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D. Dick [a], W. Gellerman [a], R. E. Benner [a] & Z. V. Vardeny [a]
[a] Dept. of Physics, Univ. of Utah, Salt Lake City, Utah, 84112
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PICOSECOND TIME RESOLVED EXCITED STATE STUDIES OF C_{60} AND C_{70} THIN FILMS

D. DICK, W. GELLERMAN, R. E. BENNER, AND Z. V. VARDENY
Dept. of Physics, Univ. of Utah, Salt Lake City, Utah 84112

Abstract We have studied photoexcitations in C_{60} and C_{70} thin films by transient photomodulation (PM) and transient photoluminesciense (PL). For 2.17 eV excitation we find photogenerated singlet excitons in C_{60} and photogenerated singlet excitons and charged carriers in C_{70}. Our results differ significantly from C_{60} and C_{70} molecules in solution.

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, C_{60} and alkali metal doped C_{60} have been the subject of extensive experimental and theoretical work. C_{70}, the second most abundant member of the fullerene family after C_{60}[1], has been the subject of substantially less theoretical and experimental investigation. Optical transitions across the HOMO-LUMO gap are dipole forbidden in C_{60} molecules, but are weakly allowed in the solid form[3]. Band structure calculations show that C_{60} 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 C_{60} 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 C_{70} relative to C_{60} leads to a much stronger absorption in the vicinity of the HOMO-LUMO gap[7]. Solid C_{70}, like solid C_{60}, is expected to retain much of its molecular character due to the weak van der Walls binding. However, studies of photoexcitations in C_{60} thin films have shown many properties which are different from those of C_{60} in solution[8-11]. The absorption spectra of charged excitations have also been observed in C_{60} and C_{70} thin films[12,13]. It is therefore of interest to study the character and dynamics of photoexcitations in C_{60} and C_{70} thin films.

Transient absorption spectra of C_{60} and C_{70} in solution have been measured on picosecond time scales[14-16]. The first excited singlet state S_1 in C_{60} has a broad photoinduced absorption (PA) band at 1.35 eV which corresponds to transitions to S_n.

S_1 has a lifetime of 1.3 ns and decays by intersystem crossing to the lowest excited triplet state T_1 which is characterized by a PA band at 1.65 eV[15,16]. The S_1 absorption in C_{70} shows a broad PA band near 1.8 eV and a smaller band near 1.5 eV. The S_1 lifetime in C_{70} is 700 ps and the T_1 absorption band is formed near 1.3 eV[14,16]. We have undertaken a study of the primary photoexcitations and their dynamics in C_{60} and C_{70} thin films by measurement of their picosecond transient absorption spectra and transient photoluminescense.

EXPERIMENT

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[17], synchronously pumped by the residual Nd:YAG fundamental, was also be 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 energy of 2.17 eV and probe 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 $3x10^{-6}$. 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.

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 $5x10^{-6}$ torr. X-ray diffraction and low resolution atomic force micrographs showed nanocrystalline films[18].

RESULTS AND DISCUSSION

The transient PM spectrum of C_{60} is shown in Fig. 1 for time delays of 0 and 2000 ps. The dominant feature is a broad PA band near 1.8 eV, and there is significant PA out to 0.8 eV. 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. The spectrum remains essentially unchanged for times up to 3 ns. 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 are shown in Fig. 2. The

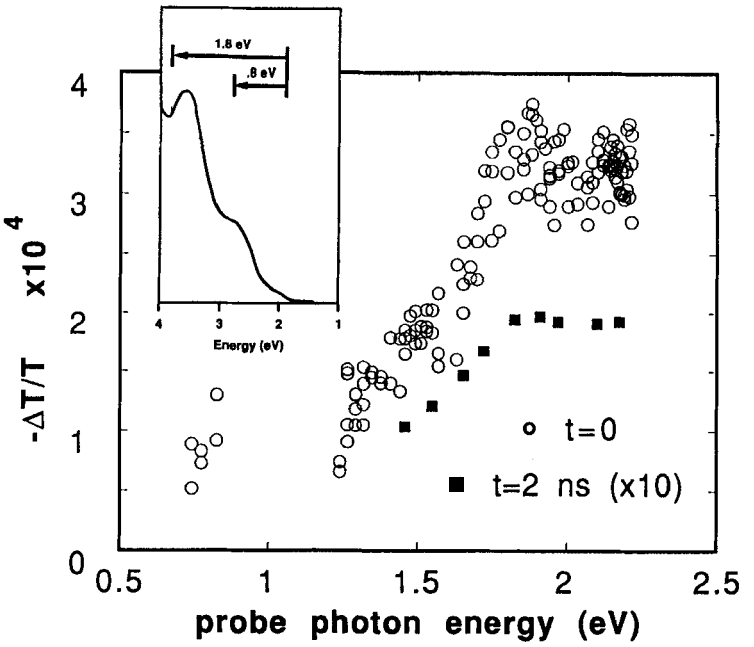

FIGURE 1 The transient photomodulation spectrum of C_{60} at t = 0 and t = 2000 ps. The inset shows the expected transitions from an exciton level at 1.8 eV.

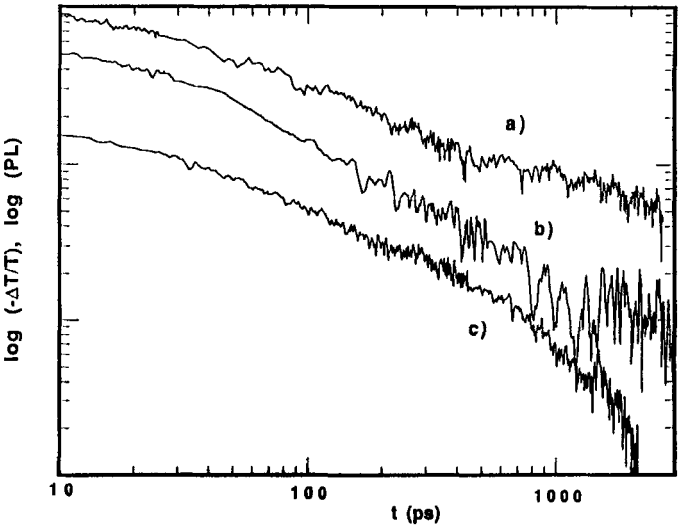

FIGURE 2 The decays of the C_{60} PA and PL: a) PA at 1.8 eV b) PA at 0.8 eV c) PL.

visible and ir PA decays and the PL decay are similar and are approximately fit by a power law decay of $t^{-.56}$. 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 excitons[8] which would be consistent with our PM spectrum. The localization may explain the delay in the intersystem crossing observed in our C_{60} thin films relative to C_{60} in solution.

The transient PM spectrum of C_{70} is shown in Fig. 3 for the time delays of 0 and 700 ps. The main feature of the spectrum is a photoinduced absorption (PA) band centered near 1.8 eV with a width of 0.4 eV. There is also evidence for a PA feature near 0.8 eV. The spectrum at 700 ps is similar to the t = 0 spectrum; however, there is a noticeable narrowing of the 1.8 eV PA band, especially on the low energy side. The 1.8 eV PA band is similar to the absorption of charged C_{70}[13], but is also consistent with singlet exciton absorption to allowed higher energy states. Measurement of the excitation spectrum of $C_{70}^{\pm}$ [19] shows that at 2.17 eV we are exciting appreciable amounts of $C_{70}^{\pm}$. Thus we expect that the 1.8 eV PA feature has contributions from both singlet exciton and $C_{70}^{\pm}$ absorption. The increase in PA spectrum near 0.8 eV 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 responsibe for the 1.8 eV PA band.

The dynamics of the PA and PL from 10 ps to 3 ns are shown in Fig. 4. The PA decays are roughly the same for probe photon energies between 1.75 and 2 eV. The decay rate increases 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. For an excitation which decays mostly radiatively one would expect $I_{pl} \sim dN/dt$. Comparing the derivative of our fit to the measured PL decay we find that the decay is first faster and then slower than the measured PL decay. However, since we have only one decade of time of the fast component available for fitting, there is some ambiguity in the fit. The fast decay also fits well to a logarithmic decay, in which case its derivative closely matches the PL decay, since it is approximately a power law decay t^{-1}. Further measurements with femtosecond time resolution will be necessary to resolve this discrepancy. The PA decay at 0.8 eV is also a good fit to a logarithmic decay over the range 10 to 3000 ps suggesting that it is correlated with the PL. 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.

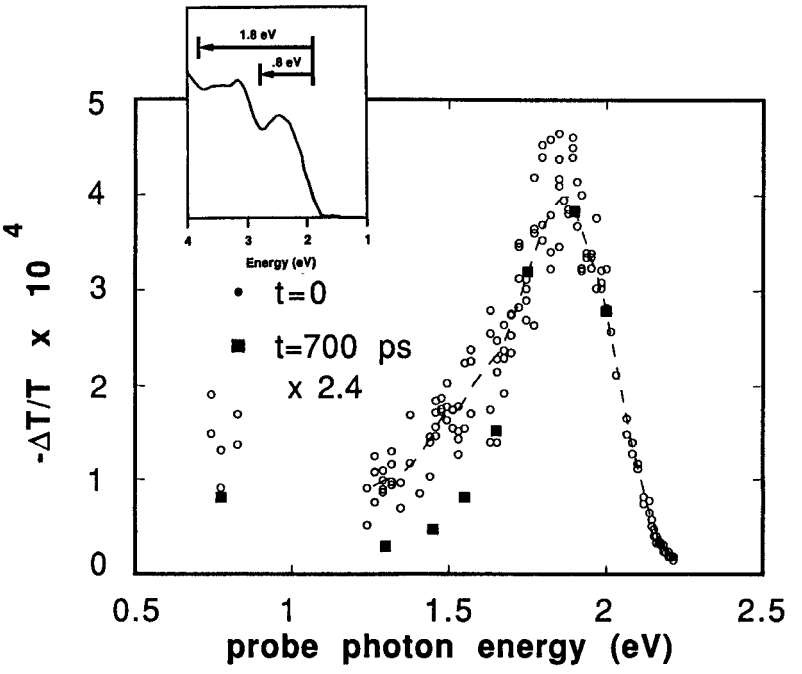

FIGURE 3 The transient photomodulation spectrum of C_{70} at t = 0 and t = 700 ps. The inset shows the expected transitions from an exciton level at 1.8 eV.

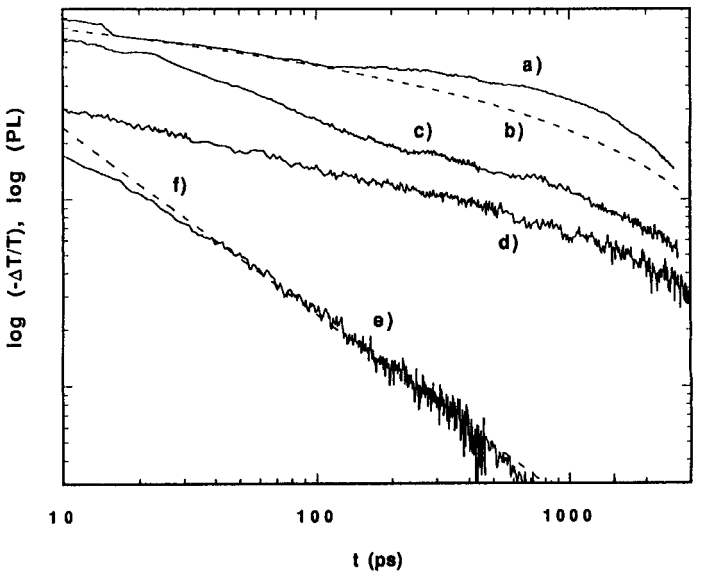

FIGURE 4 The decays of the C_{70} PA and PL: a) PA at 1.75 eV b) fit to ln(t) c) PA at 1.3 eV d) PA at 0.8 eV e)PL f) fit to t^{-1}.

CONCLUSION

Our results for photoexcitations in C_{60} thin films can be explained by the following scenario: Upon excitation singlet excitons are formed at an energy near 1.8 eV. Some of them decay radiatively giving rise to the weak photoluminescense. The self-trapped nature of the excitons results in a slow ($t \geq 3$ ns) intersystem crossing. For C_{70} the scenario is somewhat more complicated. Both singlet excitons and charged carriers are probably formed upon excitation. These excitations both have absorption bands near 1.8 eV, and thus contribute to the 1.8 eV feature in the transient PA spectrum. The singlet excitons also have an absorption band near 0.8 eV. The singlet excitons are created with excess energy, and their thermalization and decay leads to a narrowing of the 1.8 eV PA band. The excitons decay primarily radiatively giving rise to the fast PL and the fast component of the PA decay in the visible. These excitons may also be self-trappped, resulting in a delayed intersystem crossing at a time greater than 3 ns. The $C_{70}^{\pm}$ decays with a lifetime of 2.2 ns, resulting in the slow component of the decays observed in the 1.75 to 2.2 eV region.

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