen in the PA spectrum which has an almost identical lineshape [4]. Both the PA and

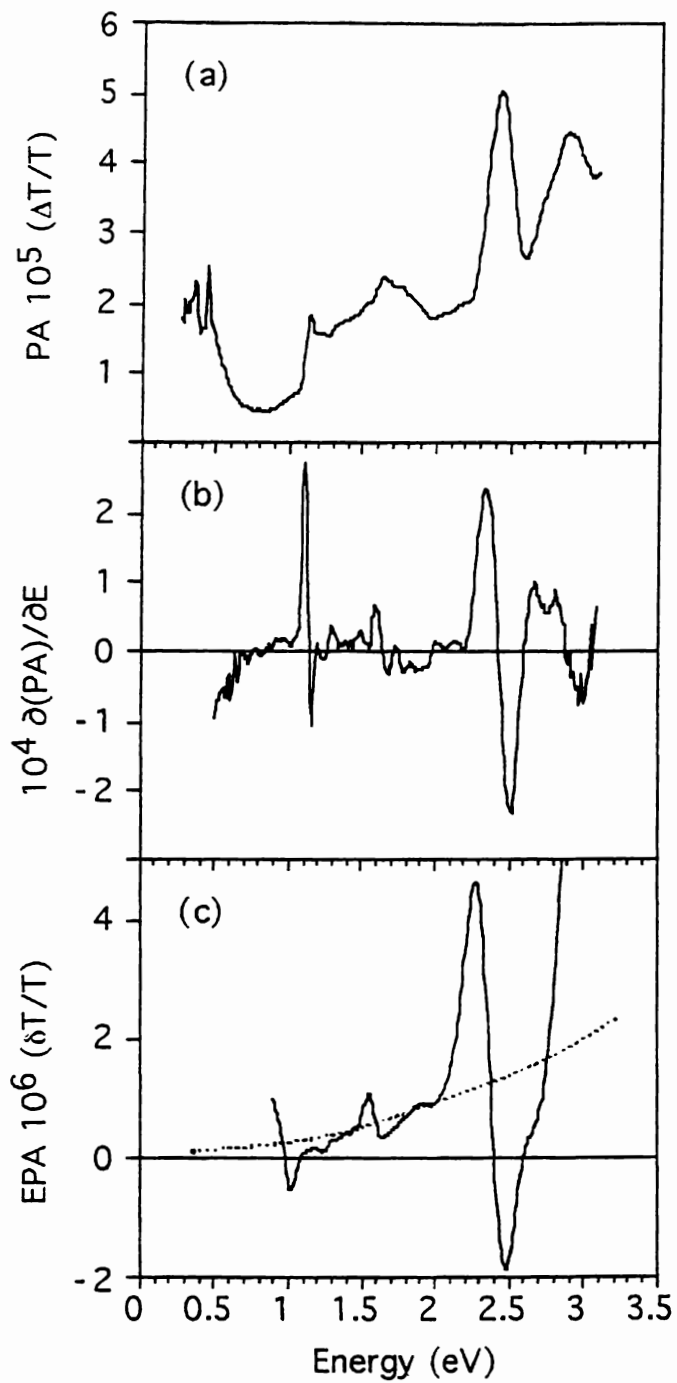


Figure 2: The PA (a), its derivative (b), and the EPA signal of C₆₀ doped PPP in comparison (c). The dotted line serves as guide to the eye to interpret the EPA spectrum.

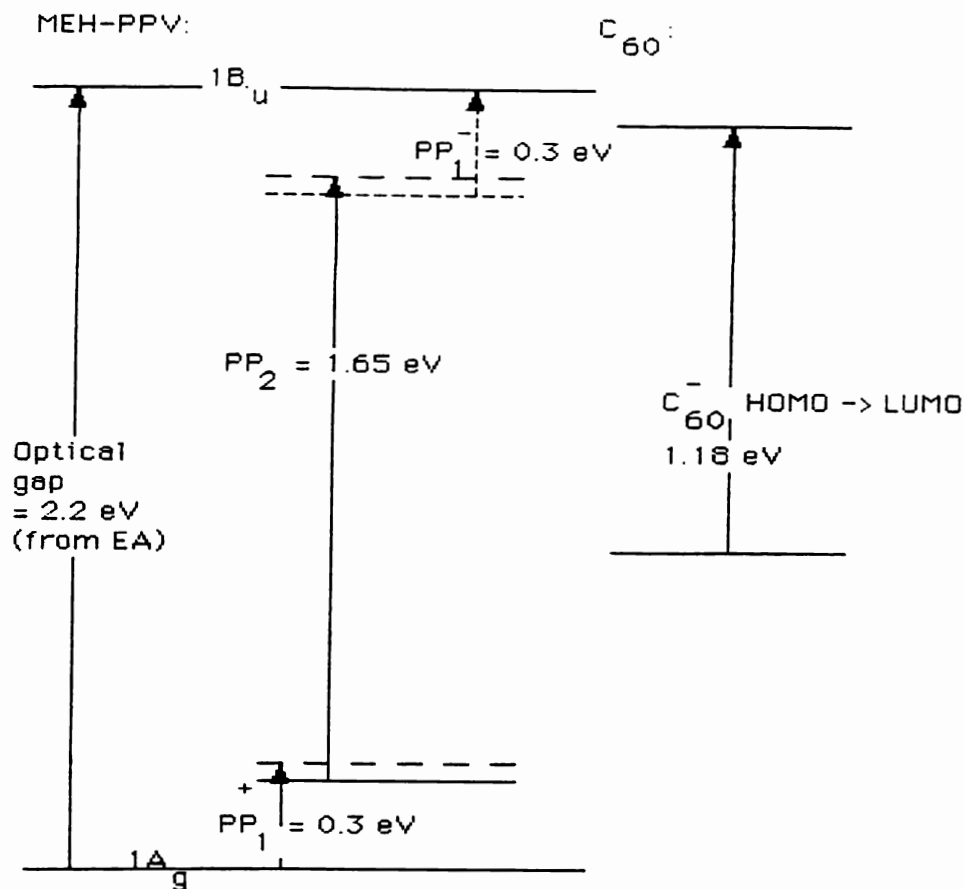


Figure 3: Energy levels of photoexcitations in MEH-PPV / C₆₀. Unrelaxed energy levels are dashed lines with long dashes. Energy levels and optical transitions which are predicted by theory but not seen in C₆₀ doped MEH-PPV are marked with short dashes.

EPA spectra show bands below 0.3 eV, at 1.25 eV, and at 1.7 eV. (The signal above 1.8 eV is due to electroabsorption of the 1B_u exciton and thermal effects.) However, a more careful analysis of the data that includes the phase of the EPA spectrum and the relative sensitivity of the photoexcitations to an electric field (EPA/PA) reveals valuable information. Both spectra (Figure 4b) show a feature at 1.15 eV and 1.7 eV. The feature at 1.15 eV is due to the C₆₀⁻ HOMO to LUMO transition [5, 6]. The C₆₀⁻ signature feature is almost not visible in the simple PA or EPA spectra. The feature at 1.7 eV also appears in the PA of P3OT. Since the EPA phase and the spectral sensitivity to an electric field (Figure 4b) correlate this signature with the C₆₀⁻ signature, it can be assigned to pp⁺ of a polaron pair-C₆₀⁻ charge transfer complex.

The PA signatures at 0.3 eV and 1.25 eV do not correlate with these complexes in lifetime (as can be seen from the EPA phase) and relative sensitivity to an electric field. Since these PA bands are below the higher PP PA band, they can be assigned to P₁ and P₂ transitions of free polarons. A summary of energy levels of photoexcitations and their optical transitions in P3OT is given in Figure 5. The mismatch of 0.15 eV between the optical gap and the polaron transitions can

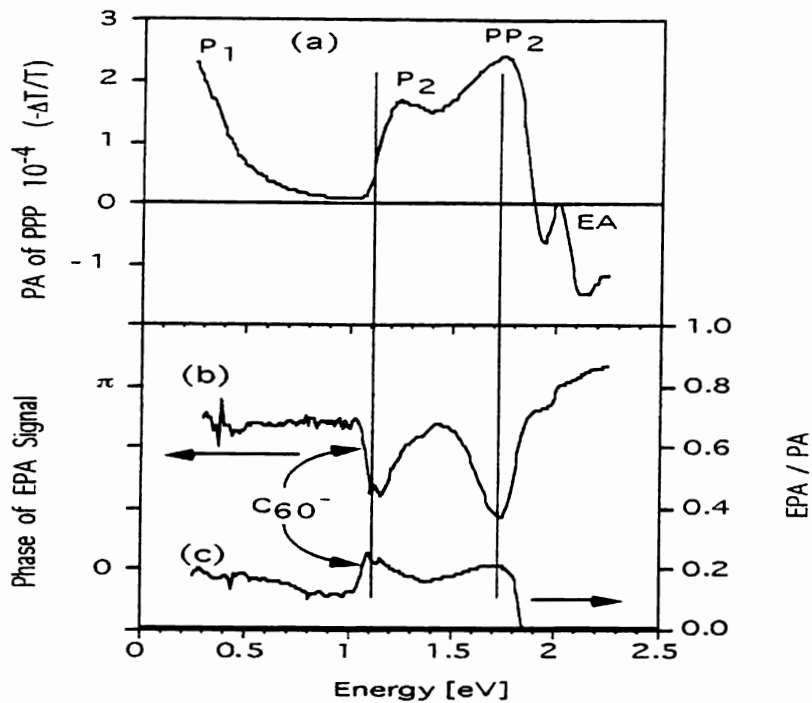


Figure 4: The EPA spectrum of P3OT/C₆₀ (a) and its phase (b) and the spectral relative sensitivity of the photoexcitations to an electric field (c).

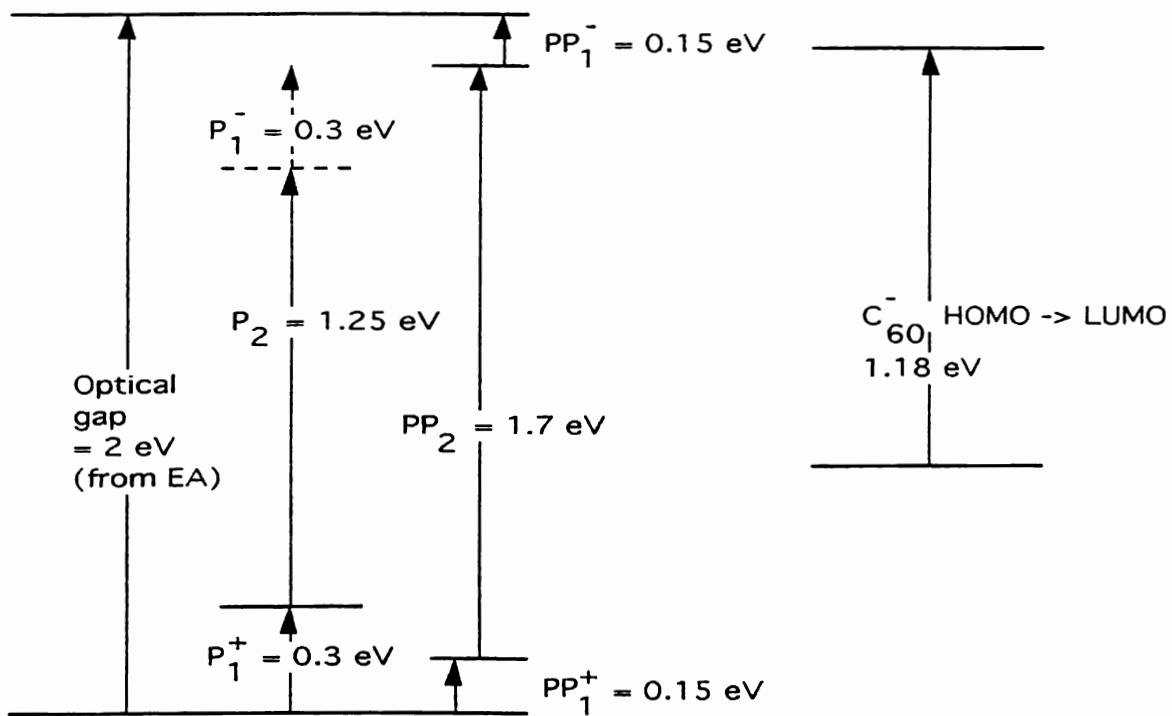


Figure 5: A diagram of energy levels of photoexcitations in P3OT and their transitions assembled using EPA and PA data.

be explained by the distribution of energy levels of the optical gap ($1B_u$) and polaronic transitions. Due to the disorder related distribution of energy levels, the average energies of transitions are difficult to exactly determine. Also the broad PP_1^+ PA band disguises the exact position of the P_1^+ PA band.

FIELD INDUCED DISSOCIATION OF SINGLET EXCITONS

The PA spectrum of the PTSi films is dominated by a broad PA band which peaks at 1.1 eV with a shoulder at 1.65 eV; there is also a distinctive band at 0.3 eV (Figure 6 (a) and Figure 7 (b)). The PADMR spectrum identifies a broad triplet which peaks at 1.1 eV and spin-1/2 bands below 0.5 eV, at 1.1 and at 1.65 (Figure 6 (b)). According to their energy and spin the bands can be assigned as follows: Below 0.5 eV there is the P_1 and PP_1 transition of PPs. at 1.1 eV, we observe the peak of the broad $1B_u^3$ (T_1) transition overlapping with the P_2 transition of polarons; and at 1.65 eV we see the PP_2 transition of PPs. The EPA spectrum of C_{60} -doped and pristine PTSi (Figure 7) shows electric field induced enhancement of the polaron and PP bands and bleaching at 1.0 eV, in pristine, and at 1.5 eV in C_{60} doped PTSi. The bleaching can be explained by the bleaching of the broad triplet absorption which is overridden by the sharp electric field induced enhancements of the P_2 , PP_2 and C_{60}^- signatures. The origin of the triplet bleaching can be determined from electromodulated photoluminescence (EPL). An electric field reduces the luminescence by enhancing the dissociation of singlet excitons and transforming them into polarons and polaron pairs. Thus the number of singlet excitons that decay into the triplet state is reduced. Excitons in π -conjugated polymers have high exciton binding energies. Thus the effect of electric field enhanced exciton dissociation can only be understood if the dissociation at defect centers and impurities is taken into account. Figure 7 shows that C_{60} doping increases the electric field enhanced bleaching of the triplet absorption. This is important to note because the triplet PA is weaker in the doped than in the undoped material. Figure 8 displays the energy levels and transitions of photoexcitations in PTSi. A more detailed analysis exclusively on PTSi is published elsewhere in this volume [2]. We note that the sum over the polaronic transitions $2 \times P_1 + P_2 \approx E(1B_u)$, as expected from theory.

CONCLUSIONS

Electro modulated photoinduced absorption is a novel technique used to investigate excitations that generate PA. In most cases perused in this study, EPA is due to an electromodulated quenching of PP-like charge transfer complexes. In one example, EPA is due to the Stark shift of PP energy levels. This allowed to determine the polarizability of PPs, which has been shown to be two orders of magnitude larger than the polarizability of the $1B_u$ exciton. In another case, EPA increases the number of polarons and PPs due to field-induced dissociation of singlet excitons. It was also shown that EPA is a useful technique which helps to further investigate the properties of PA active excitations. On the other hand EPA can demonstrate

the various effects of electric fields on photoexcitations in conductive polymers. Figure 9 summarizes the different effects observed with EPA and shows the information obtained about the polymer in the different cases.

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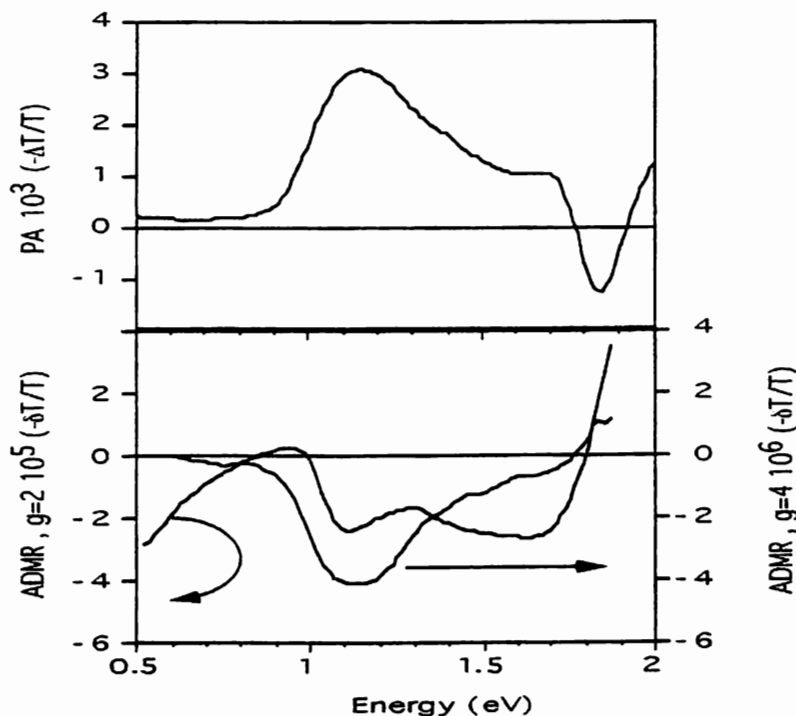


Figure 6: The PA spectrum of pristine PTSI (upper part) in comparison with the PADMR spectrum (lower part). At $g=2$, the spectrum shows $s=1/2$ (doublet) excitations and at $g=4$ it shows $s=1$ (triplet) excitations.

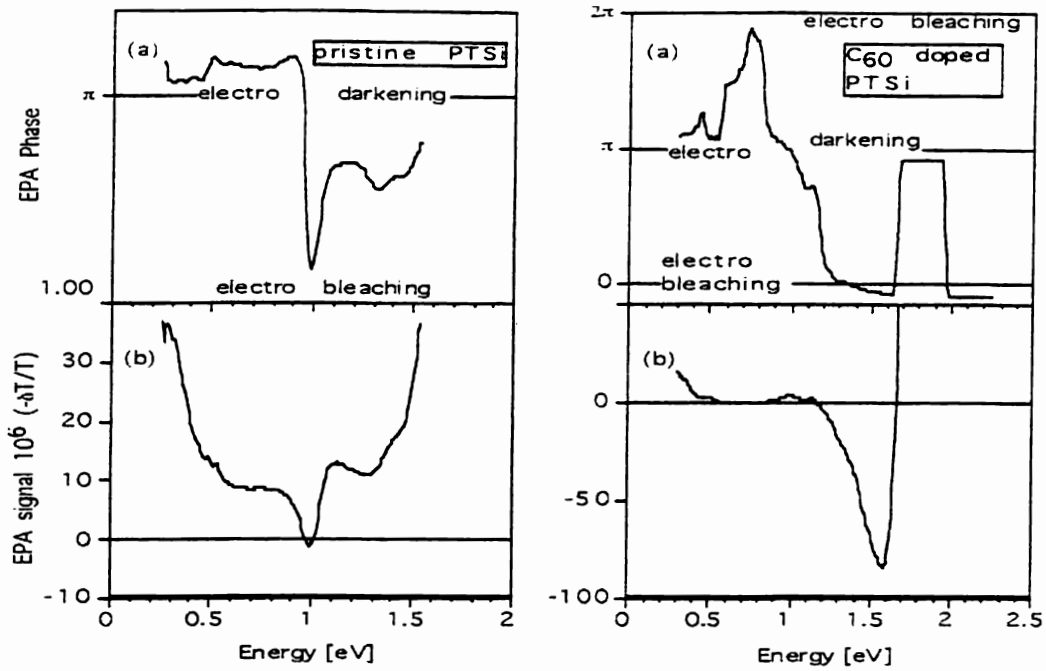


Figure 7 : In pristine and C_{60} -doped PTSi, an electric field enhances the PA features related to charge photoexcitations. Bleaching occurs outside the absorption bands of the charged photoexcitations due to bleaching of the broad triplet. Parts (a) show the phase of the signal, while parts (b) show its magnitude.

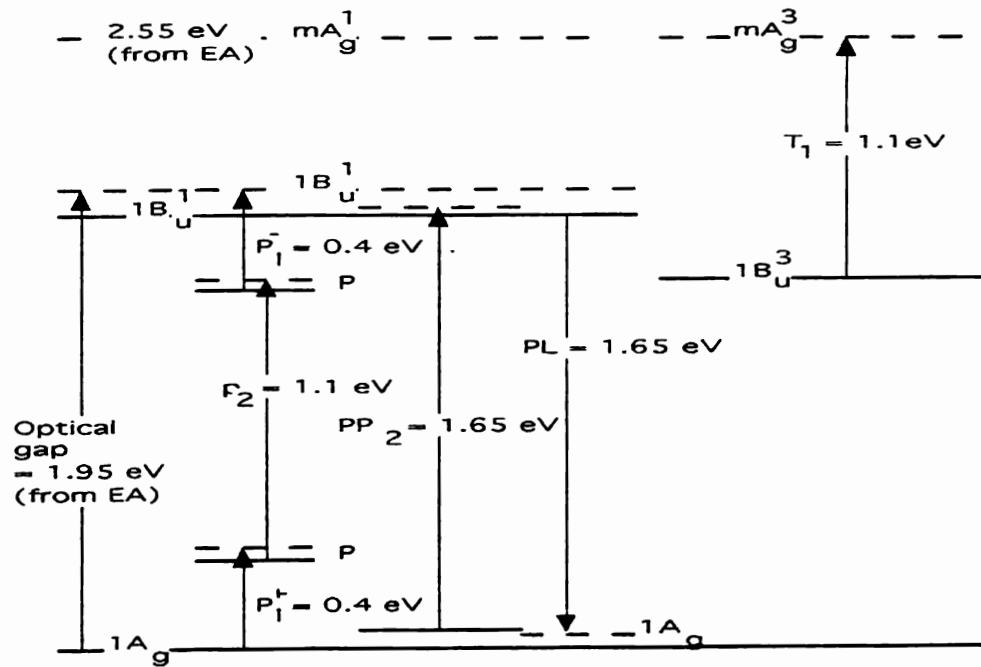


Figure 8 : Energy levels of excitons and photoexcitations and their transitions assembled from EA, PA, EPA, EPL and PADMR data of pristine and C_{60} doped PTSi. Unrelaxed energy levels are marked with dashes.

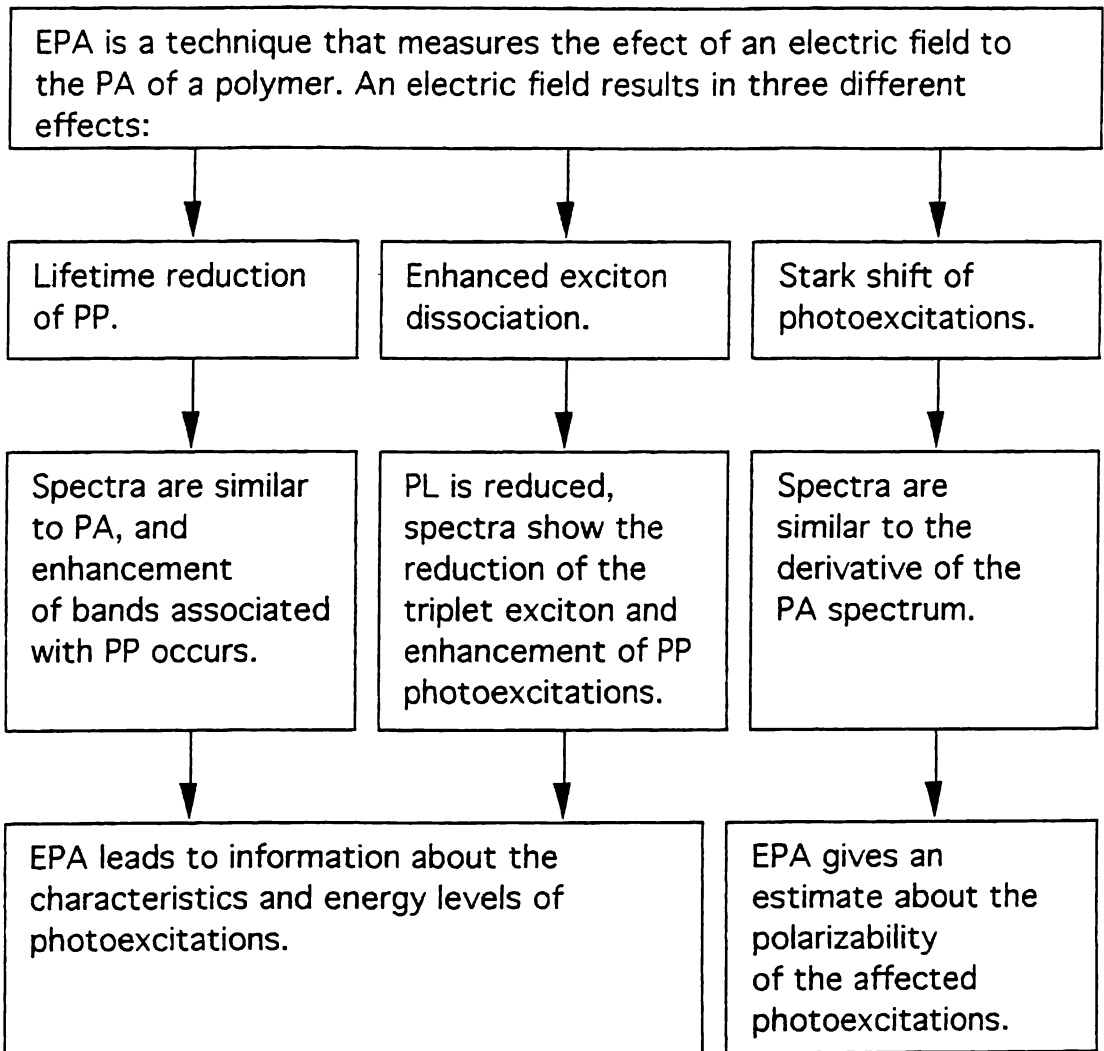


Figure 9: Different effects observed with EPA and the information obtained using EPA spectroscopy.