High-pressure study of picosecond exciton dynamics in solid C_{60}

Bret C. Hess* and Eric A. Forgy

Physics Department, California State University–Fresno, Fresno, California 93740

Sergey Frolov, David D. Dick, and Zeev V. Vardeny

Physics Department, University of Utah, Salt Lake City, Utah 84112

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We have studied the singlet exciton decay by picosecond photoinduced absorption in films of C_{60}, under pressures up to 62 kbar. The picosecond decay of excitons excited in the absorption tail continues to be dominated by broad distributions of lifetimes at high pressure. These results suggest that the distributions of lifetimes do not arise from variations in tunneling or hopping rates between C_{60} molecules as was originally suggested, but arise from distributions of recombination rates at different sites in the sample.

The dynamics of excitons in C_{60} in solution have been extensively studied. The decay of singlet excitons in solution occurs with a lifetime of about 1 ns, and is governed by the crossover into triplet excitons with a much longer lifetime.[1,2] However, the nature of the electronic structure of the solid is still uncertain. In particular, the degree of coupling between molecules and the role of electronic correlation in this coupling is of particular interest. One-electron band-structure calculations[3] of the fcc solid C_{60} suggest an energy gap of about 1.5 eV between narrow continuum bands of bandwidth $W \approx 0.4$ eV. Indeed, weak absorption is observed[4] between 1.6 and 2 eV. However, electron-electron interaction is important in C_{60} solids. Photoemission and Auger experiments give an on-site Coulomb interaction $U = 1.6$ eV, and a forbidden "gap" at 2.3 eV.[5] With $U/W \approx 4$, strongly localized Frenkel excitons are expected for the lowest electronic excited states, rather than band states or Wannier excitons.

Studying photoinduced absorption (PA) at 605 nm, Cheville and Halas[6] reported a stretched-exponential decay in the picosecond time range. They attributed the PA decay to tunneling or hopping between localized electronic states. At higher laser intensities, both transient PA (Ref. 7) and time-resolved degenerate four-wave mixing measurements[8] show a faster decay that is strongly dependent on laser intensity, followed by a slow decay lasting into the ns region. Several mechanisms have been suggested for this fast decay at high intensities, including electron-electron scattering,[7] self-trapping distortions common to conjugated polymers,[7] and singlet exciton-exciton annihilation.[8]

In this work we have studied the singlet exciton decay in C_{60} films as a function of pressure. Pressure studies have been of great interest in solid C_{60} because of the opportunity to increase intermolecular coupling. The absorption edge,[9–11] reflectivity edge,[12] and photoluminescence peak[13] are observed to redshift with pressure at rates of 5–14 meV/kbar. This gap reduction is usually interpreted as the formation and broadening of delocalized conduction and valence bands with pressure.[10–13] However, an alternative explanation of the pressure redshifting exists:[9] increased intermolecular coupling of dipole fluctuations (the "solvent" or "gas-to-crystal" effect)[14] which lowers excitonic energies in molecular crystals independent of covalent coupling.

From the PA decay we find that the exciton dynamics from 300 fs to 3 ns change with pressure, but this change can be explained by a redshift in the distribution of localized singlet excitons across the excitation photon energy. The lack of a true pressure effect, even though the separation distance between C_{60} molecules changes dramatically, suggests that exciton dynamics cannot be limited by hopping or tunneling processes.[6] The stretched-exponential and power-law decays observed over hundreds of picoseconds instead result from a distribution of molecular exciton recombination rates, independent of hopping.

C_{60} films from 99.9% pure powder were sublimated in a vacuum of less than 10^{-6} torr at a rate of about 3 Å/s from a quartz crucible near 450 °C. The film thickness was about 800 nm. Films were stored in air. The substrates were glass and 12-μm-thick mylar sheets. Mylar has been used successfully as a thin-film substrate in a number of pressure studies.[15] Pieces of C_{60} film on mylar were cut to fit in a gasketed diamond anvil cell with deoxygenated alcohol and ruby chips. Measurements were taken at room temperature.

Two picosecond laser systems were used to measure the exciton dynamics by photoinduced absorption (PA), in which the change ΔT in the probe transmission T is measured as a function of the probe delay time relative to a pump pulse. A colliding-pulse mode-locked ring dye laser (CPM) was used for measurements at high pressure and fixed wavelength. Because the absorption increases with photon energy in the tail of the absorption, the laser was operated near 615 nm rather than the usual 620–630 nm, giving pulses from 150 to 300 fs in duration. For ambient pressure measurements at variable wavelengths, we used a synchronously pumped dye laser with 5-ps resolution. For all experiments the photon densities per pulse were about 0.1 mJ/cm^2, two orders of magnitude smaller than the densities used in previous studies[7,8] which showed intensity-dependent decays.

Optical absorption at high pressure was measured by imaging on the sample a pinhole at the exit of a $\frac{1}{4}$-m

monochromator using reflective optics. Reference spectra for ratioing were taken in the diamond cell.

The transient PA in C_{60} films is shown in Fig. 1 for pressures from 0 to 62 kbar. The PA signal represents an increase in the absorption ($\Delta\alpha > 0$) which is proportional to the exciton density, due to larger transition probabilities to higher singlet exciton states $S_1 \rightarrow S_n$ than for the mostly forbidden lowest ground-state absorption $S_0 \rightarrow S_1$.

The decay curve at ambient pressure (0 kbar) is well fitted by either a stretched-exponential form for the exciton population,

$$N(t) \sim \exp[-(t/\tau)^\beta] , \qquad (1)$$

where $\beta = 0.54$ and $\tau = 160$ ps, or by another decay form common to disordered systems, [16]

$$N(t) \sim 1/[1 + (t/\tau)^\alpha] , \qquad (2)$$

where $\alpha = 0.83$ and $\tau = 87$ ps, which is the fit shown in Fig. 1 for 0 kbar. The two fits begin to differ noticeably only around 500 ps, where $t \gg \tau$. The stretched-exponential values obtained at 615 nm differ somewhat from those reported by Cheville and Halas[6] at 605 nm ($\beta = 0.42$ and $\tau = 43$ ps), but as we show below, these parameters depend on details of the disorder distributions in the sample and hence on the exciting wavelength.

With increasing pressure, both τ and α decrease, as shown in Fig. 2 (τ is simply a disorder distribution parameter, and need not have any direct physical meaning). By 28 kbar, the decay clearly approaches a power law, $N(t) \sim (t/\tau)^{-\alpha}$, the asymptotic form of (2). Even the flat tail observed after 600 ps at zero pressure becomes part of the same power-law decay, indicating that no new excitations arise within 3 ns.

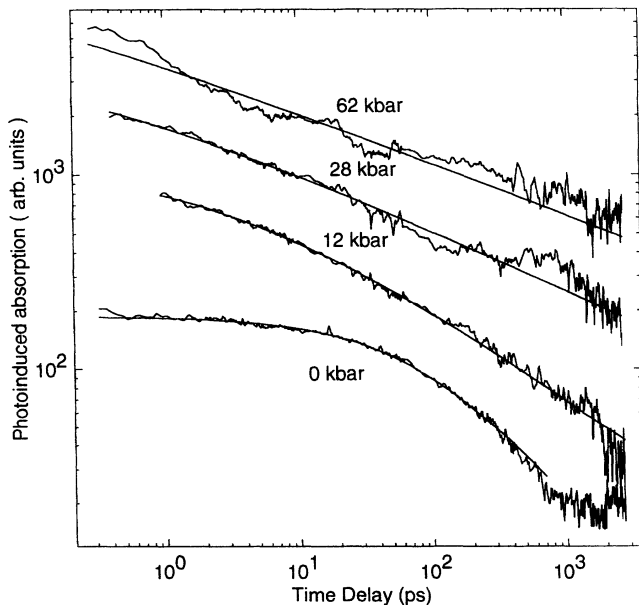Figure 3 shows the optical density of the sample at

FIG. 2. Variation with pressure of the decay parameters α and τ for the fits shown in Fig. 1.

several pressures. By 60 kbar, the CPM photon energy at 2 eV is well above the absorption threshold. The inset in Fig. 3 shows the optical-absorption threshold energy (ATE) as a function of pressure. As in Ref. 10, we define the ATE as the extrapolation of the linear portion of the absorption edge to zero absorbance. For unpressed samples, this is taken at the onset of the small shoulder near 1.9 eV. We observe a linear redshift of $dE/dP = -7$ meV/kbar, close to values reported of $dE/dP \approx 5-10$ meV/kbar for films[11] and crystals.[8,12] No hysteresis was noticed in the absorption threshold when the pressure ws released, although some broadening of the absorption edge occurred.

Since pressure redshifts the absorption edge of solid C_{60}, we explored the possibility that the changes in the decay form were simply caused by the movement of different regions of the absorption tail across the fixed CPM photon energy. Figure 4 shows the transient PA at varying photon energies in unpressed samples. These measurements of the sync-pump system demonstrate that increasing photon energy at ambient pressure is similar to increasing pressure at a fixed wavelength at ambient pressure: both the stretched-exponential decay and the slow

FIG. 1. Decay of singlet excitons in a C_{60} film at various pressures. The pump and probe wavelength was 615 nm. The curves are vertically offset for easier comparison. The dashed lines represent fits to $N(t) \sim 1/[1 + (t/\tau)^\alpha]$.
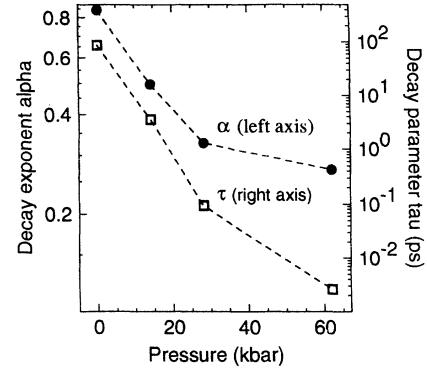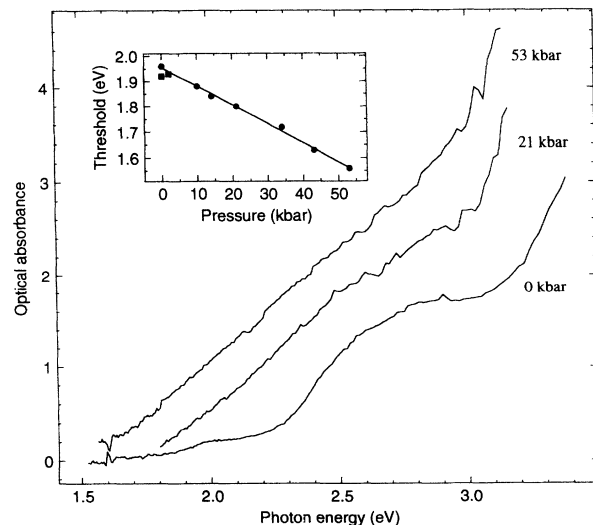

FIG. 3. Optical absorption spectra at various pressures. Inset: Absorption threshold energy as a function of pressure.
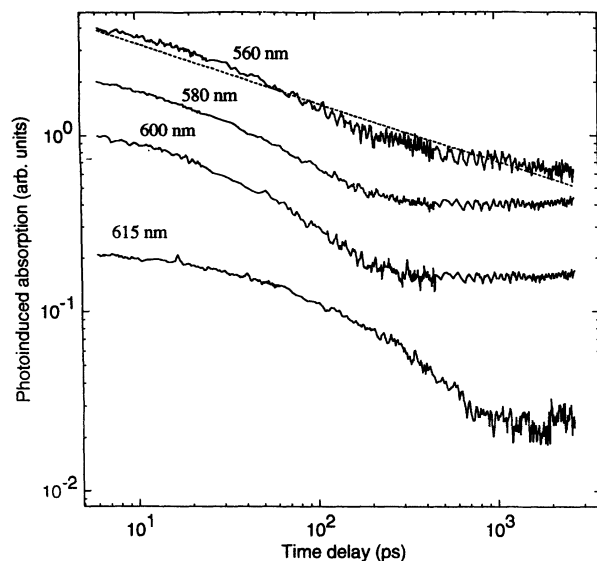
FIG. 4. Decay of singlet excitons in a C_{60} film pumped and probed at various wavelengths, at ambient pressure. The curves are vertically offset for easier comparison. The dashed line is a fit to a power-law decay, yielding an exponent $\alpha = 0.3$.

tail begin to converge to a power-law decay. Since the absorption band redshifts with pressure at a rate $dE/dP = -7$ meV/kbar, the 200-meV shift between the highest excitation energy (560 nm) and the lowest (615 nm) is equivalent to a redshift of the absorption band due to a pressure difference of about 30 kbar. The same decay exponent $\alpha = 0.3$ is found in the two "equivalent" cases: 560 nm at 0 kbar and 615 nm at 28 kbar.

Cheville and Halas[6] attributed the stretched-exponential decay to a distribution of tunneling or hopping rates between localized states. By 60 kbar, the inter-ball distance has been reduced by 30%, from 2.9 to 2.0 Å,[17,18] and tunneling or hopping rates should be strongly affected. Instead, we observe that changes with increasing pressure can be roughly imitated at ambient pressure by pumping and probing at higher photon energies. There is no substantial change in the distribution of exciton lifetimes with pressure. Instead, different portions of the distribution are probed as the distribution redshifts across the fixed CPM wavelength. The lack of a true pressure effect suggests that the exciton lifetime is not governed by dispersion in the hopping or tunneling rates between C_{60} molecules. This is consistent with the finding that the PA decay is temperature independent.[6] We conclude that the dispersion in the PA decay must be due to a distribution of exciton decay times among the excited molecules, rather than due to diffusion toward recombination centers.

Because of the disorder in the sample, these results do not shed much light on the degree of localization of excitons near 2.0–2.4 eV, although we can probably rule out a dramatic increase in mobility with pressure. There is general agreement that excitons below 2.3 eV are indeed Frenkel excitons. Studies of C $1s$ autoionization[19] show that a transition from well-localized to delocalized states occurs in the first few (core-hole) excited states. The onset of significant absorption near 2.3 eV in solid C_{60} can

be interpreted as due either to band formation or to transitions to optically "forbidden" excitons allowed by a loss of symmetry in the solid-state environment. Free carriers observed in photoconductivity[20] may be byproducts of exciton-exciton collision,[20] and are not direct evidence of the formation of bands of extended states. As mentioned above, the mechanism for the absorption redshift can be due to broadening of bands or coupling of dipolar fluctuations of Frenkel excitons to neighboring molecules. Hence the question of the localization of the excited states remains open.

It is natural to ask if the singlet exciton decay in the solid is to triplet states or to the ground state. Our data extend beyond the time range reported by Cheville and Halas,[6] and show that at ambient pressure after a few hundred ps the decay changes over to a slower decay, giving an almost constant exciton population from a few hundred ps out to at least 3 ns (Figs. 1 and 4). This slow decay has also been observed in degenerate four-wave mixing, and was attributed by Flom et al.[8] to the crossover to triplet excitons, suggesting that the singlet lifetime in the solid is governed by singlet-triplet crossover, as it is in solution. Triplet states in the solid have been detected conclusively at long times (μs to ms),[21,22] but picosecond PA spectra from 2.2 to 1.2 eV show no evidence of triplet formation or distinct dynamics out to 3 ns.[23] In the present work, we can see that there is nothing unique in the nearly flat tail that takes over after a few hundred ps. With increasing pressure or when pumped at higher energy, the tail along with the rest of the time range approaches a uniform power-law decay. This suggests that *singlet* excitons still dominate the PA out to at least 3 ns, by which time most of them have recombined to the ground state.

Finally, we comment on models proposed for the fast PA decay at high intensities. Brorson et al.[7] suggested two possibilities: electron-electron scattering or self-trapping distortions seen in the conjugated polymer polydiacetylene. Because at 2 eV excitons are the primary excitation, free carrier-carrier scattering is not a likely explanation. In addition, comparing ultrafast recombination in C_{60} to that in quasi-one-dimensional polymers is probably not appropriate; a previous pressure study[14] has shown that the fast decay (1.5 ps) of singlet excitons in polydiacetylene requires out-of-plane twisting deformations that are not available to the more interconnected C_{60} molecule. The most promising explanation for the intensity-dependent decay is singlet exciton-exciton annihilation suggested by Flom et al.[8]

In conclusion we have found that when excited near 2 eV, the exciton decay in solid C_{60} depends fundamentally on the position of the exciting wavelength in the absorption band, but not significantly on pressure. The results suggest that singlet excitons remain the dominant photoexcitation at high pressure, and that their lifetime does not depend on hopping or tunneling.

*Author to whom correspondence should be addressed; present address: Department of Physics and Astronomy, Brigham Young University, Provo, UT 84602.

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