Magnetoe-Optical Characterization of Excited States in C$_{60}$

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by

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Prepared for Publication in

Physical Review Letters

May 15, 1992
Magneto-Optical Characterization of Excited States in C_{60}

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Abstract

We have used various optical and optically detected magnetic resonance techniques to characterize excited states in C_{60} in toluene/polystyrene (T/PS) glass and C_{60} films produced by evaporation. In C_{60}: T/PS glass at 4K we found long lived (~5 ms) triplet excitons which recombine radiatively with a linear kinetics. Their relatively small zero-field-splitting (ZFS) parameters indicate delocalization over the entire C_{60} molecule. In C_{60} film, however, we found both neutral and charged excitations, with bimolecular recombination kinetics. The neutral photoexcitations are more delocalized triplets with smaller ZFS, whereas the charge carriers are spin 1/2 excitations which we identified as C_{60}^* due to their optical transitions and associated photoinduced electroabsorption.

92-14080
Since the fullerenes and in particular C$_{60}$ became available in quantity [1], they have stimulated a great deal of experimental work. Most dramatically, C$_{60}$ films show superconductivity at T$_c$ as high as 47K [2,3] when doped with alkali metals. The structure of C$_{60}$ and its aromaticity have been convincingly demonstrated with good agreement between experiment and theory [4]. Photoexcitation (or photo-doping) provides a means of charge injection at a very low concentration and this may help in separating intramolecular and intermolecular interactions in C$_{60}$ films. Although several studies of excited states in C$_{60}$ solutions have been recently reported [5-8], the nature of the photoexcitations in C$_{60}$ solids, where the intermolecular interaction is more important, have yet to be identified [9-12].

In this work we characterize the photoexcitations in C$_{60}$ in toluene/polystyrene (T/PS) glass and thin films produced by evaporation, using various optical and magneto-optical techniques. They include photomodulation (PM), photoluminescence (PL), and their optically detected magnetic resonance: the absorption detected magnetic resonance (ADMR) and the PL detected magnetic resonance (PDMR), respectively. We measured in C$_{60}$: T/PS glass long lived (~5ms) triplet excitons with photoinduced absorption (PA) bands in the triplet manifold at 1.65 and 1.8 eV, respectively, which recombine with linear kinetics. These triplets give rise to a triplet PL component and have relatively small zero-field-splitting (ZFS) parameters of D = 0.0115 cm$^{-1}$ and E = 0.0008 cm$^{-1}$, respectively, indicating delocalization over the entire C$_{60}$ molecule. In C$_{60}$ films, however, we measured both neutral and charged excitations, with bimolecular recombination kinetics. The neutral excitations form more delocalized triplet excitons with somewhat different PA bands and smaller ZFS parameters (D = 0.0098 cm$^{-1}$).
whereas the charged carriers are spin ½ excitations, with PA bands at 0.8 and 2 eV, respectively and a correlated electroabsorption due to the photogenerated electric fields in the film. Based on C₆₀ energy levels' calculation [13] we identify the charged photoexcitations as C₆₀⁺.

The PM and PL spectra have been excited by an Ar⁺ laser beam at 458 nm (pump) with intensity I₀ of 400 mWcm⁻² modulated at frequency f ranging from 20 Hz to 50 kHz by an acousto-optical modulator. The PI, from the sample and the transmission of a cw lamp (probe beam) were dispersed by a ¼ met. monochromator and measured by various solid state detectors in the spectral range of 0.3 to 2.7 eV. For the ADMR measurements the pump and probe beams constantly illuminate the sample mounted in a high Q microwave cavity at 3 GHz equipped with optical windows and a superconducting magnet producing a field H up to 3 Tesla. Microwave (μ-wave) resonant absorption modulated at a frequency between 20 to 4 KHz which leads to small change δT in the transmission proportional to δn, the change in photoexcitation density n produced by the pump beam. δn is induced by transitions in the μ-wave range that charge spin-dependent recombination rates. With suitable signal averaging, the system δT/T sensitivity was about 10⁻⁷. In PDMR we measure changes δL in the PL intensity L with sensitivity δL/L = 10⁻⁷. Two types of ADMR (PDRM) spectra were obtained: the H-ADMR spectrum, in which δT (δL) is measured at a fixed probe wavelength λ while sweeping H, and the P-ADMR spectrum in which δT is measured at a constant H, in resonance, while λ (probe) is varied.

Purified C₆₀ powder, with purity better than 99%, as established by Raman scattering spectroscopy [14], was mixed in a solution of degassed toluene/polystyrene which was
subsequently evaporated to form C_{60}: T/PS glass. The C_{60} films were deposited at 450 °C on sapphire substrates by evaporation at 5 \times 10^{-6} \text{ torr} [15]. The film thickness (1000Å to 2 μm) was controlled by the deposition time. X-ray diffraction and low resolution atomic force micrographs showed essentially amorphous to nanocrystalline type samples.

The optical and magneto-optical measurements of C_{60}: T/PS glass at 4K are shown in Fig. 1. The PM spectrum contains a strong PA band (T_{1}) which peaks at 1.65 eV [7,8] and a shoulder (T_{2}) at 1.8 eV. Both PA bands increase linearly with I_{L} showing monomolecular recombination kinetics. The H-ADMR spectrum at 1.65 eV (Fig. 1, lower inset) shows a 200 G wide triplet powder pattern at "full field" (Δm_s = ±1) around H = 1071 G with δn/n = -6 \times 10^{-3}, and a narrow (5 G) signal at "half field" (Δm_s = ±2) peaked at 531 G. To correlate the ADMR and PM spectra, we measured the P-ADMR spectra at 1010G (full field) and 531 G (half field), respectively, as shown in Fig. 1. Since the P-ADMR and PM spectra in Fig. 1 are identical, we conclude that the two PA bands in the PM spectrum are due to photoinduced triplet transitions. We note that the H-ADMR triplet powder pattern at full field is not simply an integration display of a standard thermalized triplet LESR lineshape [6], since transition probabilities as well as changes in the recombination rates among the triplet sublevels, are involved [16]. However, an accurate measure of the triplet ZFS parameters can be still obtained by taking the derivative of the H-ADMR spectrum [16]. From the six singularities, shown as arrows in Fig. 1 lower inset, we calculate for the triplets in C_{60}: T/PS, D = 0.0115 cm^{-1} and E = 0.0008 cm^{-1}, respectively, identical to the ZFS parameters determined previously by LESR [6]. The triplet state is thus nearly axially symmetric, of about 6Å in size, i.e., delocalized over...
most of the $C_{60}$ molecule (7Å in diameter). To estimate the triplets lifetime $\tau$ we measured the in-phase of out-of-phase ADMR signals at 1.65 eV, versus the $\mu$wave modulation frequency, as shown in Fig. 1 upper inset. Assuming longer spin lattice relaxation than $\tau$ [16], we determine $\tau$ at 4K to be 5 ms, an order of magnitude longer than in Ref. [6].

The PL spectrum of $C_{60}:^7T/PS$ is also shown in Fig. 1. It peaks at 1.65 eV [9-12]. Excitation frequency dependence of the PL at 4K shows that it contains a fast and slow components. The fast PL is probably due to emission of singlet excitons, whereas the slow component is due to emission of triplet excitons, as determine by its H-PDMR spectrum [12]. As shown in Fig. 1 (lower inset) the H-PDMR and H-ADMR triplet powder patterns are quite similar, however $\delta n < 0$, whereas $\Delta L > 0$. Also the in phase and out-of-phase ADMR and PDMR frequency dependencies are identical (Fig. 1, upper inset). These two measurements show that the $\mu$wave induced increase in the triplet recombination rate, which results in $\delta n < 0$ is mostly radiative in nature, in agreement with $\delta L > 0$. In fact from the values of $\delta L/L (\sim 10^4)$ and $\delta n/n (\sim -6 \times 10^3)$ we calculate that the triplet PL component is only 1/60 of the total PL signal. This is consistent with our measurements of the PL frequency dependence, separating the slow and fast components.

The PM spectrum of the $C_{60}$ film, however, is much more complicated [10,11] since it contains at least 5 PA features, as shown in Fig. 2 (b). These are PA bands $C_1$ and $C_2$ at 0.8 and 2 eV, respectively, $T_1$ and $T_2$ at 1.2 and 1.8 eV, respectively, and a derivative-like feature (E) with zero crossing at 2.4 eV. We found in $C_{60}$ films that all PA bands increase as $I_U^{14}$,
indicating a bimolecular recombination kinetics. However the PA bands do not share a common origin due to their distinctly different laser modulation frequency \( f \) and temperature \( T \) dependencies. \( C_1, C_2 \) and \( E \) depend stronger with \( f \) than \( T_1 \) and \( T_2 \) (Figs. 2(a) and 2(b)). Also \( T_1 \) and \( T_2 \) have a stronger \( T \) dependence than \( C_1, C_2 \) and \( E \); in fact at \( T = 300 \) K (Fig. 2(c)) \( T_1 \) and \( T_2 \) completely disappear from the PM spectrum.

The inset of Fig. 2 (c) shows our electro-absorption (EA) spectrum measured at 300 K on the same \( C_{60} \) film, with fields of 20K V/cm, which were modulated at 1 kHz. The EA spectrum shows strong derivative-like features [10,11] which at their lower energy side are identical with band \( E \) in the PM spectrum. We therefore identify \( E \) as due to EA caused by photogenerated electric fields in the film due to photoinduced charge separation. Since the band \( E \) is more correlated with \( C_1 \) and \( C_2 \), we tentatively identify \( C_1 \) and \( C_2 \) PA bands as due to photogenerated charge carriers; \( T_1 \) and \( T_2 \) PA bands, on the other hand, are due to neutral photoexcitations. Their spin states are analyzed with the following magneto-optical measurements.

Three typical H-ADMR spectra of \( C_{60} \) film measured at different probe photon energies are shown in Fig. 3. Each spectrum contains two components with opposite signs and different P-ADMR spectrum (Fig. 3): a broad (powder pattern) component \( (\Delta H = 180G) \) with \( \delta n/n = 2 \times 10^{-3} \) and a narrow component \( (\Delta H = 15 G) \) with \( \delta n/n = 10^{-2} \). Correlated with the broad component, centered at \( H = 1071 \) G, there is a negative H-ADMR signal at "half field" at \( H = 531 \) G. This clearly identifies the negative ADMR at full field and half fields as \( \Delta m_s = \pm 1 \).
The P-ADMR spectra of the $S = \frac{1}{2}$ and $S = 1$ ADMR components are shown in Fig. 3. The triplet spectrum contains two $\delta n < 0$ bands at 1.1 and 1.8 eV, identical to the $T_1$ and $T_2$ PA bands in the PM spectrum (Fig. 2(a) and (b)); we conclude that the long-lived neutral photoexcitations in $C_{60}$ film are triplet excitons. Their optical transitions in the triplet manifold are further split compared to the triplets in $C_{60}; T/PS$ glass (Fig. 1), probably due to additional energy relaxation in the film, consistent with their smaller ZFS parameters that we measured. Also since $T_1$ and $T_2$ PA bands in $C_{60}$ films and glass are both due to triplets, we can calculate the triplet-triplet annihilation or bimolecular recombination rate $b$ in $C_{60}$ films. This is based on the triplet steady state density in $T/PS$ glass ($N_p$) and in film ($N_p^f$), the laser excitation intensity $\chi$, and the triplet lifetime ($\tau$) in glass, and using the relation $b = N_p^f / (N_p^2 \tau)$. We obtain $b = 10^9 \text{ cm}^2/\text{sec}$, one of the largest exciton bimolecular recombination rate constants measured in solids.

By contrast, the spin $\frac{1}{2}$ P-ADMR spectrum (Fig. 3) contains three spectral features: two
\( \delta n \) bands at 0.8 and 2.1 eV, respectively, and a derivative-like \( \delta n \) band with zero crossing at 2.4 eV. The \( \delta n \) bands are identical to the \( C_1, C_2 \) and \( E \) bands of charge carriers in the PM spectrum (Fig. 3 (b) and (c)). Similar (but not identical) optical transitions have been measured in the absorption spectra of \( C_{60}^{*} \) produced by \( \gamma \) irradiation [17], alkali metal doping [18] and charge transfer from semiconductors colloids [19]. We therefore identify the charge carriers as spin \( \frac{1}{2} C_{60}^{*} \).

We have also measured the PL and its H-PDMR spectrum in \( C_{60} \) film. In the \( C_{60} \) films, as in glass, the PL at 4K contains also two components; a fast component due to singlet excitons and a slow component due to triplet excitons; both PL components increase as \( I_L \). We measured a positive PDMR with an H spectrum identical to the H-ADMR spectrum at 1.6 eV (Fig. 3, lower inset), which contains only the triplet powder pattern; no spin \( \frac{1}{2} \) component was identified in H-PDMR.

Our results for excited states in \( C_{60} \) films can be explained by the following scenario: Upon excitation, singlet excitons are formed. Some of them decay radiatively giving rise to the fast PL component with no PDMR signal. However a significant fraction of the singlet excitons decay into the triplet manifold. Fast triplet recombination occurs via bimolecular kinetics, which also may produce charge separation into \( C_{60}^{*} \). This can explain the seemingly contradictory results for the charge excitations in \( C_{60} \) films, in that their density increase as \( I_L^{1/6} \) but their ADMR signal is positive, indicating geminate recombination [12]. This can be reasonably reconciled assuming that \( C_{60}^{*} \) generation, not recombination, has a bimolecular kinetics. The
long-lived surviving triplets recombine monomolecularly; some of them decay radiatively giving rise to the triplet PL component that we have observed.

An attempt to identify the various transitions in the PM spectrum using the C\textsubscript{60} energy levels calculation based on CNDO/S, and assuming rigid band approximation, is shown in Fig. 2 (b); the energy levels notation is based on the C\textsubscript{60} icosahedral point group symmetry [13]. The HOMO (h\textsubscript{1u}) and LUMO (t\textsubscript{1u}), both with odd parity u, give rise to a \( \pi - \pi^* \) forbidden transition which, however, can be enhanced by the EA spectrum (Fig. 3 (c)) [11]. In C\textsubscript{60} films it appears that this transition is located at 2.4 eV. Then the important C\textsubscript{60} optical transition, (when an electron is added at the LUMO level at t\textsubscript{1u}) is the C\textsubscript{1} transition (t\textsubscript{1u} \rightarrow t\textsubscript{1g}) at 0.8 eV, which also appears upon alkali metal doping [18]. Moreover, the important transitions of C\textsubscript{60}\textsuperscript{+} (when a hole is added at the HOMO level at h\textsubscript{1u}) is the C\textsubscript{2} transition (g\textsubscript{u} \rightarrow h\textsubscript{u}) at 2 eV. The almost rigid band approximation can also explain the two optical transitions associated with the photoinduced triplets. When an electron is promoted to the LUMO level, a hole appears at the HOMO level.

If the relaxation energy associated with the excited states in the triplet manifold is relatively small (as depicted in Fig. 2 (b)), then the two triplet transitions T\textsubscript{1} and T\textsubscript{2} are not far from the C\textsubscript{1} and C\textsubscript{2} transitions of C\textsubscript{60}\textsuperscript{+}; this is in agreement with the experiment where C\textsubscript{1} and C\textsubscript{2} peak at 0.8 and 2 eV, respectively, whereas T\textsubscript{1} and T\textsubscript{2} are at 1.1 and 1.8 eV, respectively.

We thank J. Shinar for sending us his paper prior to publication. The work at the University of Utah was supported in part by BP America, the DOE grant no. DE-FG 02-89 ER 45409 and by ONR grant no. N00014-91-C-0104. The work at UCSB was supported by DMR.
88-20933, NSF grant no. CHE 89-08323. V.I.S. acknowledges support by the NSF QUEST program at UCSB.
References

12. P.A. Lane et al., preprint.
Figure Captions

Fig. 1: PM, PL and P-ADMR spectra of C\textsubscript{60}: T/PS glass at 4K; the PA bands T\textsubscript{1} and T\textsubscript{2} are assigned. Lower inset shows the H-ADMR at 1.65 eV (T\textsubscript{1}) and the H-PDMR spectra of the PL band at "half" and "full" fields, respectively. Upper inset shows the in-phase and out-of-phase ADMR and PDMR signals vs. the \( \mu \)wave modulation frequency.

Fig. 2: PM spectra of C\textsubscript{60} film at different modulation frequency \( f \) and sample temperature \( \theta \). (a) \( f = 20 \) kHz, \( \theta = 80 \) K; (b) \( f = 20 \) Hz, \( \theta = 80 \) K; (c) \( f = 500 \) Hz, \( \theta = 300 \) K. The PA bands C\textsubscript{1}, C\textsubscript{2}, T\textsubscript{1}, T\textsubscript{2} and E are assigned. The inset of Fig. 2 (b) shows the C\textsubscript{60} energy levels as calculated in Ref. 13; singlet and triplet manifolds are depicted on the left and right hand sides, respectively. The inset in Fig. 2 (c) shows our electro-absorption spectrum, measured on the same C\textsubscript{60} films; the bands C\textsubscript{2} and E are derived from the PM spectrum based on the EA spectrum in the inset.

Fig. 3: P-ADMR spectra of the \( S = 1/2 \) (at H = 1071 G) and \( S = 1 \) (at H = 1050 G) components of the ADMR signal. The bands C\textsubscript{1}, C\textsubscript{2}, T\textsubscript{1}, T\textsubscript{2} and E are as in Fig. 2; C\textsubscript{2} and E bands are derived from the ADMR spectrum as in Fig. 2 (c). Three typical H-ADMR spectra at 0.8, 1.6 and 2.3 eV, respectively are also shown 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 \( S = 1/2 \) photoexcitations.
Fig. 1
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