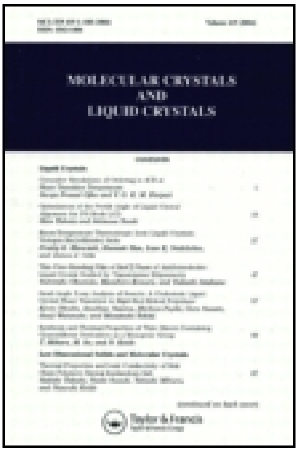

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Exciton Dynamics in Solid C_{60} at High Pressure

Bret C. Hess [a], Eric A. Forgy [a], Sergey Frolov [b], David D. Dick [b] & Zeev V. Vardeny [b]

[a] Physics Department, California State University, Fresno, CA, 93740

[b] Physics Department, University of Utah, Salt Lake City, Utah, 84112

Version of record first published: 04 Oct 2006.

To cite this article: Bret C. Hess , Eric A. Forgy , Sergey Frolov , David D. Dick & Zeev V. Vardeny (1994): Exciton Dynamics in Solid C_{60} at High Pressure, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 256:1, 775-782

To link to this article: http://dx.doi.org/10.1080/10587259408039324

Mol. Cryst. Liq. Cryst. 1994, Vol. 256, pp. 775–782
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EXCITON DYNAMICS IN SOLID C_{60} AT HIGH PRESSURE

BRET C. HESS and ERIC A. FORGY
Physics Department, California State University, Fresno, CA 93740

SERGEY FROLOV, DAVID D. DICK, and ZEEV V. VARDENY
Physics Department, University of Utah, Salt Lake City, Utah 84112

Abstract

We have studied the singlet exciton decay by picosecond photoinduced absorption (PA) in films of C_{60}, under pressures up to 62 kbar. When excited at 2 eV, the exciton lifetime distribution broadens with pressure. A similar broadening occurs when changing the exciting wavelength at ambient pressure. This suggests that the lifetimes of the lowest-energy excitons do not depend upon hopping or tunneling between C_{60} molecules. We see no evidence in the dynamics of the lowest energy excitons for the evolution of extended states or bands with pressure up to 60 kbar, even though we excite states well above the absorption edge.

INTRODUCTION

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.

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, [9,10] reflectivity edge,[11] and photoluminescence peak[12] are observed to redshift with pressure at rates of 5-14 meV/ kbar. This gap reduction is widely interpreted as the formation and broadening of delocalized conduction and valence bands with pressure.

From the PA decay[13] 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 the 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.

EXPERIMENT

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. 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.[14] 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 DT in the probe transmission T is measured as a function of the probe delay time relative to a pump pulse. A colliding-pulse modelocked 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 wavelength, 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.

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 photoexcited exciton density, due to larger transition probabilities to higher singlet exciton states $S_1 \to S_n$ than for the mostly forbidden lowest ground state absorption $S_0 \to S_1$.

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[12]

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

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 later, these parameters depend on the details of the disorder distributions in the sample and hence on exciting wavelength.

With increasing pressure, both τ and α decrease, reflecting a broadening in the distribution of exciton lifetimes. By 28 kbar, the decay clearly approaches a power-law, $N(t) \sim (t/\tau)^{-\alpha}$, the asymptotic form of (2).

By 60 kbar, the CPM photon energy at 2 eV is well above the absorption threshold.[11] We observe a linear redshift[11] of $dE/dP = -7$ meV/kbar, similar to that reported[8] (-5.5 meV/kbar) for a thicker film deposited directly on a diamond anvil.

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. Fig. 2 shows the transient PA at varying photon energies in unpressed samples. These measurements on the sync pump system demonstrate that increasing photon energy at ambient pressure is similar to increasing pressure at a fixed wavength at ambient pressure: both the stretched-exponential decay and the slow 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 0kbar, and 615nm 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,[14,15] and tunneling or hopping rates should be strongly affected. Instead, we observe that the changes with increasing pressure can be roughly immitated 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 dispersive diffusion of excitations toward recombination centers.

ACKNOWLEDGEMENTS

We thank D. V. Bowersox for preparing the samples. This research was funded in part by a grant from Research Corporation and D.O.E. grant no. DE-FG 03-93 ER 45490 and by ONR grant no. N00014-91-C-0104.

REFERENCES

1. R. J. Sension, C. M. Phillips, A. Z. Szarka, W. J. Romanow, A. R. McGie, J. P. Cauley, Jr., A. B. Smith III, and R. M Hocstrasser, J. Phys. Chem. 95, 6075-6078 (1991).
2. T. W. Ebbesen, K. Tanigaki and S. Kuroshima, Chem. Phys. Lett. 181, 501 (1991)
3. W. Y. Ching, M.-Z. Huange, and Y.-N. Xu, Phys. Rev. Lett. 67, 2045, 1991.
4. A. Skumanich, Chem. Phys. Lett. 182, 486 (1991)
5. R. W. Lof, M. A. van Veenendaal, B. Koopmans, H. T. Jonkman, and G. A. Sawatzky, Phys. Rev. Lett. 68, 3924 (1992).
6. R. A. Cheville and N. J. Halas, Phys. Rev. B 45, 4548 (1992).
7. D. W. Snoke, K. Syassen, and A. Mittelbach, Phys. Rev. B 47, 4146 (1993).
8. F. Moshary, N. H. Chen, I. F. Silvera, c. A. Brown, H. C. Dorn, M. S. deVries, and D. S. Bethune Phys. Rev. Lett. 69, 466 (1992).
9. D. W. Snoke, Y. S. Raptis, and K. Syassen, Phys. Rev. B 45, 14419 (1992)
10. A. K. Sood, N. Chandrabhas, D. V. S. Muthu, A. Jayaraman, M. Kumar, H. R. Krishnamurthy, T. Pradeep and C. N. R. Rao, Solid State Commun. 81, 89 (1992).
11. B. C. Hess et al., to be published (more complete paper on this work).
12. a) B. C. Hess, G. S. Kanner, Z. V. Vardeny, and G. L. Baker, Phys. Rev. Lett. 66, 2364 (1991) b) L. X. Zheng, B. C. Hess, R. F. Benner and Z. V. Vardeny, Phys. Rev. B 47, 3070 (1993) c) B. C. Hess, G. S. Kanner and Z. V. Vardney, Phys. Rev. B 47, 1407 (1993)
13. For a review, see Z. Vardeny and J. Tauc in Semiconductors Probed by Ultrafast Laser Spectroscopy, Vol.II, (Academic Press, 1984).
14. J. E. Fischer, P. A. Heiney, A. R. McGhie, W. J. Romanow, A. M. Denenstein, J. P. McCauley, Jr;, A. B. Smith III, Science 252, 1288 (1992)
15. Y. Wang, D. Tomanek and G. F. Bertach, Phys. Rev. B 44, 6562 (1991)

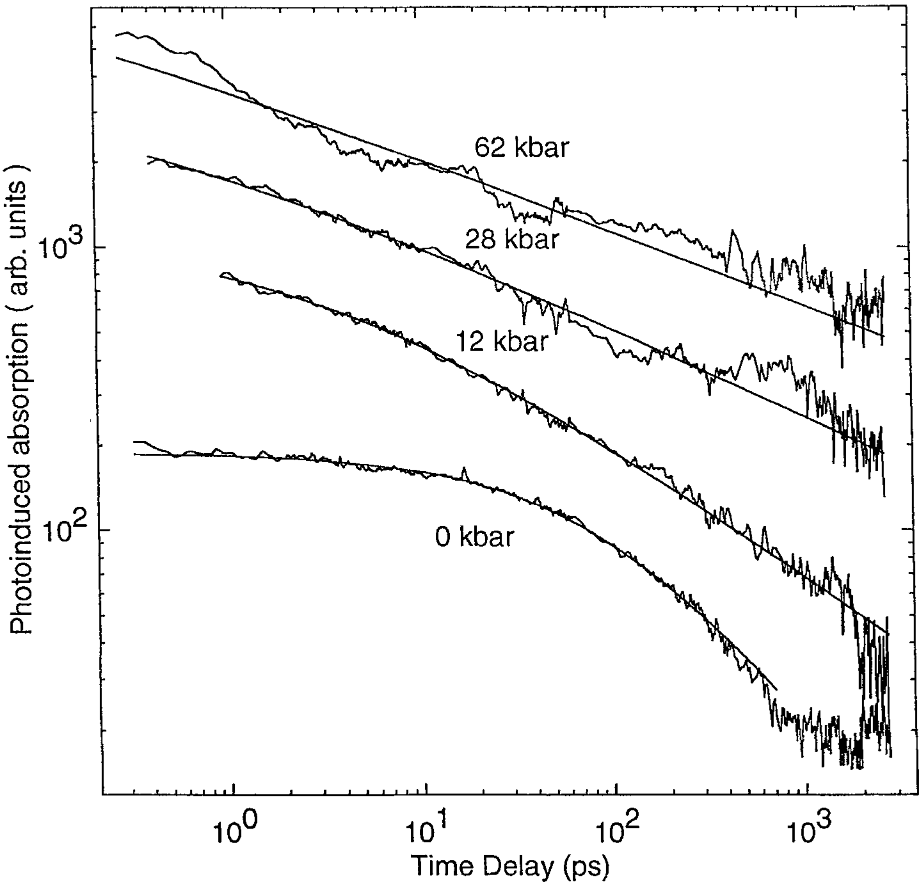
Figure Captions

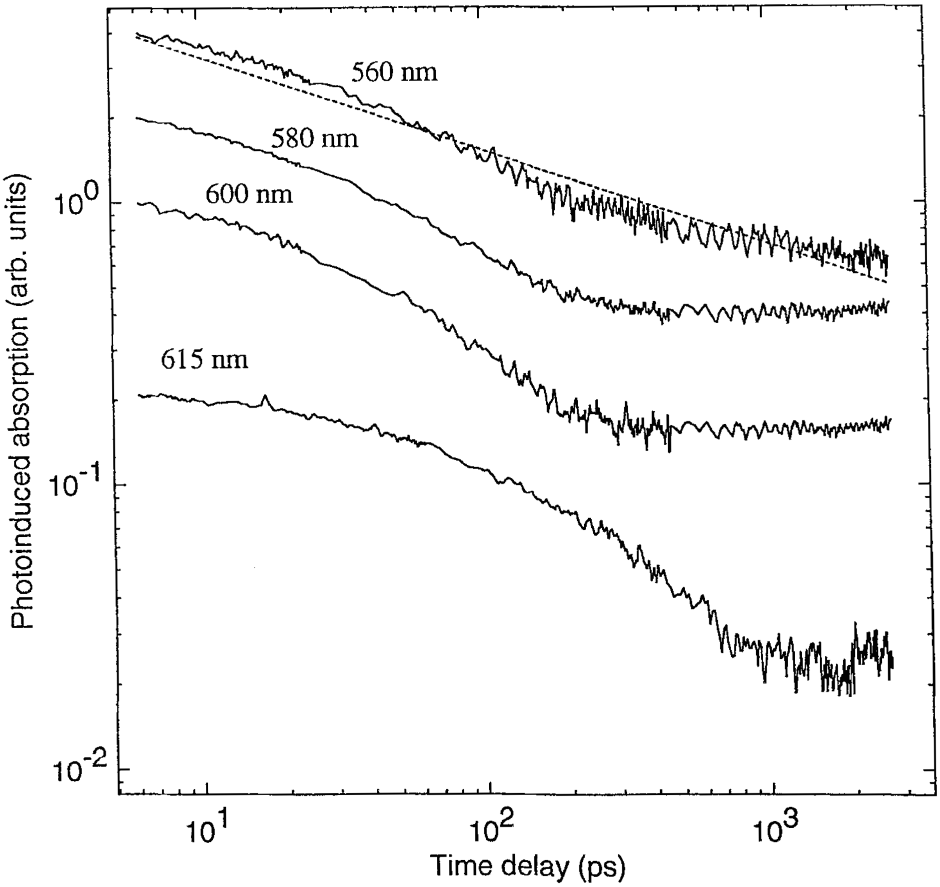
Figure 1:

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 $N(t) \sim 1/[1+(t/\tau)^{\alpha}]$

Figure 2:

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 $\alpha = 0.3$.


62 kbar
28 kbar
12 kbar
0 kbar
Photoinduced absorption (arb. units)
10^3
10^2
10^0
10^1
10^2
10^3
Time Delay (ps)


560 nm
580 nm
600 nm
615 nm
Photoinduced absorption (arb. units)
10^0
10^{-1}
10^{-2}
10^1
10^2
10^3
Time delay (ps)