Absorption-detected magnetic-resonance studies of photoexcitations in conjugated-polymer/C_{60} composites

X. Wei* and Z. V. Vardeny
Department of Physics, University of Utah, Salt Lake City, Utah 84112

N. S. Sariciftci and A. J. Heeger
Institute for Polymers and Organic Solids, University of California, Santa Barbara, California 93106
(Received 7 August 1995)

Photoexcitations in poly[2-methoxy-5-(2′-ethyl-hexyloxy)-*p*-phenylene vinylene] (MEH-PPV) and composites of MEH-PPV and C_{60} (MEH-PPV/C_{60}) were studied by photoinduced absorption and absorption-detected magnetic-resonance spectroscopies. We report direct evidence that the prominent triplet photoexcitations in pristine MEH-PPV are effectively quenched in MEH-PPV/C_{60}. In contrast, the dominant photoexcitations in MEH-PPV/C_{60} are spin-1/2 excitations: polarons on the polymer chains; and polarons on the C_{60} (C_{60}^{-}).

INTRODUCTION

Photoexcitations is conjugated-polymer/C_{60} composites have been extensively investigated since the report that photoinduced charge transfer was observed in this class of composites.[1,2] The photophysics of composites made of non-degenerate ground-state conjugated polymers and C_{60} differs substantially from that of the pristine polymers. In polymer-C_{60} composites, the following photophysical phenomena have been observed: (1) the strong photoluminescence (PL) originating from the polymer is quenched by more than three orders of magnitude;[1,3] (2) photoconductivity is enhanced by at least two orders of magnitude;[4,5] (3) light-induced electron-spin resonance (LESR) shows two spin-1/2 signals with different g values, which are attributed to C_{60} anions (with $g \approx 1.995$) and positive polarons (with $g \approx 2.000$) on the polymer chains, respectively.[3] These results have been well explained within a model of ultrafast (i.e., less than a picosecond) photoinduced charge transfer[1] in which the charge-transfer process, with a quantum yield of near unity, efficiently quenches the formation of the neutral singlet excitons that yield PL. The steady-state photoinduced absorption (PA) shows clear changes in many conjugated polymers upon addition of C_{60} as compared to the pristine materials.[6,7] The changes in PA of poly[2-methoxy-5-2′-ethyl-hexyloxy)-*p*-phenylene vinylene] (MEH-PPV) has not been clearly elucidated because MEH-PPV has a band peaked at 1.35 eV in both the pristine and C_{60} composite films. The 1.35 eV PA band in pristine PPV has been identified as due to triplet excitons. Therefore direct evidence of the *absence* of triplet photoexcitation in MEH-PPV/C_{60} is needed to establish the quenching of neutral photoexcitations in the polymer-C_{60} composites. For example, as shown in the study of poly(3-alkylthiophene)-C_{60} in solution, quenching of the PA band that is associated with the triplet photoexcitation in the polymer results from triplet energy transfer rather than from a charge-transfer process.[8] The proposed photoinduced charge-transfer process in the composites is expected to enhance the generation of polarons with spin-1/2 within the polymer, as suggested by the $g \approx 2.000$ spin-1/2 LESR signal in conjugated polymer-C_{60} composites.[2] If this LESR signal is directly correlated with the charged PA spectral bands in conjugated polymer-C_{60} composites, then the charged photoexcitations (whether polarons or bipolarons) will be identified and hence the mechanism of the enhanced PC will be clarified.

Absorption detected magnetic resonance spectroscopy[9] (ADMR) which combines the advantages of both PA (spectral resolution) and LESR (spin information), is thus an ideal technique to answer these questions. In this work, we report the comparative studies of MEH-PPV and its C_{60} composite (MEH-PPV/C_{60} using the techniques of PA and ADMR. The triplet photoexcitations that are prominent in the pristine MEH-PPV are indeed *absent* in MEH-PPV/C_{60}. On the contrary, spin-1/2 photoexcitations, which are assigned to polarons, dominate the PA spectrum of MEH-PPV/C_{60}.

EXPERIMENTAL

The synthesis, structure, and properties of MEH-PPV have been reported earlier.[10] Films of MEH-PPV were prepared by spin-casting the solution of MEH-PPV in chloroform onto sapphire or KBr substrates. C_{60} powder was purchased in high purity (99.99%) from Polygon Enterprises, Texas. The MEH-PPV/C_{60} composite films were obtained by dissolving MEH-PPV and C_{60} (1:1 by weight) in toluene (typically 1% solution) and spin casting onto sapphire or KBr substrates.

The photoinduced absorption spectroscopy uses standard phase-sensitive lock-in techniques with a chopped Ar^+ laser beam as source. Photoinduced changes ΔT in the sample transmission T are recorded to obtain the normalized changes in transmission ($-\Delta T/T \approx \Delta \alpha d$, where d is the sample thickness). The ADMR technique[9,11] uses a cw pump beam (from an Ar^+ laser) and a probe beam (from a tungsten lamp) to constantly illuminate the sample, which is mounted in a high Q microwave cavity (at 3 and 16 GHz) equipped with optical windows, and a superconducting magnet producing a field H. Microwave resonant absorption, modulated nominally at 500 Hz, leads to small changes, δT, in the probe transmission T. This δT is proportional to δn, the

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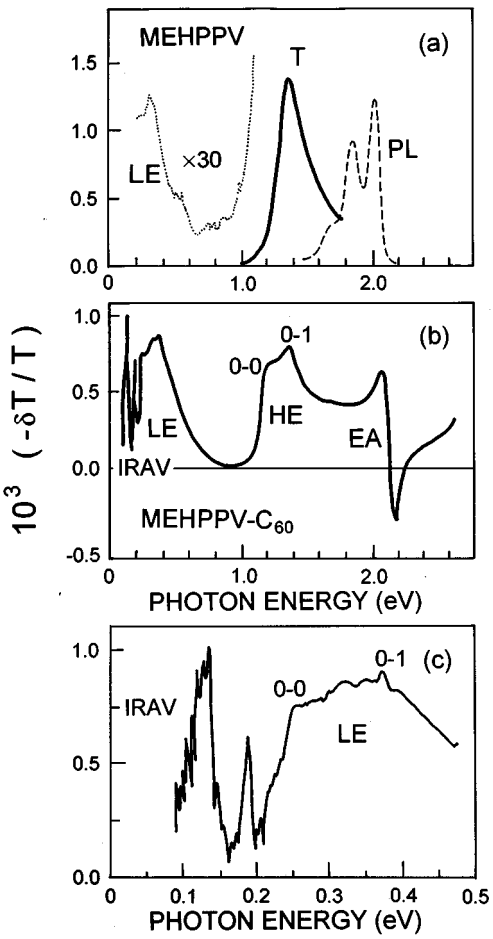

FIG. 1. (a) PA and PL spectra of MEH-PPV at 80 K, (b) and (c) PA spectra of MEH-PPV/C_{60}, at 4 K, with an Ar^+ laser modulated at 200 Hz. **T**, **IRAV**, **LE**, **HE**, and **EA** PA features are assigned.

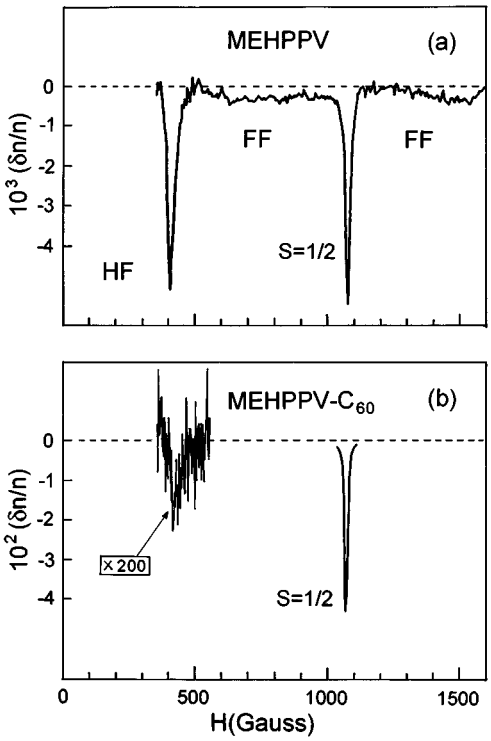

FIG. 2. (a) H-ADMR spectrum of MEH-PPV, showing the "full field" (**FF**) and "half field" (**HF**) triplet (spin-1) resonance signals as well as the spin-1/2 resonance signal. (b) H-ADMR spectrum of MEH-PPV/C_{60} showing the spin-1/2 resonance; the spin-1 **HF** resonance ($\times 200$) is also shown for comparison. Both spectra were measured at probe photon energy of 1.35 eV, temperature of 4 K and 3 GHz resonant microwave frequency.

change in the photoexcitation density n produced by the pump. δn is induced by transitions in the microwave range that change spin-dependent recombination rates. Two types of ADMR spectra were obtained: the H-ADMR spectrum, in which δT is measured at a fixed probe wavelength λ, while sweeping H, and the λ-ADMR spectrum in which δT is measured at a constant H, in resonance, while λ (probe) is varied.

RESULTS AND DISCUSSION

The PA spectra of the pristine MEH-PPV and MEH-PPV/C_{60} composites are shown in Fig. 1. The dominant PA band [feature **T** in Fig. 1(a)] which peaks at 1.35 eV in MEH-PPV arises from triplet exciton transition. The strong PL band in MEH-PPV [in Fig. 1(a)] is only faintly observable in MEH-PPV/C_{60}.[9,12] The PA band associated with charged photoexcitations in MEH-PPV below 0.5 eV is very small, consistent with previous studies.[9,12] In contrast, the PA spectrum in MEH-PPV/C_{60} is dominated by two bands with onsets at 0.25 eV (LE band) and 1.18 eV (HE band), respectively. The two PA bands are correlated: this was verified by their similar modulation frequency dependence and intensity dependence of the excitation beam, which are also similar to those of the strong photoinduced infrared-active vibration (IRAV) modes below 0.2 eV [Fig. 1(c)]. The photoinduced IRAV modes are the same as those found in doped MEH-PPV,[13,14] showing that they arise from charged photoexcitations. At higher photon energies, the HE PA band is followed by a derivativelike structure that has the same spectral shape as the electroabsorption of MEH-PPV.[3,15]

The HE and LE PA bands of the C_{60} composite show similar structures: a sharp edge (0-0) at 0.25 eV (LE) and 1.18 eV (HE), respectively, followed by a gradual increase to a respective peak (0-1) at 0.38 eV (LE) [Fig. 1(c)] and 1.38 eV (HE) [Fig. 1(b)]. The HE band in the composite is known to have different dynamics than that of the triplet excitons in MEH-PPV.[16] On the other hand, since C_{60}^- is known to have an optical transition at $\sim$1.1 eV,[17] and the pristine polymer has an optical transition due to the charged photoexcitations at $\sim$1.3 eV,[9] we carried out detailed PA studies to try separating the possible different 0-0 and 0-1 transitions of the LE and HE PA bands. We found, however, that the 0-0 and 0-1 transitions are correlated: (1) both 0-0 and 0-1 transitions have the same excitation frequency dependence, from 10 Hz to 50 kHz, and the same excitation intensity dependence, from 10 to 200 mW/cm^2; (2) the spectral shape of the HE and LE PA bands remains unchanged when excited at 514.5 nm (2.41 eV), 457.9 nm (2.71 eV) and 351 nm (3.5 eV), respectively; and (3) the 0-0 transitions slightly gain strength relative to the 0-1 transitions when the temperature is raised from 4 to 250 K.

More definite spectral identifications have been obtained

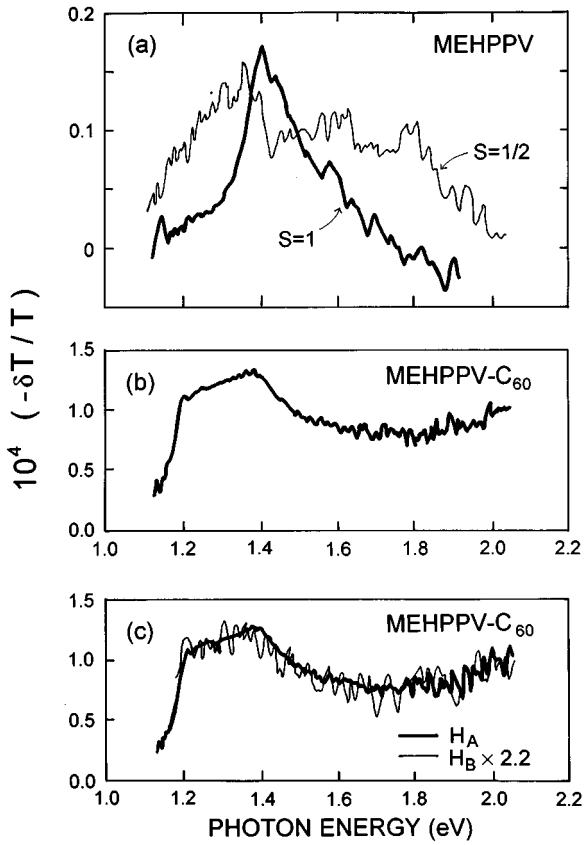

FIG. 3. λ-ADMR spectra of MEH-PPV at 3 GHz (a) and MEH-PPV/C_{60} at 3 GHz (b) and MEH-PPV/C_{60} at 16 GHz (c). (a) shows both spin-1/2 and spin-1 resonances whereas (b) and (c) are spin-1/2 only. The fields $\mathbf{H}_A$ and $\mathbf{H}_B$ in (c) are defined in Fig. 4(b).

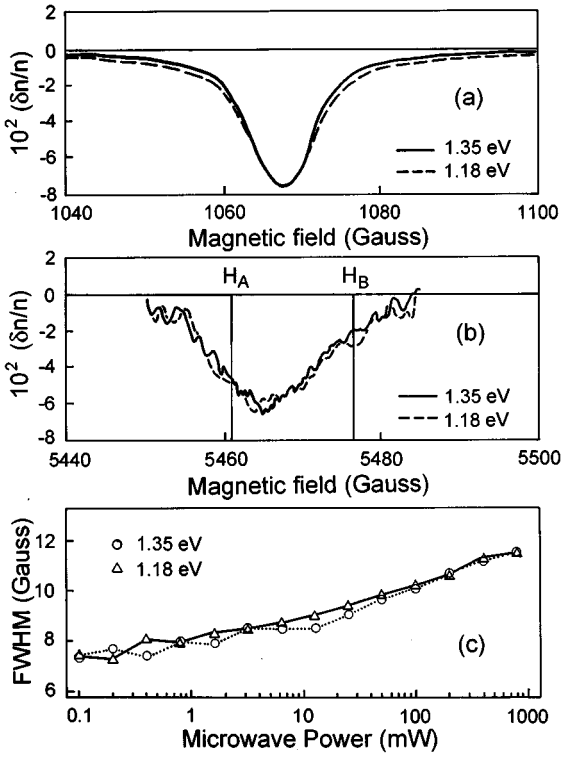

FIG. 4. H-ADMR spectra at 1.18 and 1.35 eV, respectively, of MEH-PPV/C_{60}, measured at 3 GHz (a) and 16 GHz (b). In (b), $\mathbf{H}_A$ and $\mathbf{H}_B$ are the resonant magnetic fields expected for $g \approx 2.002$ (p^+ on the polymer chain) and 1.997 (C_{60}^-), respectively. (c) shows the FWHM of the 3 GHz H-ADMR resonance at 1.18 and 1.35 eV, respectively, versus the microwave power intensity.

by the ADMR spectroscopy. The H-ADMR spectra (at probe photon energy of 1.35 eV) of MEH-PPV and MEH-PPV/C_{60}, respectively, are shown in Figs. 2(a) and 2(b). Three resonance bands with $\delta n < 0$ were observed in pristine MEH-PPV: (1) a prominent band at 1067 G which is associated with spin-1/2 at $g \approx 2.002$; (2) another prominent band peaked at 410 G which is the "half-field" powder pattern resonance signal associated with photoinduced spin-triplet excitons;[18] and (3) a weak broad band between 550 G to 1600 G which is the "full-field" powder pattern[18] of the triplet exciton, respectively. In contrast, the H-ADMR spectrum in MEH-PPV/C_{60} is dominated by the resonance band at 1067 G with $\delta n < 0$, which is associated with spin-1/2 at $g \approx 2.002$; its relative intensity $\delta n/n$ in MEH-PPV/C_{60} is enhanced by an order of magnitude compared to that of pristine MEH-PPV, with $\delta n/n \approx -4 \times 10^{-2}$ and -5×10^{-3} in MEH-PPV/C_{60} and MEH-PPV, respectively. (Note that the absolute intensities δn differ even more since the charged photoexcitation density n is much larger in MEH-PPV/C_{60} than in MEH/PPV.) The triplet powder pattern at "half field" in MEH-PPV/C_{60} is of order $\delta n/n \approx -10^{-4}$; and the relative magnitude of $\delta T_{410\,\mathrm{G}}/\delta T_{1067\,\mathrm{G}}$ is less than 2×10^{-3}.

In Fig. 3, λ- ADMR spectra at 1067 G (for spin-1/2) and 410 G (for spin-1) confirm that while both triplet and spin-1/2 photoexcitations exist in MEH-PPV, whereas spin-1/2 photoexcitations dominate the spectrum in MEH-PPV/C_{60}. Moreover, the spin-1/2 λ-ADMR spectrum of MEH-PPV/C_{60} at 1067 G has the same shape as the PA spectrum itself [Fig. 1(b)], indicating that the dominate photoexcitations in the MEH-PPV/C_{60} composites are associated with the spin-1/2 species. For MEH-PPV, on the other hand, the λ-ADMR spectrum at 410 G is the same as the 1.35 eV PA band, confirming that the dominant photoexcitations in pristine MEH-PPV are triplet excitons. It is noteworthy that in pristine MEH-PPV, λ-ADMR spectrum at 1067 G also shows two bands similar to that of MEH-PPV/C_{60}, indicating that the charged photoexcitations in MEH-PPV/C_{60} are not different from those observed in pristine MEH-PPV.

We assign, therefore, the spin-1/2 charged photoexcitations in both pristine MEH-PPV and MEH-PPV/C_{60} composites to polarons on the polymer chains. This assignment is in agreement with the following experimental observations: (1) LESR measurement in MEH-PPV/C_{60} shows long lived spin-1/2 polarons;[3] (2) in ADMR, we expect $\delta n < 0$ for polarons and $\delta n > 0$ for bipolarons. This is true because spin-dependent recombination of polarons is enhanced at resonance, leading to a decrease of polar population for polaron pairs (p^+-p^-, p^+-p^+, and p^--p^-) and resulting in an increase of bipolaron population due to $p^+ + p^+ \rightarrow BP^{++}$ and $p^- + p^- \rightarrow BP^{--}$.[19]

We also made efforts to separate the 0-0 and 0-1 transitions at LE and HE PA bands of MEH-PPV/C_{60} using the ADMR spectroscopy. H-ADMR spectra using resonant microwave frequencies of 3 and 16 GHz, respectively, were measured (Fig. 4). We note that a possible difference Δg of ≈ 2.000–1.995 [i.e., g values of PPV^+ and C_{60}^-, respectively, found in LESR (Ref. 3)] would result in field difference of

3.2 G with 3 GHz resonant microwave frequency and 17 G with 16 GHz resonant microwave frequency. The H-ADMR spectra at photon energies of 0.4, 1.18, 1.35, and 1.91 eV, however, are *identical* and contain only a single band at $g \approx 2.002$ [Figs. 4(a) and 4(b)]. Its full width at half maximum (FWHM), measured with 16 GHz microwave, is only 14 G [Fig. 4(b)]. This indicates that the single spin-1/2 band is not composed of two overlapping spin-1/2 bands with $g \approx 1.995$ and 2.000, respectively. Moreover, as shown in Fig. 3(c), the λ-ADMR spectrum at 5460 G [H_A in Fig. 4(b), corresponding to $g \approx 2.002$] is identical to that at 5476 G [H_B in Fig. 4(b), corresponding to $g \approx 1.997$]. Furthermore, the FWHM of the H-ADMR spectra at 1.18 and 1.35 eV show identical changes when 3 GHz resonant microwave power is varied from 0.1 to 1000 mW [Fig. 4(c)], resulting in change of FWHM from 7.4 to 11.5 G. Neither splitting nor shifting in the g value was observed. In addition, we checked that the ADMR signals at 1.18 and 1.35 eV also show identical microwave intensity and modulation frequency dependence. We noted the possibility that if there is a strong spin-exchange interaction between PPV^+ and C_{60}^-, the ADMR signal of PPV^+ can be indistinguishable from that of C_{60}^-,[20] in contrast of the two spin-1/2 signals observed in LESR, which detects the long-lived photoexcitations (i.e., PPV^+ and C_{60}^- have been well separated).

On the other hand, it has been reported that the optical transitions of C_{60}^- are small compared with that of the charged photoexcitations in oligothiophene/C_{60} composites.[8] Therefore, we conclude tentatively that the 0-0 and 0-1 transitions in HE PA band in MEH-PPV/C_{60} are associated with the same spin-1/2 photoexcitations as in MEH-PPV, and that no optical transitions associated with C_{60}^- were identified.

The splitting value of the 0-0 and 0-1 transitions is about 0.13 eV for the LE PA band of 0.18 eV for the HE PA band, respectively. We believe that the 0-1 transitions are due to vibrational sidebands of the 0-0 transitions. The possibility that the respective LE and HE 0-1 PA transitions are due to p^+-p^- charge symmetry breaking in PPV can be ruled out, since the intraband polaron transition (the HE band) would be the same for p^+ and p^-, contrary to our experimental findings. Note that the LE band splitting is very close to the energy (0.12 eV) of the first strong photoinduced IRAV band, suggesting that the 0-1 transition is a vibronic sideband. The difference in the 0-0 and 0-1 splitting between the HE PA band and the LE PA band thus indicates a photon frequency hardening for the polaron.

CONCLUSION

Comparative studies of pristine MEH-PPV and MEH-PPV/C_{60} composite by ADMR spectroscopy have shown direct evidence that the triplet excitons of the MEH-PPV are quenched in MEH-PPV/C_{60}. This is in agreement with the general model that a photoinduced charge-transfer process dominates the photophysics of MEH-PPV/C_{60}, thus inhibiting the intersystem crossing channel between the singlet and triplet excitons. As a result, the PA spectrum of MEH-PPV/C_{60} predominantly arises from charged photoexcitations, identified as photogenerated spin-1/2 polarons on the polymer chain.

ACKNOWLEDGMENTS

We appreciate useful discussion and experimental assistance of D. Moses, J. M. Leng, D. Mao, W. Ohlsen, and P. C. Taylor. The work was supported in part by DOE FG-03-93ER45490 and ONR No. N00014-94-1-0853.

*Present address: Dr. Xing Wei, CST-4, MS-C345, Los Alamos National Laboratory, Los Alamos, NM 87545.

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