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Invited Paper

Spin dependent spectroscopy of photoexcitations in conducting polymers and fullerenes

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ABSTRACT

We have used the novel technique of absorption detected magnetic resonance (ADMR) to investigate the photoexcitation properties in conducting polymers and fullerene C_{60} films. In conducting polymers we have identified both charged and neutral long-lived photoexcitations with distinct different properties in polymers with degenerate (trans polyacetylene; t-$(CH)_x$) and nondegenerate (polyparaphenylene vinylene; PPV) ground state backbone structure. In t-$(CH)_x$ the photocarriers are charged solitons and the neutral photoexcitations are spin ½ soliton pairs, whereas the photoexcitations in PPV form charge bipolarons and triplet excitons. The neutral photoexcitations in C_{60}/polystyrene "glass" are triplet excitons identified in ADMR through the triplet "powder-pattern" around g = 2.003.

1. INTRODUCTION

Electron spin resonance (ESR) spectroscopy is a fundamental method for studying electronic states and structural properties in condensed matter. Various optical techniques have been used in conjunction with ESR to study the properties of excited states. Among them, most frequently used is ODMR[1] (optically detected magnetic resonance), in which

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photoluminescence (PL) is used to detect the microwave induced changes in emission due to magnetic resonances. Since photomodulation (PM) spectroscopy has been a very powerful technique in studying photoexcited states in semiconductors[2], we discuss in this paper its use to monitor magnetic resonances; in particular, its application to study photoexcitations in conducting polymers and in C_{60} fullerene. The technique is called absorption detected magnetic resonance (ADMR) where spin dependent recombination and generation processes are used to observe changes in the steady state PM spectra due to μwave absorption in resonance[3]. We applied the ADMR technique to study the nature of photoexcitations in conducting polymers with degenerate (trans polyacetylene, t-$(CH)_x$) and nondegenerate (polyparaphenylenevinylene, PPV) backbone ground states and in C_{60} "glass". In t-$(CH)_x$ we identified photogenerated charged and neutral solitons, whereas the photoexcitations in PPV are charged bipolarons and neutral triplet excitons; all of these excitations have strong photoinduced absorption (PA) bands in the gap. This shows that the nature of the primary photoexcitations in degenerate and nondegenerate conducting polymers are fundamentally different. We have also applied the ADMR technique to the novel C_{60} and C_{70}/polystyrene "glass". We show that the long-lived photoexcitations in them are triplet excitons with strong optical transitions in the triplet manifold.

In ADMR we detect changes in the steady state photomodulation (PM) spectrum associated with induced changes in the photoexcitation recombination kinetics. This is caused by resonant μ-wave absorption among Zeeman splitted electronic energy levels in a moderately strong magnetic field. This technique is similar to another optical detected magnetic resonance, the phosphorescence detected magnetic resonance (PDMR), except that in ADMR changes in PM intensity are detected, whereas in PDMR changes in photoluminescence (PL) intensity are recorded. ADMR is therefore more versatile because it does not require radiative recombination.

2. EXPERIMENTAL

Our ADMR set-up (Fig. 1) consists of a pump beam, from an Ar^+ laser at 488nm, and a probe beam from an incandescent light source dispersed by a monochromator, in the spectral range of 0.25 to 2 eV. The sample was placed in a high Q value μwave cavity with resonance at about 3 GHz (S band), equipped with optical windows for transmission. The cavity was placed in a dewar in a superconducting magnet with a field H up to 3 Tesla. We used an RF field at 2.99

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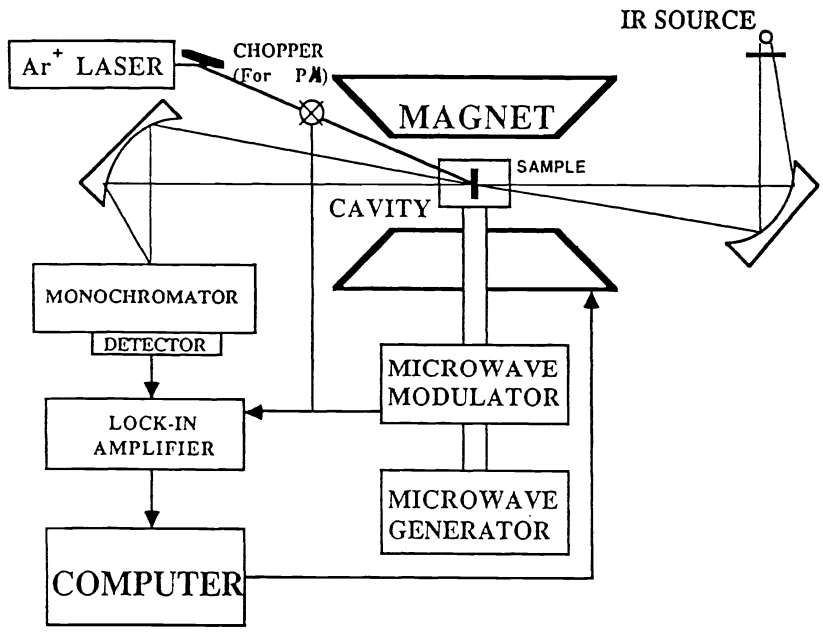


Fig. 1: Block diagram of the ADMR experimental set-up.

GHz with power up to 200 mW which was modulated at 500 Hz. After proper signal averaging, the sensitivity $\delta T/T$ (where T is the transmission and δT is its spin modulation change) of our apparatus was about 3×10^{-8} in the Si-detector spectral range, which decreased to 2×10^{-7} in the InSb ir range. The PM spectra were detected by modulating the Ar^+ laser beam, whereas the ADMR spectra were obtained by modulating the RF field. Two types of ADMR spectra were obtained: the H-ADMR spectrum for which H was swept at a fixed probe wavelength, and the P-ADMR spectrum for which the probe wavelength was changed at a constant H, in resonance.

The samples studied were a soluble t-$(CH)_x$ film and two solution-cast films of alkoxy derivatives of PPV:DOO and DHO[3], all deposited on sapphire substrates. The C_{60} "glass" was obtained by mixing 2% C_{60} powder in a solution of polystyrene in toluene. Active evaporation yielded flexible films with an effective optical density of 0.5 at 2.5 eV.

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3. APPLICATIONS OF ADMR SPECTROSCOPY TO CONDUCTING POLYMERS

Considerable PM and light induced ESR (LESR) studies have been carried out to investigate the photoexcited states in conducting polymers with degenerate and nondegenerate backbone ground state structures[4], in order to observe the quasiparticles predicted by various theoretical studies. In general, the main feature of the PM spectra consists of high energy (HE) and low energy (LE) PA bands and a PB (photobleaching) band of the interband transitions[5].

3.1 *t-$(CH)_x$*

The PM spectrum of t-$(CH)_x$ at 4K is shown in Fig. 2. It consists of a LE band (0.45 eV) identified as due to spinless charged solitons S^+ and S^- [4,5]; correlated with it is a prominent oscillation above 1.45 eV, identified[5] as due to electroabsorption (EA) caused by the photogenerated $S^{\pm}$. The HE band (1.35 eV), which is associated with neutral photoexcitations[5], however, has still remained a mystery for over a decade. Recent careful LESR studies of t-$(CH)_x$[6] have conclusively shown that spin ½ species are photogenerated. It was speculated[6] that they are neutral solitons S° associated with the HE band. The following ADMR studies can prove this assumption.

The ADMR spectrum of t-$(CH)_x$ is shown in Fig. 2. The inset shows the H-ADMR signal at 1.35 eV (at the peak of the HE band). A single symmetrical band, with a reduction of PA ($\delta n/n \approx -6 \times 10^{-3}$), was observed at 1067 Gauss (s = ½, g ≈ 2.003). The P-ADMR spectrum at a fixed H of 1067 Gauss, which is also shown in Fig. 2, consists of the following features[3].

1) A HE band, with a relatively large δn reduction: $\delta n/n \approx -6 \times 10^{-3}$, with the same spectral shape as the HE band in the PM spectrum.
2) A smaller increase in the $S^{\pm}$ population at the LE band: $\delta n/n \approx 10^{-3}$ and a correlated small EA oscillation above 1.45 eV.

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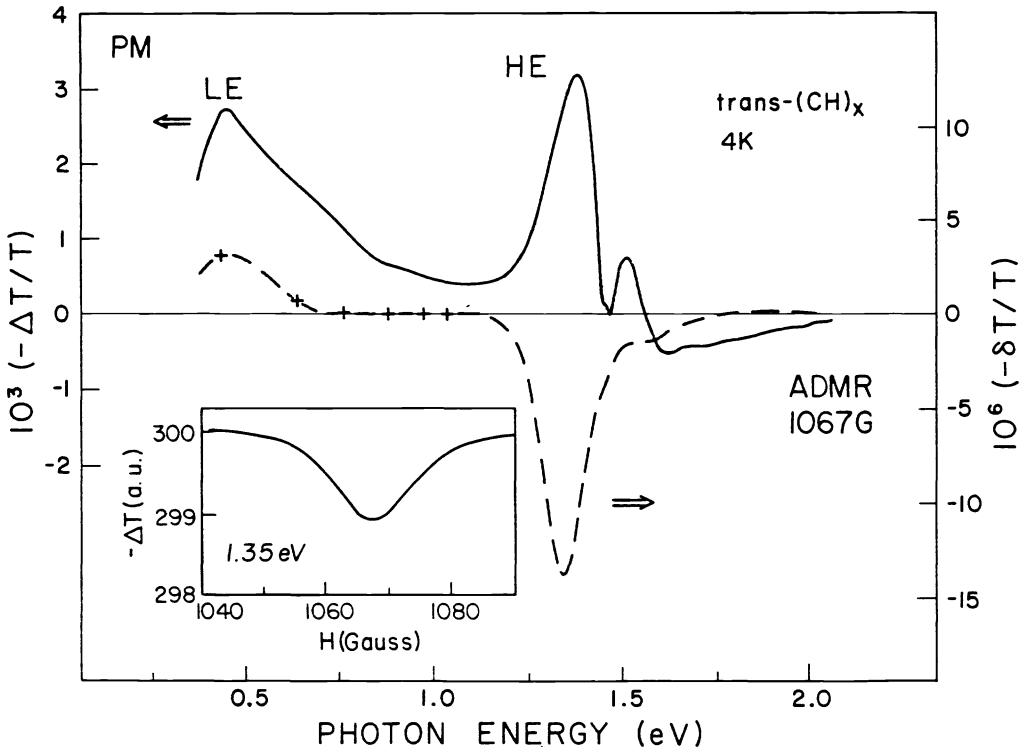


Fig. 2: PM spectrum (solid line) and P-ADMR spectrum (broken line) at 1067 Gauss of soluble trans-$(CH)_x$ film at 4K. The inset shows the H-ADMR spectrum at 1.35 eV (HE peak).

3) A small reduction of the PB band, suggesting enhanced recombination to the ground state. δn(HE) is correlated with δn(LE) as verified[3] by their same dependencies on the pump excitation intensity I_L, the microwave modulation frequency f and sample temperature Θ. For example, in the PM spectrum, the HE and the LE PA bands do not decrease with Θ in the same way[5]; their δn signals, however, decrease together[3] with Θ.

The ADMR spectrum shows, therefore, that a spin ½ excitation is associated with the HE band as well as with the LE band. Resonant microwave absorption reduces the photoexcitation population associated with the HE band and enhances the population of charged solitons (LE) and the ground state. The only viable candidate for this spin ½ signal is a neutral soliton (S°)[3].

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Several theoretical studies have shown that in many conducting polymers there is a reversed order of the excited $2A_g$ and $1B_u$ states. The $2A_g$ state is therefore lower in energy and in a degenerate ground state system such as t-$(CH)_x$, it can decay into two neutral solitons[7]. Another decay mechanism into $S^\circ\bar{S}^\circ$ pairs is a fast intersystem crossing of the singlet ^1B_u to a triplet ^3B_u state, followed by a triplet fision into a $S^\circ\bar{S}^\circ$ pair[8]. These decay channels into S° explain the PM and ADMR result which show in t-$(CH)_x$ both charged and neutral photoexcitations. An excited ^1B_u forms $S^+\bar{S}^-$ pairs, whereas other decay channels may produce $S^\circ\bar{S}^\circ$ pairs.

3.2 PPV

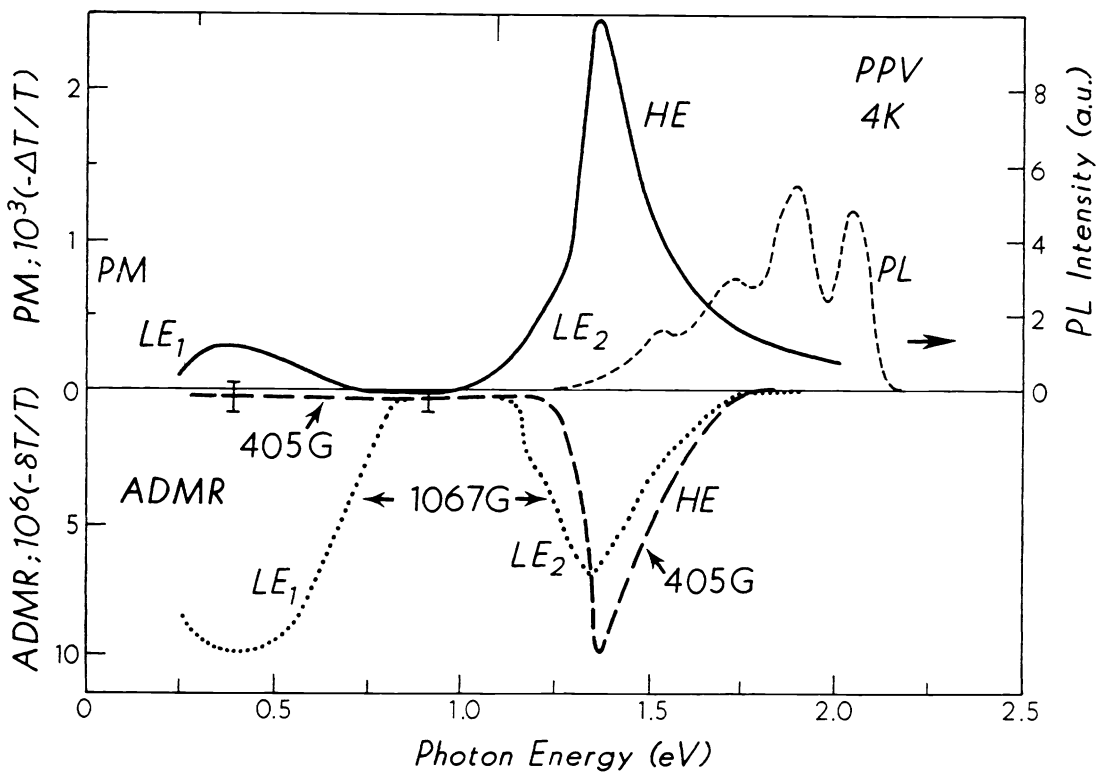


Fig. 3: PM spectrum (solid line) and P-ADMR spectra at 427 Gauss (broken line) and at 1067 Gauss (dotted line), of unoriented DOO-PPV film at 4K.

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The photoexcitation dynamics in polymers with nondegenerate ground state, such as PPV and its alkoxy derivatives, is very different from that of t-$(CH)_x$. Triplet excitons, formed either via the decomposition of $2A_g$ state[7] or through an intersystem crossing from the singlet manifold[8], cannot further produce $S^{\circ}\bar{S}^{\circ}$pairs because of the confinement of the backbone structure[4]. We expect therefore that triplet excitons would dominate the PM and ADMR spectra for neutral excitations. This is shown in Fig. 3 for the DOO derivative of PPV at 4K. The PM spectrum is composed of two main PA bands: LE_1 band at 0.35 eV and HE band at 1.36 eV; a shoulder (LE_2) is also evident at about 1.3 eV. The LE_1 and HE PA bands in PPV do not share any common origin as evidenced by their distinct I_L, Θ and modulation frequency dependencies[3]. In fact the LE_1 band is due to charged photoexcitations, whereas the HE band is due to neutral excitations.

The P-ADMR spectra taken at 1067 Gauss (S = ½) and at 405 Gauss (S = 1) are also shown in Fig. 3. The triplet ADMR spectrum contains a single band peaked at 1.36 eV with the same spectral shape as the HE band in the PM spectrum. The spin ½ ADMR spectrum, however, contains two bands peaked at 0.3 and 1.3 eV which are equivalent to the LE_1 band and LE_2 shoulder, respectively, in the PM spectrum. We therefore identify the LE_1 and LE_2 PA bands as due to optical transitions associated with photogenerated bipolarons ($BP^{2\pm}$)[4]. The HE band, on the other hand, is due to optical transitions in the triplet manifold, associated with photogenerated triplet excitons in PPV[9].

According to the above theoretical pictures, in nondegenerate ground state systems an excited $1B_u$ state can decay into spin ½ polarons ($P^{\pm}$), which are not topological defects and are therefore relatively mobile in the sample. Polarons can either directly recombine, or form bipolarons. Resonant microwave absorption induces "spin-flip" which enhances polaron recombination[1], and consequently reduces the population of bipolarons. For the triplets, resonant microwave absorption induces spin-flip among the triplet sublevels which in turn enhances recombination[10]. The ADMR signal is thus also negative due to the decrease in the triplet steady state population.

4. APPLICATION OF ADMR SPECTROSCOPY TO C_{60}

The recent synthesis of macroscopic amounts of the spherical all-carbon molecule C_{60}[11] has stimulated a variety of studies on their chemical and physical properties. This new form of solid carbon has a graphitic closed cage structure

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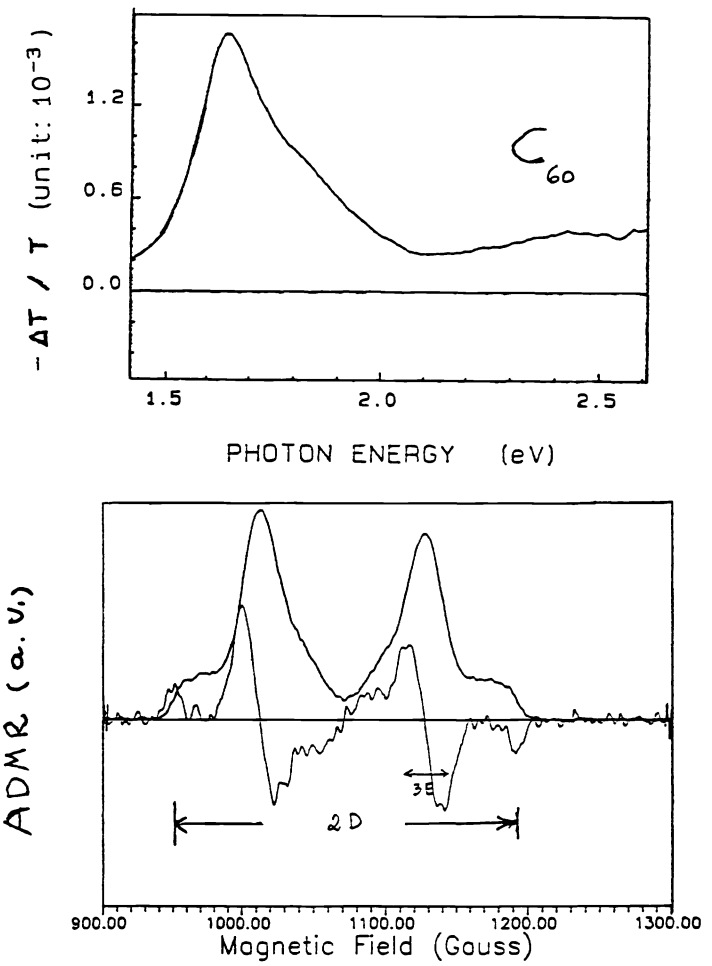


Fig. 4: The PM spectrum of C_{60}/polystyrene "glass" at 4K and the H-ADMR spectrum at 1.65 eV (at the peak of the PA band). The derivative of the H-ADMR spectrum and the way to extract the triplet parameter D and E are also shown.

consisting of 12 five-membered rings separated by 20 benzenoid six-membered rings. The molecule, which contains 60 carbon atoms lying at the vertices of a truncated icosahedron is known as Buckminster-fullerene because it reminds of the geodesic structures of the famous architect (Buckminster Fuller), which led to the initial proposal of the C_{60} structure[12]. Since there are alternate single a double bonded carbon atoms along special directions on the C_{60} surface, with delocalized π-electrons, C_{60} must bear some similarities to π-conjugated polymers and we have embarked to study its optical properties to unravel these similarities.

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Solutions of C_{60} can be readily prepared; the long-wavelength absorption edge lies at about 620 nm. The triplet-triplet absorption spectrum (1.1 to 3 eV) has been recently measured in C_{60} solutions by the transient absorption technique in the picosecond to millisecond time range. Transient light induced ESR (LESR)[13] and triplet oxygen quenching have been utilized to verify that the primary long lived photoexcitations in C_{60} solutions are triplet excitons.

Recently we have studied the photoexcitations in C_{60} and C_{70} "glasses" by the PM and ADMR techniques. In C_{60} "glass", prepared by mixing 2% C_{60} with polystyrene, we measured one PA band in the PM spectrum, peaking at 1.65 eV, as is seen in Fig. 4. According to previous studies[14] this PA band is due to triplet absorption in the triplet manifold, but no direct proof has been given. The H-ADMR spectrum in Fig. 4 measured at 1.65 eV (the PA band peak) can provide this missing information.

The ADMR is negative corresponding to reduction in n with $\delta n/n \approx -3 \times 10^{-3}$. The H-ADMR is composed of two symmetric bands each starting with a pronounced step. The magnetic resonance is centered around 1070 Gauss and therefore we identify it as a triplet "powder pattern" associated with $\Delta m_s = \pm 1$ transitions among the triplet sublevels with g=2.003. We have also observed the correlated $\Delta m_s = \pm 2$ transition ("½ field" signal) centered around 530 Gauss. The deviation from the exact "½ field" value of 535 Gauss is due to the D and E spin dipolar interaction parameters in the triplet Hamiltonian[10]. The D and E parameters can be obtained from the derivative of the powder pattern[13] as seen in Fig. 4. We obtained D = 122 Gauss ($=115 \times 10^{-4}$ cm^{-1}) and E = 9 Gauss ($=6 \times 10^{-4}$ cm^{-1}), consistent with LESR results of C_{60} powder[13].

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