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Dynamics of Photoexcited States in C_{60}: An Optically Detected Magnetic Resonance, ESR, and Light-Induced ESR Study

P. A. Lane, L. S. Swanson, Q.-X. Ni, and J. Shinar
Ames Laboratory—U.S. DOE and Physics Department, Iowa State University, Ames, Iowa 50011

J. P. Engel,[a] T. J. Barton,[a] and L. Jones
Ames Laboratory—U.S. DOE, Iowa State University, Ames, Iowa 50011

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The photoluminescence, X-band optically detected magnetic resonance (ODMR), ESR, and light-induced ESR (LESR) of C_{60} films and C_{60} in toluene/polystyrene glass (C_{60}:T/PS) are described. The ESR at $g=1.998$ and delocalized triplet LESR and ODMR of C_{60}:T/PS are similar to previously reported spectra. In films, the ODMR indicates that the delocalized triplet is larger and distorted by neighboring molecules. In addition, another, more localized triplet and a narrow photoluminescence-enhancing line at $g=2.0017\pm0.0005$, consistent with intermolecular polaron recombination, are also observed in films but not glasses.

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The novel fullerenes in general, and C_{60} in particular, are attracting intense attention. Recent studies include optical absorption [1-5], photoluminescence (PL) [2,5], ESR [4,6-8], and light-induced ESR (LESR) [9] of films, solution, and glasses. Both absorption and emission spectra [2] clearly displayed the totally symmetric pentagonal pinch vibrations. The emission spectrum, however, did not reveal the additional 0.09-eV ($\sim$740 cm^{-1}) vibronic progression observed in the absorption and in resonant Raman scattering [9]. These additional lines are believed to result from nontotally symmetric phonons [5,10] possibly associated with a Jahn-Teller distortion [2]. This work reveals this vibronic structure in the emission spectra of films; it broadens with increasing temperature much more rapidly than the pentagonal pinch vibration replica, and is unobservable above 150 K.

While X-band ESR studies yielded varying g values and satellite structures, the main narrow line was invariably attributed to the radical anion $C_{60}{}^{\cdot-}$ [6-8]. The g value of $C_{60}{}^{\cdot-}$ trapped in a molecular sieve was 1.9995, with satellites at ±10 G [8]. The interpretation of the satellites was inconclusive, since they appeared to be consistent both with a hyperfine interaction with five equivalent neighboring ^{13}C nuclei, and with a triplet state of a pair of $C_{60}{}^{\cdot-}$ ions. The intense triplet powder pattern LESR [9] of C_{60} in a toluene/polystyrene (C_{60}:T/PS) glass matrix at 9 K yielded zero-field parameters $D=122$ G (0.0114 cm^{-1}) and $E\approx7.4$ G (0.00069 cm^{-1}) indicating a nearly axially symmetric triplet delocalized over the C_{60} molecule. Transient LESR yielded a lifetime of $\sim$0.4 ms [9]. The triplet energy level had been determined to be $\sim$1.6 eV [1,3,11]; the absence of observable phosphorescence suggested that its decay is dominated by nonradiative processes [9].

In addition to the novel PL spectra and LESR consistent with previous results, the PL (i.e., optically) detected magnetic resonance (ODMR or PLDMR) of films described in this work reveal novel features of excited states strikingly reminiscent of those in π-conjugated polymers [12-14]. They include (i) a delocalized triplet exciton distinct from that in C_{60}:T/PS [9], (ii) another, more localized triplet, possibly pinned at a distorted region of the molecule, and (iii) a narrow PL-enhancing resonance tentatively attributed to intermolecular polaron recombination. A strong "dip" at $g=2.000\pm0.003$ exhibited by the C_{60}:T/PS glass is speculated to result from nonradiative trapping of polarons photogenerated on $C_{60}{}^{\cdot-}$ radical anions.

C_{60} was synthesized by a $\sim$110-A, $\sim$22-V ac, 100-torr He arc discharge between two $\frac{1}{4}$-in.-diam high-purity graphite rods in a water-cooled chamber [15-19]. The resultant soot was extracted with toluene in a soxhlet apparatus under a N_2 atmosphere. Purification of the C_{60} was accomplished by eluting the soluble material through a neutral alumina column and collecting the resolved magenta band [19]. The 99.5 at.% purity of the C_{60}/toluene solution was established by UV and photoacoustic IR spectroscopy [20]. Films were prepared by degassing the solution and evaporating the toluene in evacuated quartz tubes. The C_{60}:T/PS glasses were similarly prepared.

An optically accessed Bruker spectrometer equipped with a He-gas flow cryostat was used for ESR and LESR. The LESR was measured by double lock-in detection of the signal from 100-kHz field modulation and 727-Hz laser chopping. The ODMR system is described elsewhere [12-14].

Figure 1(a) displays the X-band ESR of a film and LESR of C_{60}:T/PS, obtained by 100-mW excitation at 457.9 nm. The g value of the ESR agrees closely with that of electrolyzed [6] C_{60} and C_{60} trapped in a molecular sieve [8]. The LESR, with derivative peaks at ±43, ±68, and ±115 G from $g=1.999$, is similar to that previously reported [9] and attributed to a triplet exciton of zero-field parameters $D\approx122$ G (0.0114 cm^{-1}) and $E\approx7.4$ G (0.00069 cm^{-1}) [21]. It is thus nearly axially

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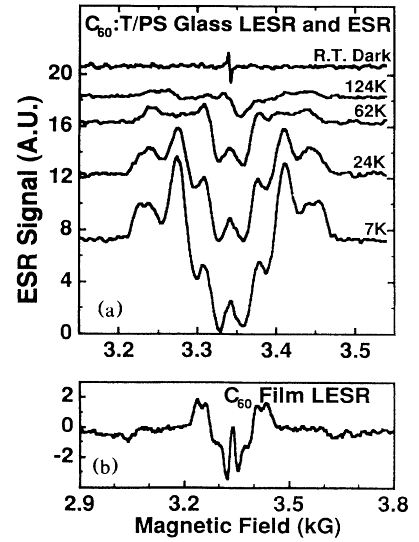

FIG. 1. (a) The X-band room-temperature ESR (top trace) and light-induced ESR (other traces) of C_{60}:T/PS excited by 100 mW at 457.9 nm and 2 mW microwave power. (b) The LESR of a C_{60} film at 38 K, showing weak shoulders ± 300 G from $g \approx 2.00$, also observable in the ODMR of films (see Fig. 4).

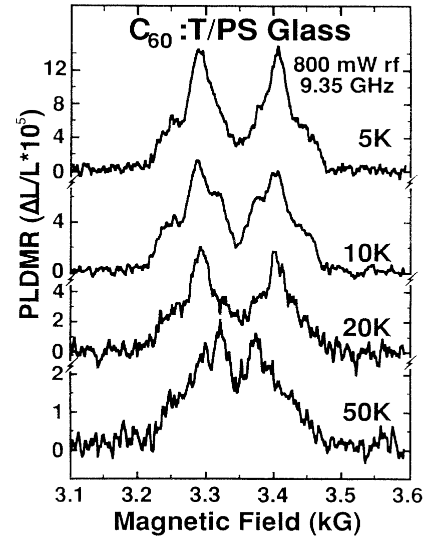

FIG. 2. Full-field ODMR of C_{60}:T/PS. Note the strong "dip" at $g \cong 2.000 \pm 0.003$. The temperature dependence of this dip clearly differs from that of the triplet powder pattern.

symmetric and about 5-6 Å large, i.e., delocalized over the C_{60} molecule [9].

The LESR of the glass also includes a weak narrow peak at $g = 1.999 \pm 0.001$, i.e., at the dark ESR position. This line is more prominent in the LESR of films [Fig. 1(b)]. The triplet pattern is somewhat narrower in the films than in the glass, as the peaks at ± 122 G have shifted to ± 100 G from $g = 1.999$. Finally, ~600-G-wide shoulders attributable to another, more localized triplet exciton are also faintly discernible. This feature was striking in the ODMR of films (see below).

At 10 K, the amplitude of the triplet pattern strongly decreased with increasing microwave power above ~1.5 mW. This strong saturation behavior yields a spin-lattice relaxation time of $T_1 \sim 0.4$ ms at that temperature [22], i.e., a value close to the measured lifetime of the triplet [9].

The total PL-detected ODMR (i.e., PLDMR) of C_{60}:T/PS is shown in Fig. 2. The narrow, delocalized triplet powder pattern, resulting in D and E values similar to those determined by LESR (Ref. [9] and Fig. 1 above), is clearly observable. However, there is a striking "dip" at $g \cong 2.000 \pm 0.003$. Although the powder pattern of triplets generally includes a broad, flat "valley" between the singularities at $\pm(D-3E)/2$ [21], the shape and temperature dependence of this dip rule out its assignment to such a valley. Some speculations on its nature are offered below.

Figure 3 shows the PL spectra of a film excited at 488 nm and 5 mW at several temperatures. Below 100 K, bands at 1.77, 1.68, 1.59, and 1.50 eV are clearly seen. While both 0.18 and 0.09 eV progressions were previously observed in absorption spectra of films, the emission spectra displayed only the 0.18-eV replicas. These were assigned to the totally symmetric soccerball pentagonal pinch mode [2,5]. The 0.09-eV mode is apparently due to a nontotally symmetric [2] phonon of gerade parity in the ground state [10] possibly resulting from a dynamic Jahn-Teller distortion. Its strong temperature dependence is consistent with this interpretation [2].

The full-field PLDMR of films is shown in Fig. 4(a). Three distinct features are prominent. The narrow ($\Delta H_{1/2} \sim 5$ G) peak at $g = 2.0017 \pm 0.0005$ coincides with the central LESR (Fig. 1). Its intensity abruptly decreases from 30 to 40 K, but it is observable up to 296 K. It is strongly reminiscent of the narrow PL-enhancing ODMR observed in several π-conjugated polymers, where it was attributed to intrachain "distant pair" polaron

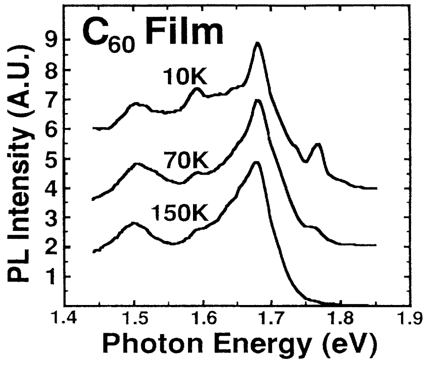

FIG. 3. The photoluminescence (PL) of C_{60} films. Note that the 1.59- and 1.77-eV bands rapidly weaken from 10 to 150 K, while the bands at 1.68 and 1.50 eV are still prominent at 150 K. The PL yield is ~0.07%.

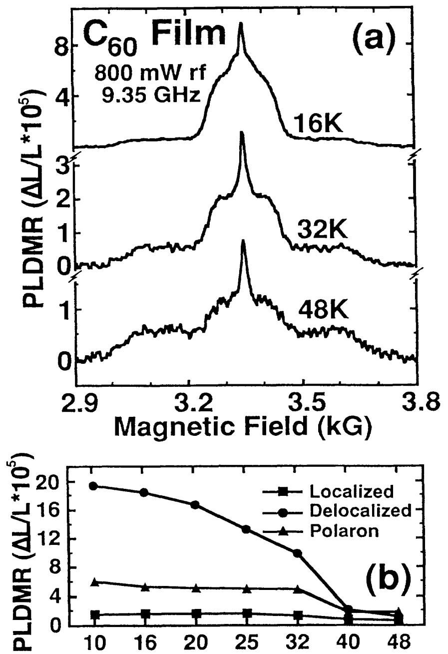

FIG. 4. (a) The full-field (i.e., $g \sim 2$) X-band PLDMR (i.e., ODMR) of C_{60} films excited by 25 mW at 488 nm. (b) The temperature dependence of the three resonances.

recombination [12–14], presumably via nongeminate singlet exciton formation.

The second feature is the ~200-G-wide delocalized triplet powder pattern. It yields a D value of ~96 G, similar to that of the LESR of films [Fig. 1(b)], i.e., distinctly smaller than that of glasses [Ref. [9] and Fig. 1(a)]. The pattern did not enable the determination of E; however, it appears to be significantly greater than 7 G.

The third feature is an additional ~600-G-wide (localized) triplet powder pattern, also faintly observable as a broad LESR [Fig. 1(b)]. In contrast to the narrow triplet, its intensity decreases moderately with temperature. It is also similar to the triplet ODMR of poly(3-alkylthiophene) [12] and poly(2,5-dialkoxyparaphenylenevinylene) [13], where it was attributed to low-lying triplet excitons localized on a thiophene or phenylene ring, respectively.

The temperature dependence of the amplitudes of the three foregoing resonances is displayed in Fig. 4(b). The rapid decrease in the intensity of the delocalized exciton above 16 K relative to that of the other features is not surprising, in view of its delocalized nature.

Figure 5(a) exhibits the half-field PLDMR resulting from the $\Delta m_S = 2$ transitions of the two triplets in C_{60} film. As expected from the behavior of the full-field PLDMR (Fig. 4), the narrow, higher-field, delocalized triplet resonance decays more rapidly with increasing temperature than the broader, lower-field line associated with the localized exciton. Since the $\Delta m_S = 2$ transition probability scales roughly as $(D/h\nu)^2$, the localized exciton pattern is much more prominent at half field than at full field. The amplitude $\Delta L/L$ of the delocalized half-field line sharply decreased with increasing 488-nm excitation power above ~8 mW; that of the localized half-field line moderately decreased at excitation intensities above ~25 mW. The lower excitation power corresponds to absorption of roughly 10^3 photons per C_{60} per second, and is therefore consistent with the measured (primarily nonradiative) delocalized triplet decay time of ~0.4 ms [9].

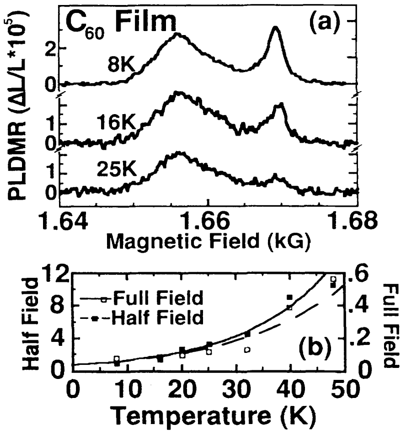

FIG. 5. (a) The half-field resonance of C_{60} films due to the $\Delta m_S = 2$ transitions of two distinct triplet excitons. (b) The temperature dependence of the ratio of the two full-field (see Fig. 4) and half-field patterns.

The temperature dependence of the ratios of the amplitudes of the full- and half-field broad (localized) triplet pattern to that of the narrow (delocalized) triplet is shown in Fig. 5(b). As expected, the temperature dependence of the ratio of the full-field patterns is similar to that of the half-field resonances. In either case, it clearly shows the distinct dynamics of the two triplets, as the narrow pattern decays more rapidly with increasing temperature.

The PL is apparently due to singlet exciton recombination [5]. Its quantum yield is ~0.07%. This low yield is not surprising, since the decay rate from the singlet exciton level at ~1.80 eV [2,5] to the triplet level at ~1.60 eV is very fast (1.5×10^9 to 3×10^{10} sec^{-1} in toluene solutions at 295 K [3,9]) and the quantum yield for triplet formation is consequently close to unity [1,3].

As in conjugated polymers [13,14], the observation of triplet powder patterns in the PLDMR is probably due to magnetic resonance enhancement of triplet fusion producing excited triplets and singlets; some singlets then decay radiatively to the ground state. Previous LESR measurements on C_{60}:T/PS, however, only revealed the presence of the low-lying triplet state delocalized over the C_{60} molecule. The lower value of D and nonzero value of E in films apparent from the PLDMR [Fig. 4(a) vs Figs. 1(a) and 2(a)] indicate that this triplet state is larger and resides on distorted C_{60} molecules, probably resulting from intermolecular coupling.

The full-field, and more strikingly the half-field, PLDMR of the films also clearly reveals the presence of an additional, more localized triplet exciton. As mentioned above, this triplet is very similar to those observed in π-conjugated polymers [12–14], and is therefore tentatively attributed to an exciton localized around a five- or six-membered ring. Yet no localized exciton was observed in C_{60}:T/PS. We therefore speculate that it may possibly be pinned at sites distorted by intermolecular interactions.

The third PLDMR feature displayed by films [Fig. 4(a)], but not by glasses (Fig. 2), is the narrow PL-enhancing resonance at $g \approx 2.0017 \pm 0.0005$. It also strongly resembles the main narrow resonance displayed by π-conjugated polymer films, solutions, and blends [12–14], where it was assigned to "distant pair" *intrachain* polaron recombination, presumably via singlet formation. In this case, however, it is *not* exhibited by glasses (Fig. 2), and is therefore assigned to *intermolecular* polaron recombination. The narrow LESR of films and glasses at $g \approx 1.999$ [Fig. 1(b)] is not clear at present, but could conceivably include contributions from either polarons or short-lived photoinduced radial anions.

The nature of the "dip" of the PLDMR of glasses at $g \approx 2.000$ (Fig. 2) is presently not established. It may, however, be speculated to result from spin-dependent nonradiative trapping of carriers photogenerated on native $C_{60}^{\cdot -}$ radical anions responsible for the dark ESR [Fig. 1(a)]. This process would be reminiscent of the dominant PL-quenching ODMR of *a*-Si:H, established to result from nonradiative trapping of band-tail carriers by neutral spin-$\frac{1}{2}$ dangling bonds [23].

In summary, the photoluminescence (PL), dark ESR, light-induced ESR (LESR), and PL (i.e., optically) detected magnetic resonance (PLDMR or ODMR) of C_{60} isolated in toluene/polystyrene glass (C_{60}:T/PS) and C_{60} films have been described. Below 100 K, the PL clearly exhibits the 0.09-eV phonon replicas suspected to be due to a nontotally symmetric vibration associated with a dynamic Jahn-Teller distortion, in addition to the prominent 0.18-eV phonons attributed to the totally symmetric soccerball pentagonal pinch mode. The LESR and dark ESR at $g = 1.999 \pm 0.001$ are consistent with previous studies; the latter is attributed to native $C_{60}^{\cdot -}$ in films and glasses. The ODMR of glasses clearly exhibits the triplet pattern previously observed in LESR and attributed to a triplet exciton delocalized over the C_{60} molecule. The lower D value in films indicates greater delocalization than in the glass; the larger value of E suggests that the molecule is more distorted in films, presumably by intermolecular interactions. The additional ~600-G-wide powder pattern centered at $g \sim 2$ in films is due to a localized exciton, possibly pinned to a five- or six-membered ring at a local molecular deformation site. The ODMR spectra clearly display the half-field $\Delta m_S = 2$ patterns of both excitons. The ODMR of films also displays a narrow resonance similar to that of π-conjugated polymers and attributed to polaron recombination. The absence of this narrow resonance from the ODMR of the C_{60}:T/PS glass suggests that it is intermolecular. A "dip" at $g \approx 2.000$ in the ODMR of the glass is suspected to reflect spin-dependent nonradiative trapping of polarons by $C_{60}^{\cdot -}$.

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(a) Also at the Chemistry Department, Iowa State University, Ames, IA 50011.

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