Magneto-optical studies of photoexcitations in C_{61}

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We have used a variety of cw optical and optically detected magnetic-resonance techniques to characterize long-lived photoexcitations in methanofullerene (C_{61}) as a dispersion in polystyrene glass, at temperatures below 10 K. We identify triplet excitons with zero-field-splitting (ZFS) parameters $D=105\times10^{-4}$ cm^{-1} and $E=9\times10^{-4}$ cm^{-1}. The triplet excitons are characterized by two photoinduced absorption (PA) bands in the triplet manifold at 1.5 and 1.7 eV, both with a lifetime of 160 μsec, and a phosphorescence emission (PL) band with onset at 1.85 eV and a lifetime of 10 μsec. The difference in lifetimes between PA and PL is explained as being due to different recombination kinetics of the triplet sublevels. This and the finite axial symmetry ZFS parameter $E\neq0$ compared to $E=0$ for triplets in C_{60} show the lower symmetry of triplets in C_{61}, consistent with its postulated distortions from icosahedral symmetry in the ground-state structure.

The recent synthesis of macroscopic amounts of the all-carbon fullerenes C_{60} and C_{70}[1] has stimulated a great deal of experimental work. Most dramatically, C_{60} films show superconductivity at T_c as high as 33 K,[2,3] when doped with alkali metals. The icosahedral (I_h) symmetry of C_{60}, the prolate spheroid with D_{5h} symmetry of C_{70}, and their electronic energy bands, have been measured with good agreement between experiment and theory.[4,5] Recent optical studies of C_{60} and C_{70} include optical absorption of the ground[6-8] and excited states,[9-12] photoluminescence,[13-17] light-induced ESR,[16] and optically detected magnetic resonance of solutions and glasses,[15] where the role of triplet excitons has been emphasized.

In this work we extend our recent magneto-optical studies of photoexcitations in fullerenes[18] to another member of the family, namely the diphenyl methano fullerene (C_{61}). The chemical structure of this fullerene is shown in the inset of Fig. 1.[19] Of all the 61 carbon (C) atoms, 58 of them are in nearly sp_2 molecular orbitals forming the regular icosahedral structure, and three of them have an sp_3 molecular orbital, of which one sticks out of the C_{60} sphere to bridge the C_{60} and two other phenyl rings. Success in synthesizing this methanofullerene not only adds to the diversity of the materials in this family, but also opens a way to synthesize the C_{60} polymer.[19] Based on the schematic C_{61} structure shown in Fig. 1, we expect that a reduction of the icosahedral C_{60} symmetry occurs in C_{61}, probably into the symmetry group C_{2v}. The consequent effect of such a symmetry reduction on the properties of C_{61} excited states, compared to those of C_{60}, should be interesting.

Similar to C_{60} and C_{70},[18] we found that the long-lived photoexcitations in C_{61} molecules are triplet excitons ($^3C_{61}^*$). These are characterized by two photoinduced absorption (PA) bands in the triplet manifold at 1.5 and 1.7 eV, respectively, and a phosphorescence emission band with onset at 1.85 eV, followed by several phonon sidebands down to 1.3 eV. One manifestation of the expected symmetry breaking in $^3C_{61}^*$ is that at 9 K the triplet sublevel lifetimes are 10 and 160 μsec, respectively, for the fastest and slowest sublevels. Another is that the nonaxial symmetric zero-field parameter $E\neq0$.

In our work we study photoexcitations in C_{61} as a dispersion in toluene/polystyrene (PS) glass using a variety of cw optical measurement techniques. This includes[18,20] photomodulation (PM), photoluminescence (PL), and their respective versions of optically detected magnetic resonance (ODMR): absorption-detected magnetic resonance (ADMR) (Ref. 20) and the PL-detected

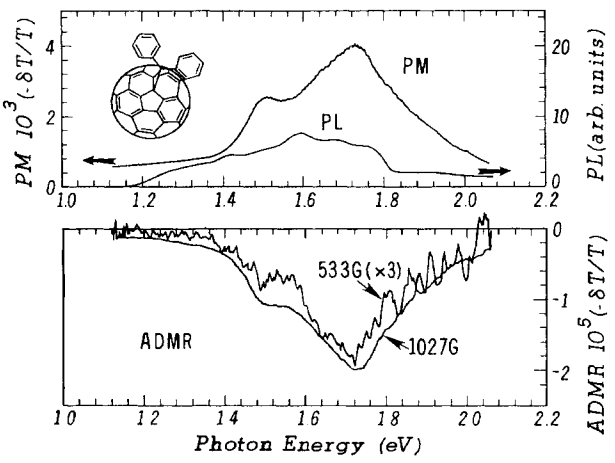

FIG. 1. PM, PL, and two *P*-ADMR spectra of C_{61}:PS glass at 4 K. The inset shows the proposed C_{61} molecular structure (Ref. 19).

magnetic resonance (PDMR).[15] The PM and PL spectra have been excited by an Ar^+ laser beam at 458 nm (pump) with intensity I_L of 200 mW cm^{-2}, which was modulated at frequency f ranging from 20 Hz to 50 kHz by an acousto-optical modulator. The PL from the sample and the transmission of a cw lamp (probe beam) were dispersed by a $\frac{1}{4}$-m monochromator and measured by various solid-state detectors in the spectral range of 0.3–2.7 eV. For the ADMR measurements the pump and probe beams constantly illuminate the sample mounted at 3 GHz in a high-Q microwave cavity equipped with optical windows and a superconducting magnet producing a field H up to 3 T. Microwave (μ wave) resonant absorption, modulated at a frequency between 20 Hz and 4 KHz, leads to small changes δT in the transmission T 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 change spin-dependent recombination rates. With suitable signal averaging, the system $\delta T/T$ sensitivity was about 10^{-7}. In PDMR we measure changes δL in the PL intensity L with sensitivity $\delta L/L \simeq 10^{-5}$. Two types of ADMR (PDMR) 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.

The details of synthesizing C_{61} has been reported in Ref. 19. In short, a reaction of C_{60} with more than one equivalent of diphenyldiazomethane in toluene at room temperature for ~ 1 h produced a monoadduct diphenyl methanofullerene C_{61}. For our magneto-optical studies the C_{61} powder was mixed in a solution of degassed toluene/polystyrene (PS), which was subsequently evaporated to form C_{61}:PS glass.

The optical and magneto-optical measurements of C_{61}:PS glass at 4 K are shown in Figs. 1 and 2. The PM spectrum (Fig. 1) contains two PA bands at 1.5 and 1.7 eV, respectively. We note that in C_{60} similar PA bands were observed at 1.65 and 1.8 eV, respectively.[18] The changes in the PA-band energies demonstrate the sensitivity of the excited energy levels to small variation of the fullerene structure. Both PA bands increase linearly with I_L, showing a monomolecular recombination kinetics for the photoexcitations. The H-ADMR spectrum at 1.7 eV (Fig. 2) shows a 200-G-wide triplet powder pattern at "full field" (FF) ($\Delta m_s = \pm 1$) around $H_0 = 1071$ G with $\delta n/n = -5 \times 10^{-3}$, and a narrow (5 G) signal at "half field" ($\Delta m_s = \pm 2$) peaked at 533 G. To correlate the ADMR and PM spectra, we measured the P-ADMR spectra at 1027 G (FF) and 533 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 triplet transitions of photogenerated triplet excitons $^3C_{61}^*$.

The PL spectrum of C_{61}:PS is also shown in Fig. 1. It contains several maxima at 1.78, 1.68, 1.5, 1.4, and 1.3 eV, which we consider to be phonon sidebands of a weak 0-0 transition at about 1.85 eV, the onset of the PL band. In a recent experimental work where the detailed C_{60} absorption bands were unraveled, the elusive 1.85-eV energy level was identified[21] as due to a $^3T_{2g}$-^1A_g weak transition, involving triplet-singlet intersystem crossing caused by the spin-orbit interaction. Therefore, we tentatively assign the PL band as due to phosphorescence coming from a triplet level at 1.85 eV. The H-PDMR spectrum shown in Fig. 2 and the PL lifetime determined from the excitation modulation frequency dependence shown in Fig. 3 are in agreement with our model.

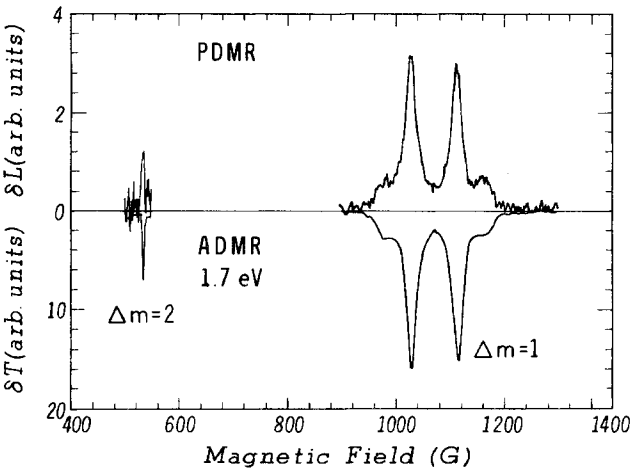

FIG. 2. The H-ADMR and H-PDMR spectra of $^3C_{61}^*$ at 4 K. The half-field ($\Delta m = \pm 2$) and full-field ($\Delta m = \pm 1$) powder patterns are assigned.

The H-PDMR spectrum (Fig. 2) of the full PL band (Fig. 2), which shows both $\Delta m_s = \pm 1$ and $\Delta m_s = \pm 2$ powder pattern resonances, is identical to the H-ADMR spectrum of $^3C_{61}^*$ at 1.7 eV (also shown in Fig. 2) except the sign; $\delta L > 0$, whereas $\Delta n < 0$. The similar magnetic-resonance spectra indicate that the same photoexcited states, namely triplets, are involved in the PA and PL bands. To check this assumption we measured the laser excitation modulation frequency dependence of the PL and PA bands as shown in Figs. 3 and 4, respectively.

The photoexcitation lifetime τ can be determined for a monomolecular recombination kinetics[22] by measuring the in-phase and out-of-phase signals as a function of the laser modulation frequency $f(=\omega/2\pi)$. In such a case the in-phase signal follows a $(1+\omega^2\tau^2)^{-1}$ functional dependence, whereas the out-of-phase response gets a maximum at $\omega\tau = 1$, at half the value of the in-phase signal at $\omega \to 0$. Figures 3 (inset) and 4 show that the PL and PA dynamics at 9 K indeed follow the predicted monomolecular frequency dependence given above. From Figs. 3 and 4 we therefore determine the PL and PA lifetimes to be 10 and 160 μs, respectively. Moreover, the similar in-phase and out-of-phase PL spectra at 100 Hz shown in Fig. 3 indicate that a single excited electronic band is involved in the PL emission.

The seemingly apparent difficulty of different PL and PA lifetimes (Figs. 3 and 4) but otherwise identical triplet magnetic-resonance spectra (Fig. 2) can be self-

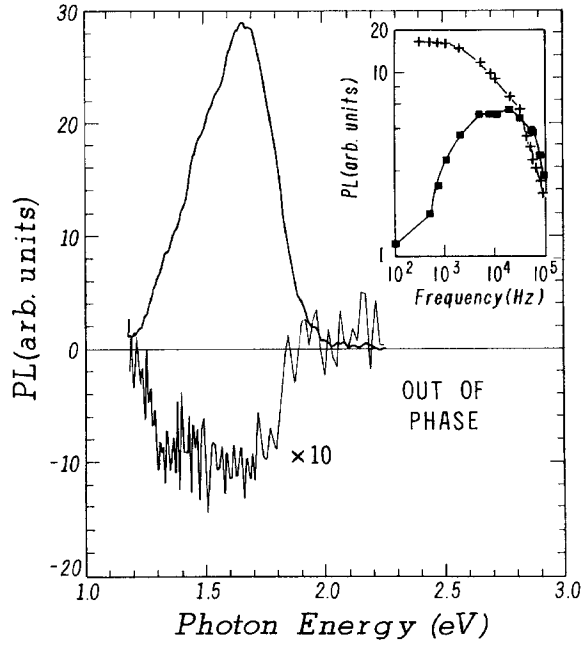

FIG. 3. The in-phase and out-of-phase PL spectra of $^3C_{61}^*$ at 9-K and 100-Hz modulation. The inset shows the in-phase and out-of-phase PL signals vs modulation frequency.

consistently explained using the fact that different triplet sublevels are involved in the PL and PA responses. The phosphorescence emission predominantly comes from the triplet sublevel which is the most strongly coupled (by the spin-orbit interaction) to the singlet ground state and therefore has a relatively short lifetime, consistent with the shorter τ (PL). On the other hand, the PA intensity is proportional to the total triplet population, which in turn is dominated by the slowest triplet sublevel. This sublevel is only weakly coupled to the ground state, and is therefore dominated by a nonradiative recombination. This is consistent with the longer τ (PA). Then the identical ADMR and PDMR spectra can readily be explained since μ-wave transitions from the slowest to the fastest triplet sublevels decrease the overall triplet population causing $\delta n < 0$, but at the same time increase the triplet radiative recombination channel, resulting in $\delta L > 0$, as in Fig. 2. This model has been further substantiated by detailed solutions of the respective PL and PA rate equations under magnetic-resonance conditions.[22]

Our measurements of the $^3C_{61}^*$ lifetime are similar to those of $^3C_{60}^*$ measured in C_{60}/PS by transient-light-induced ESR.[16] It was found that $\tau_x = 410$ μs and $\tau_z = 290$ μs, and these values compare favorably with $\tau_x \simeq \tau_y = 160$ μs that we measured for $^3C_{61}^*$.

The deep valley at H in between the two central peaks in the FF triplet powder pattern shown in Fig. 2 does not agree with the triplet powder pattern of thermalized spins having sublevel populations with a Boltzmann distribution.[15] We note that triplet powder patterns in ODMR spectroscopy at low temperatures are in general not due to thermalized spins.[23] Instead the triplet sublevel populations n_i are determined by their respective generation rates G_i and recombination rates R_i to the ground state,[23] where $n_i = G_i/R_i$. As in C_{60},[24] we could fit the FF powder pattern of $^3C_{61}^*$ to unequal steady-state populations n_x, n_y, and n_z of triplet sublevels T_x, T_y, and T_z, respectively, as follows.

The triplet Hamiltonian H in a magnetic field $\mathbf{H}$ is given by[3]

$$H = g\beta \mathbf{S}\cdot\mathbf{H} + D[S_z^2 - \tfrac{1}{3}S(S+1)] + E(S_x^2 - S_y^2) , \quad (1)$$

where g and β are the gyromagnetic constant and Bohr

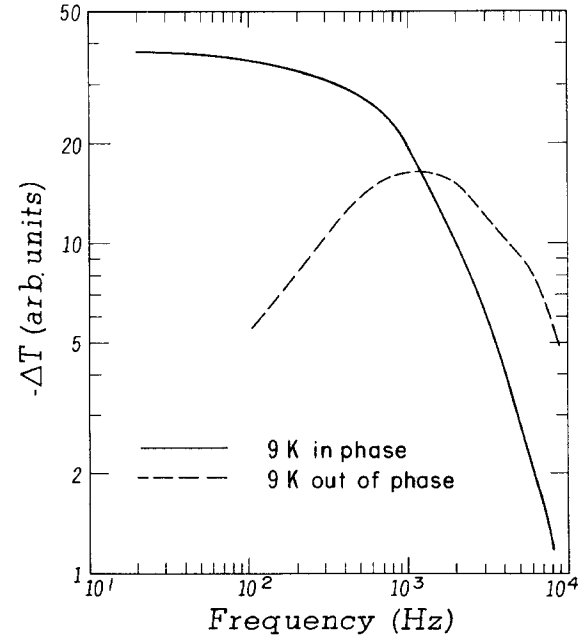

FIG. 4. The $^3C_{61}^*$ in-phase and out-of-phase PM signals at 1.7 eV vs modulation frequency at 9 K.

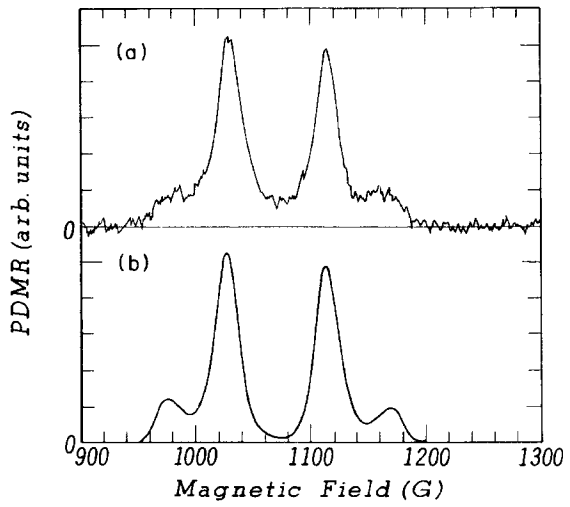

FIG. 5. The H-PDMR FF powder pattern of $^3C_{61}^*$ (a) and its fit (b); the parameters used in the fit are given in the text.

magneton, respectively, and D and E are the triplet zero-field-splitting (ZFS) parameters, given by averages in the triplet excited states; $D \sim \langle (r^2-3z^2)/r^5 \rangle$ and $E \sim \langle (y^2-x^2)/r^5 \rangle$. The triplet FF powder pattern contains, in the general case,[23] six singularities at $\pm D$, $\pm(D+3E)/2$, and $(D-3E)/2$, around H_0. From Fig. 2 it seems that the FF powder pattern for $^3C_{61}^*$ contains fewer singularities. This happens since $\tau_x \simeq \tau_y \gg \tau_z$. We could satisfactorily fit the H-PDMR FF powder pattern of $^3C_{61}^*$ as shown in Fig. 5 with the following parameters: $D=105\times10^{-4}$ cm^{-1}, $E=9\times10^{-4}$ cm^{-1}, spin-spin relaxation time $T_2=22$ ns, relative generation rates $G_x=0.1$ and $G_y=G_z=0.4$, respectively, and relative recombination rates $R_x=R_y=0.1$ and $R_z=1.6$, respectively, corresponding to their respective measured lifetimes: $\tau_x=\tau_y=160$ μs, and $\tau_z=10$ μs.

We could previously fit the FF powder pattern of $^3C_{60}^*$ at 2 K with an axial symmetric ZFS tensor ($E=0$) so that it contains four main singularities at $\pm D$ and $\pm D/2$, respectively, around H_0, with $D=115\times10^{-4}$ cm^{-1}.[22,24] Assuming that D is determined by the bipolar interaction between spin-$\frac{1}{2}$ electron (e) and hole (h) on the fullerene, from our measured D we obtain an e-h distance of 6.3 Å for $^3C_{61}^*$ compared to 6.1 Å for $^3C_{60}^*$.[24] This indicates that a larger Jahn-Teller (JT) distortion exists in the C_{61} excited state,[25] in agreement with the reduced symmetry postulated for its ground state.[19] The fact that for $^3C_{61}^*$ the nonaxial symmetric ZFS parameter $E\neq0$, whereas $E\simeq0$ for $^3C_{60}^*$,[24] shows that $^3C_{61}^*$ and its associated JT distortions[25] has a lower symmetry than $^3C_{60}^*$ and its JT distortions.[25-27]

In summary, using a variety of optical and magneto-optical techniques, we have measured the characteristic properties of $^3C_{61}^*$. From the onset of the phosphorescence emission band we have determined that the $^3C_{61}^*$ energy level is at about 1.85 eV from the ground state. The PM spectrum shows two triplet-triplet transitions at 1.5 and 1.7 eV, respectively. We have also found a pronounced asymmetry between the $^3C_{61}^*$ sublevels, with radiative and nonradiative lifetimes of 10 and 160 μs, respectively, for the respective fastest and slowest sublevels. We also determined the ZFS parameters from the fit to the FF powder pattern; we found $D=105\times10^{-4}$ cm^{-1} and $E=9\times10^{-4}$ cm^{-1}. These ZFS parameters show that $^3C_{61}^*$ has a lower symmetry than $^3C_{60}^*$, in agreement with its distorted ground state with lower symmetry than I_h.

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