

Optical probes of photoexcitations in fullerene thin films
from femtoseconds to milliseconds

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ABSTRACT

We have studied photoexcitations in various fullerene thin films using transient photomodulation and photoluminescence from 100 fs to 50 ms and absorption-detected magnetic resonance (ADMR). We show that singlet Frenkel type excitons are the primary photoexcitations; their recombination kinetics in the picosecond time domain are dispersive as a result of inhomogeneity. The long-lived photoexcitations, however, are shown to be triplet excitons and charged polarons, identified by the correlation found between their associated optical transitions and ADMR signals with spin 1 and $\frac{1}{2}$, respectively.

Keywords: Fullerenes, photoexcitations, photomodulation, photoluminescence, optically detected magnetic resonance, picosecond transients.

1. INTRODUCTION

The discovery of the fullerenes,¹ and their subsequent production in gram quantities,² have resulted in an intensive effort to understand their chemical and physical properties. So far, C₆₀ and alkali metal doped C₆₀ have been the subject of extensive experimental and theoretical work. C₇₀, the second most abundant member of the fullerene family after C₆₀,¹ has been the subject of substantially less theoretical and experimental investigation. Optical transitions across the HOMO-LUMO gap are dipole forbidden in C₆₀ molecules, but are weakly allowed in the solid form.³ Band structure calculations show that C₆₀ solid is a molecular semiconductor with a direct bandgap of 1.5 eV between narrow (~0.5 eV) continuum bands.⁴ However, recent experiments indicate that the bandgap of C₆₀ is 2.3 eV,^{5,6} and therefore the weak optical absorption below 2.3 eV corresponds to intramolecular Frenkel type excitons. The reduced symmetry of C₇₀ relative to C₆₀ leads to a much stronger absorption in the vicinity of the HOMO-LUMO gap.⁷ Solid C₇₀, like solid C₆₀, is expected to retain much of its molecular character due to the weak van der Waals binding. However, studies of photoexcitations in C₆₀ thin films have shown many properties which are different from those of C₆₀ in solution.⁸⁻¹¹ For example the absorption spectra of charged excitations have also been observed in C₆₀ and C₇₀ thin films.^{12,13} It is therefore of interest to study the character and dynamics of photoexcitations in C₆₀ and C₇₀ thin films.

Transient absorption spectra of C₆₀ and C₇₀ molecules in solution have been measured before on picosecond time scales.¹⁴⁻¹⁶ The first excited singlet state S₁ in C₆₀ has a broad photoinduced absorption (PA) band at 1.35 eV which corresponds to transitions to S_n. S₁ has a lifetime of 1.3 ns and decays by intersystem crossing to the lowest excited triplet state T₁, which is characterized by a PA band at 1.65 eV.¹⁵⁻¹⁶ The S₁ absorption in C₇₀ shows a broad PA band near 1.8 eV and a smaller band near 1.5 eV. The S₁ lifetime in C₇₀ is 700 ps and the T₁ absorption band is formed near 1.3 eV.^{14,16} We have undertaken a study of the primary photoexcitations and their dynamics in C₆₀ and C₇₀ thin films by

measurement of their picosecond transient PA spectra and transient photoluminescence. To complement our studies we have measured the transient PA spectra in the millisecond time domain and also used an optically magnetic resonance (ODMR) technique to identify the photoexcitations.

2. EXPERIMENTAL

We have applied a variety of cw and transient optical probes to study the primary photoexcitations and their byproducts, in a vast time domain from 100 femtoseconds (fs) to 50 milliseconds (ms) and spectral range of 0.25 to 2.6 eV. To cover such a large time domain, we have used several experimental techniques. In the fs and picosecond (ps) domains we have used the transient photomodulation (PM) and photoluminescence (PL) techniques. PM measures the excited state absorption and is therefore sensitive to all photoexcitations, whereas PL measures only radiative photoexcitations; the comparison between the transient PM and PL decays, however, is instructive.¹⁷ For the long-lived photoexcitations we have used the cw PM technique.¹⁸ Charged excitations in the PM spectrum are identified by a characteristic PA feature which resembles the electro-absorption spectrum caused by applying an external electric field.¹⁹ Other excitations in the PM spectrum are separated by measuring their associated spin state, using the absorption-detected magnetic resonance (ADMR) technique.²⁰ This technique is sensitive to spin-dependent recombination processes identifying therefore photoexcitation optical transitions in the PM spectrum associated with spin zero, $\frac{1}{2}$, and 1, respectively.

The spectral evolution of the excited states in the picosecond time domain was studied by the pump-and-probe correlation technique using two dye lasers synchronously pumped by a frequency-doubled modelocked Nd:YAG laser at a repetition rate of 76 MHz. A NaCl (F_2^+)_H color center laser,²¹ synchronously pumped by the residual Nd:YAG fundamental, was also used in place of one of the dye lasers. The pump-probe system had a cross correlation of about 5 ps and the probe pulse could be delayed by up to 3 ns relative to pump pulse. Transient spectra of the photoinduced change (ΔT) in the sample transmission (T) were obtained at a fixed pump photon energy of 2.17 eV and probe photon energies in the range 1.2-2.3 eV (dye laser) and .74-.83 eV (color center laser) with a sensitivity in $\Delta T/T$ of 3×10^{-6} .¹⁷ The transient PL was measured with a streak camera which had a resolution of 10 ps and a time range of up to 2.5 ns. For the PM measurements in the femtosecond time domain we used a colliding pulse modelocked (CPM) dye laser with 60 fs pulse duration at 620 nm (2 eV). The time interval between 1 μ s to 50 ms was studied using a cw PM apparatus.¹⁸ The excitation was an Ar⁺ laser beam modulated at frequency f between 20 Hz and 1 MHz by an acousto-optic modulator, and the probe beam was a premonochromatized incandescent lamp in the spectral range of 0.25 to 2.6 eV. $\Delta T(f)$ was measured by a set of fast detectors with matched preamplifiers and a lock-in amplifier.

The ADMR technique²⁰ 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 GHz) equipped with optical windows, and a superconducting magnet producing a field H . Microwave (μ -wave) resonant absorption, modulated at 500 Hz, leads to small changes, δT , in the probe transmission T . This δT is proportional to δn , the change in the photoexcitation density n produced by the pump. δn is induced by transitions in the μ wave range that change spin-dependent recombination rates.

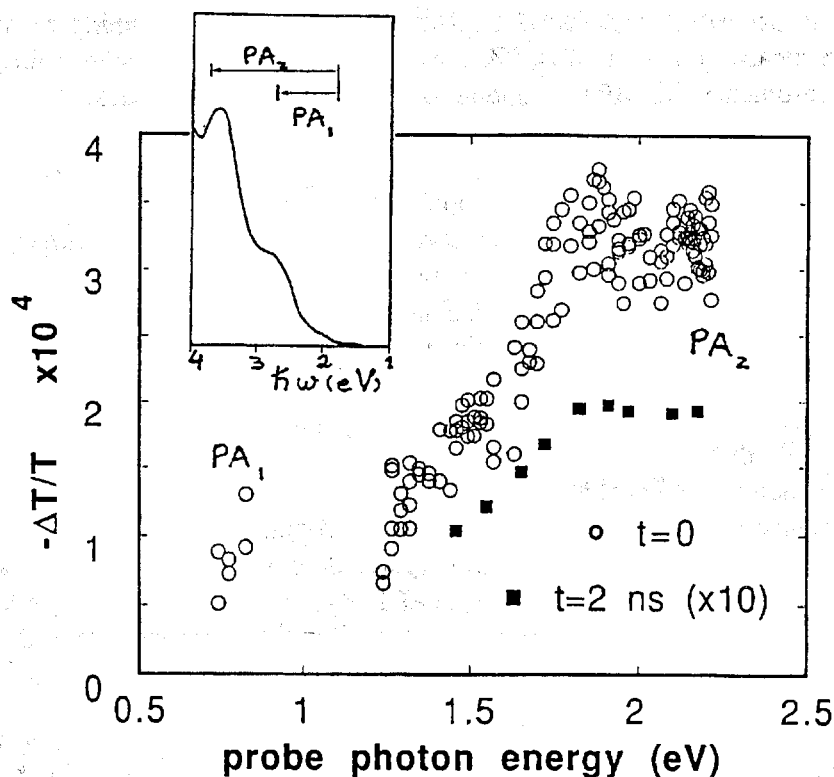


Fig. 1: The transient photomodulation spectrum of C_{60} film at $t = 0$ circles, and $t = 2000$ ps squares, respectively. The inset shows the expected transitions PA_1 and PA_2 from an exciton level at 1.8 eV.

Purified C_{60} and C_{70} powders, from MER Corporation, with purity better than 99% as established by Raman scattering, were deposited at 450°C on sapphire substrates by evaporation at 5×10^{-6} torr. X-ray diffraction and low resolution atomic force micrographs showed nanocrystalline films.²² The film thickness was about 1000 \AA as determined from the film absorption spectrum. The films were kept in air.

3. RESULTS AND DISCUSSION

3.1 C_{60}

The transient PM spectrum of C_{60} is shown in Fig. 1 for time delays of 0 and 2000 ps, respectively. The dominant feature is a broad PA band near 1.8 eV (PA_2), and there is significant PA out to 0.8 eV (PA_1). Since the first excited state has the same parity as the ground state, absorption to the first excited state is dipole forbidden, but the first excited state should have the same allowed transitions as the ground state. Therefore we expect to observe excited state absorption similar to the ground state absorption but shifted by the exciton energy (see Fig. 1, inset). Using the CPM laser, we found that PA_2 is formed instantaneously; no initial photobleaching is observed.²³⁻²⁵ This shows that the PA response is dominated by excited state absorption. The PA spectrum remains essentially unchanged for times up to

3ns. The intransigence of the PM spectrum in our C_{60} thin films is in marked contrast to the results for C_{60} in solution where a triplet PA band forms in 1.3 ns.¹⁵

The dynamics of the PA and PL from 10 ps to 3 ns were measured and compared. The visible and ir PA decays and the PL decay were found to be similar and could be approximately fit by a power law decay of $t^{-5.6}$. Since the PL is weak in C_{60} , the primary decay channel is probably non-radiative. In this case, both the PL and PA should be proportional to N , the number density of excitations, and from the similarity of the decays we can conclude that the three components share a common origin. The PL in C_{60} has been attributed to self-trapped polaronic excitons⁸ which would be consistent with our PM spectrum. The localization may explain the delay in the intersystem crossing observed in the C_{60} thin films relative to C_{60} in solution. We conclude, therefore, that the primary photoexcitations in C_{60} films are Frenkel type excitons.

Because of the known inhomogeneity in C_{60} films,²⁶ we consider that the Frenkel excitons recombine with a characteristic distribution $G(\tau)$ of recombination times τ . Then, the surviving exciton density $N(t)$ is given by:¹⁷

$$N(t) = N(0) \int_{\tau_1}^{\tau_2} d\tau G(\tau) e^{-t/\tau} \quad (1)$$

where the upper integration limit τ_2 is determined by the pump modulation frequency f ($\tau_2 = 1/f = 100$ ns), whereas the lower limit τ_1 is set by the resolution of the experiment (5 ps). Using Eq. (1) and a broad distribution $G(\tau)$ of the form $G \sim \tau^{-(1+\alpha)}$,¹⁷ we calculate $N(t) \sim (t/\tau_1)^{-\alpha}$, consistent with the power law decay observed at $\lambda_{ex} = 570$ nm, where $\alpha = 0.57$. A narrower $G(\tau)$ of the form $G \sim \exp[-(\tau)^\nu]$ results in $N(t) \sim \exp[-(t/\tau_0)^\beta]$, where $\beta = \nu/(1+\nu)$,²⁵ consistent with the stretched exponential PA decay at $\lambda_{ex} = 620$ nm observed in Ref. 23.

We now turn to the long lived photoexcitations, studied by the PM technique; their spin states have been studied by the ADMR technique.²⁵ Three typical H-dependent ADMR spectra of the C_{60} film measured at different probe photon energies are shown in Fig. 2 (insets). Each H-dependent spectrum contains two components with opposite signs and different photon energy spectrum: a broad (powder pattern) component ($\Delta H = 180$ G) with $\delta n/n \approx -2 \times 10^{-3}$ and a narrow component ($\Delta H = 15$ G) with $\delta n/n \approx 10^{-2}$. Correlated with the broad component, centered at $H = 1071$ G, there is a negative "half field" signal at $H = 531$ G (not shown). This clearly identifies the negative ADMR component at full and half fields as $\Delta m_s = \pm 1$ and $\Delta m_s = \pm 2$ transitions, respectively, associated with μ wave absorption by triplet exciton sublevels. We identify the narrow positive ADMR component peaked at 1071 G, as being due to spin $1/2$ excitations with $g \approx 2.000$, similar to the PL ODMR results in C_{60} films.²⁷

The different photon energy dependent spectra of the $S = 1/2$ and $S = 1$ components in ADMR are also shown in Fig. 2. The triplet spectrum contains two $\delta n < 0$ bands at 1.1 and 1.8 eV, respectively (T_1

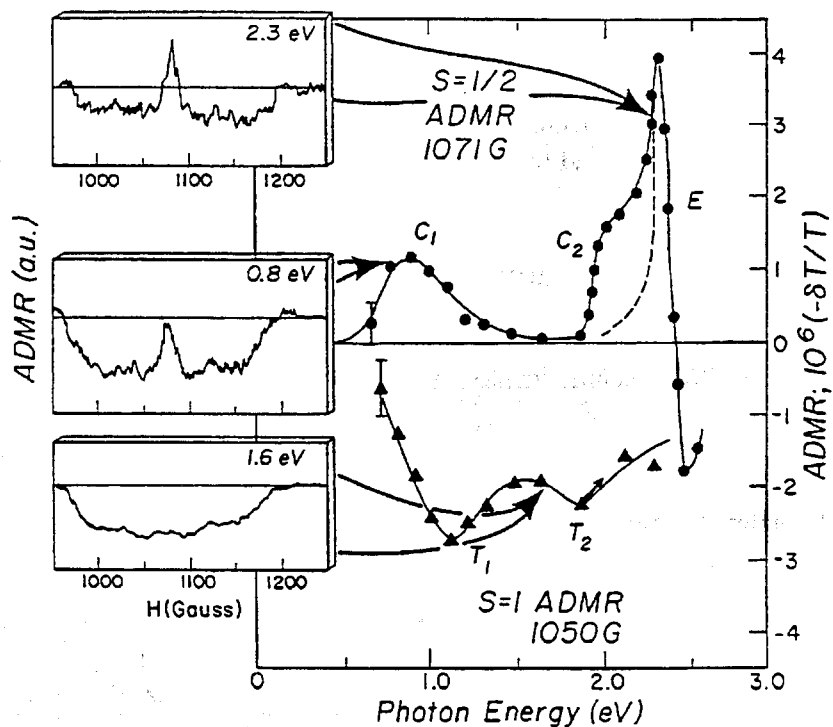


Fig. 2: Spectra of the $S = \frac{1}{2}$ (positive, peaked at $H = 1071$ G) and $S = 1$ (negative, measured at $H = 1050$ G) components of the ADMR signal of C_{60} film. The bands C_1 , C_2 , T_1 , T_2 , and E are assigned. The insets show three typical H -dependent ADMR measured at probe photon energy of 0.8, 1.6, and 2.3 eV, respectively, to demonstrate the different spectra of the two ADMR components.

and T_2 PA bands in the PM spectrum). We conclude that the long-lived neutral photoexcitations in C_{60} films are triplet excitons. The spin $1/2$ ADMR spectrum (Fig. 2), on the other hand, contains three spectral features: two δn bands with energies of 0.8 and 2 eV, respectively, and a derivative-like δn band with zero crossing at 2.4 eV. These δn bands are assigned respectively C_1 , C_2 , and E PA bands of charge carriers in the PM spectrum.²⁵ Similar optical transitions have been measured in the absorption spectra of C_{60} films doped with alkali metal.^{28,29} We also note that recent theoretical calculations have shown that polarons (C_{60}^{\pm}) are stable in C_{60} , with binding energy of order 0.1 eV.^{30,31} Their optical absorption spectra contain two new bands at 0.7-1.0 eV and at 2.5-2.8 eV, respectively, similar to the C_1 and C_2 PA bands associated with spin $1/2$ carriers observed here. We thus tentatively identify the long-lived charge carriers in C_{60} films as spin $1/2$ polarons, C_{60}^{\pm} . Neither the polaron PA spectrum (C_1 , C_2 and E) nor the triplet PA spectrum (T_1 and T_2) are similar to the ps PA transient shown in Fig. 1, in agreement with the different origin of the primary excitations in C_{60} films identified as singlet excitons.

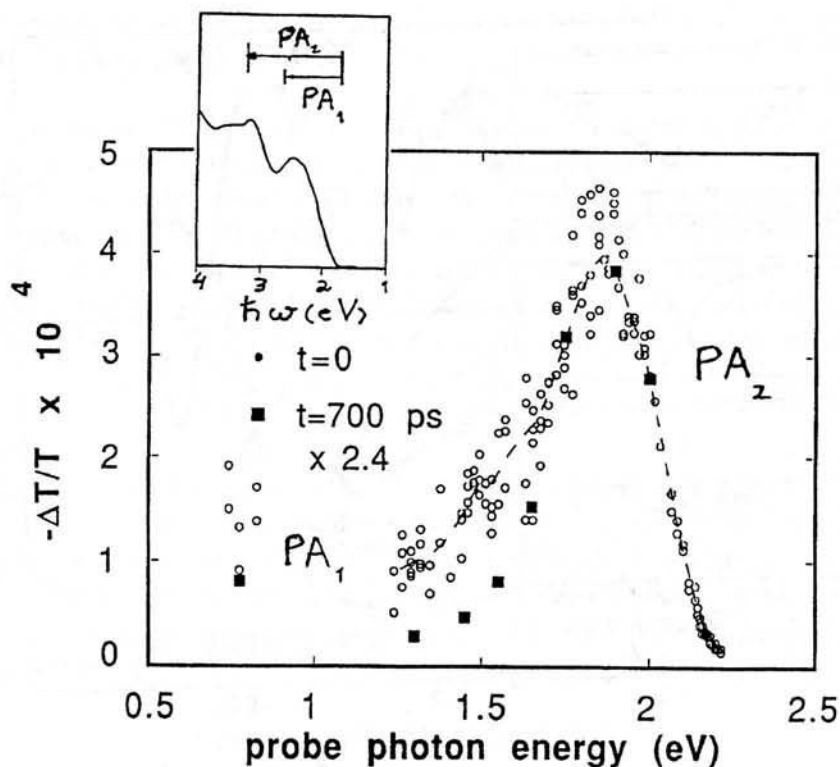


Fig. 3: The transient PM spectrum of C_{70} film at $t = 0$ (circles) and $t = 700$ ps (squares), respectively. The line through the data points is a guide to the eyes. The inset shows the expected transitions, PA_1 and PA_2 , from an exciton level at 1.7 eV.

3.2 C_{70}

The transient PM spectrum of C_{70} is shown in Fig. 3 for the time delays of 0 and 700 ps, respectively. The main feature of the spectrum is a photoinduced absorption (PA) band, PA_2 , centered near 1.8 eV with a width of 0.4 eV. There is also evidence for a PA feature near 0.8 eV, PA_1 . The spectrum at 700 ps is similar to the $t = 0$ spectrum; however, there is a noticeable narrowing of PA_2 . PA_2 is similar to the absorption of charged C_{70} ,¹³ but is also consistent with singlet exciton absorption to allowed higher energy states (Fig. 3, inset). Measurement of the excitation spectrum of C_{70}^{\pm} ³² shows that at 2.17 eV we are exciting appreciable amounts of C_{70}^{\pm} . Thus we expect that PA_2 has contributions from both singlet exciton and C_{70}^{\pm} absorptions. PA_1 may correspond to a 0.6 eV feature in the C_{70}^{\pm} absorption spectrum,¹³ but there is also the possibility of singlet exciton absorption to states at lower energies than the ones responsible for PA_2 (Fig. 3, inset).

The dynamics of the PA and PL from 10 ps to 3 ns have been also measured.³² The PA decays are roughly the same for probe photon energies between 1.75 and 2 eV. The decay rate increases

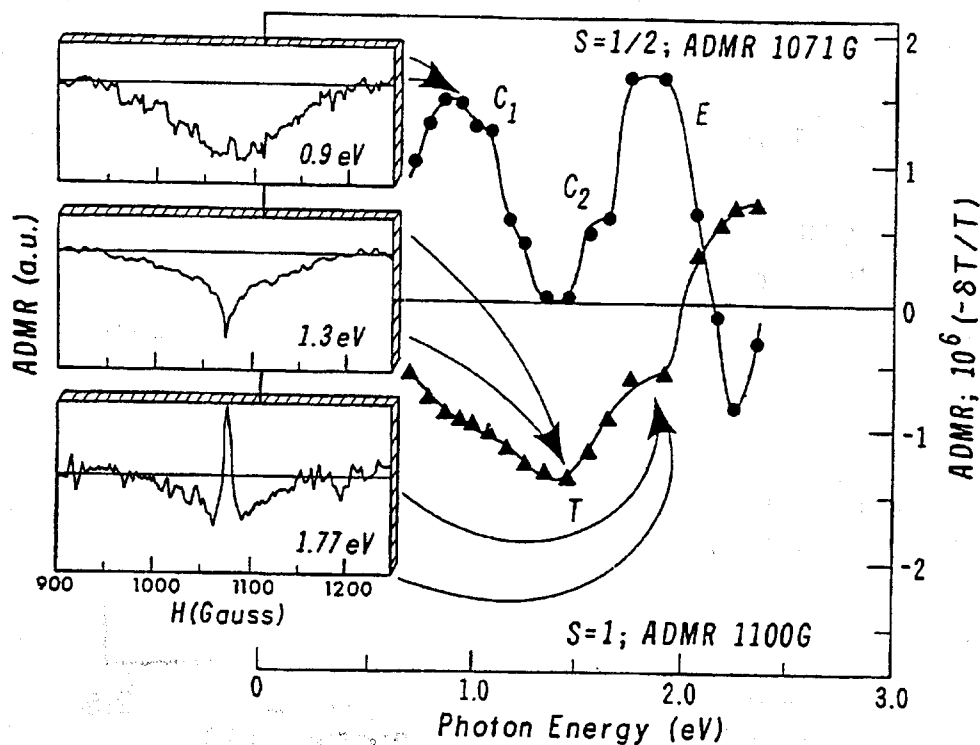


Fig. 4: P-ADMR spectra of $S = \frac{1}{2}$ (at $H = 1071$ G) and $S = 1$ (at $H = 1050$ G) components of the ADMR in C_{70} films. The band C_1 , C_2 , T and E are assigned. Three typical H-ADMR spectra at 0.9, 1.3 and 1.77 eV, respectively are also shown in the insets to demonstrate the two ADMR components in the spectrum: the broad negative component is due to triplets, whereas the narrow, positive component is due to $S = \frac{1}{2}$ photoexcitations.

monotonically with decreasing probe energy in the range 1.3 to 1.75 eV. The PA decay at 0.8 eV is slower than that at 1.3 eV, but faster than the decay at 1.75 eV, also suggesting that there is a separate PA feature near this energy. The 1.75 eV PA decay shows a change in dynamics near 100 ps, suggesting that there are two components to the decay. This change is less dramatic in the 1.5 eV decay, and is not observable in the 0.8 eV decay. A fit to the 1.75 eV decay as the sum of two exponentials gives lifetimes of 52 ps and 2.2 ns for the fast and slow components, respectively. Again there is no evidence for the formation of a triplet absorption band for $t \leq 3$ ns, in contrast to the results for C_{70} in solution.

Three typical H-ADMR spectra of the C_{70} film measured at different probe photon energies are shown in Fig. 4. Each spectrum contains two ADMR components with opposite signs and different P-ADMR spectrum: a broad (powder pattern) component ($\Delta H = 120$ G) with $\delta n/n \approx -3 \times 10^{-2}$ and a narrow component ($\Delta H = 15$ G) with $\delta n/n \approx 8 \times 10^{-2}$. Correlated with the broad component, centered at $H_0 = 1071$ G, there is a negative H-ADMR signal at $H = 532$ G (half field). This clearly identifies the negative H-ADMR bands as $\Delta m_s = \pm 1$ and $\Delta m_s = \pm 2$ transitions, respectively, associated with μ -wave

absorptions of triplet excitons. In contrast, we identify the narrow, positive ADMR component peaked at 1071 G, as due to spin $\frac{1}{2}$ excitations with $g \approx 2.000$.

The P-ADMR spectra of the $S = \frac{1}{2}$ and $S = 1$ ADMR components are also shown in Fig. 4. The triplet spectrum contains a broad band peaked at 1.5 eV (band T is the PM spectrum),³³ hence we conclude that the long-lived neutral photoexcitations in C_{70} films are also triplet excitons. By contrast, the spin $\frac{1}{2}$ P-ADMR spectrum (Fig. 4) contains three spectral features: two δn bands at 0.8 and 1.7 eV, respectively, and a derivative like δn band with zero crossing at 2.2 eV. The $\delta n > 0$ bands are C_1 , C_2 and E bands of charge carriers in the PM spectrum.³³ From the similarity of the PM spectrum in C_{70} films to that in C_{60} films [9], we identify the C_1 and C_2 bands as due to optical transitions of C_{70}^- and C_{70}^+ , respectively,³⁴ whereas the E band is due to electroabsorption associated with photoinduced electric fields in the film^{19,35} caused by the photogenerated C_{70}^\pm .

From the similarity of band E (Fig. 4) to the main PA band (PA_2) in the ps transient PA (Fig. 3), we conclude that PA_2 in the ps transient PA is due either to photogenerated electric fields in the C_{70} film²⁵ or to transient strains produced by the ps pulses.³⁶ In both cases the PA decay should be much slower than the decays due to exciton and carrier recombination. We therefore conclude that the excitonic PA spectrum in C_{70} films has two main components peaking at 0.8 and 1.4 eV, respectively, consistent with the two possible transitions depicted in Fig. 3 inset.³⁷

4. CONCLUSIONS

Our results for photoexcitations in C_{60} thin films can be explained by the following scenario:³⁷ Upon excitation, singlet Frenkel type excitons are formed at an energy near 1.8 eV. Some of them decay radiatively giving rise to the weak photoluminescence. The self-trapped nature of the excitons results in a slow ($t \geq 3$ ns) intersystem crossing. For C_{70} films the scenario is somewhat more complicated. Singlet excitons are the primary excitations in C_{70} as well.³² However their PA spectrum is weaker than a dominant PA band, which is caused by transient strains or electric fields, which are generated in the film by the ps pulses.³⁶ The excitons in C_{70} films decay primarily radiatively giving rise to the fast PL and the fast component of the PA decay in the visible.²⁵ These excitons may also be self-trapped, resulting in a delayed intersystem crossing at a time greater than 3 ns.

The cw PM and ADMR spectra show that the long-lived photoexcitations in C_{60} and C_{70} films are polarons (C_{60}^\pm and C_{70}^\pm) and triplet excitons, respectively, which are indirectly photogenerated, with very different PA bands than those of the primary singlet excitons in the ps time scale.

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