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Time-resolved carrier relaxation in solid C_{60} thin films

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The time dependence of the carrier relaxation in undoped solid C_{60} thin films has been studied by monitoring changes in the optical transmission upon photoexcitation at the HOMO-LUMO band edge. The relaxation closely follows a Kohlrausch-Williams-Watts decay with an exponent of $\beta = 0.4$. This functional form is typical of carrier relaxation associated with states of localized rather than extended character. In addition, we observe this relaxation behavior to be independent of temperature, which indicates that a hopping mechanism may be important in the carrier recombination process in solid C_{60}.

The discovery of the fullerene family of carbon cluster molecules, the third elemental form of carbon, has generated much recent interest.[1] Breakthroughs in the capability of synthesizing large quantities of mass-selected fullerenes[2] has led to several investigations of the geometric and electronic structural properties of the condensed phase of fullerenes, specifically solid C_{60} and C_{70}.[3–5] In solid C_{60}, the C_{60} clusters condense into an fcc lattice, which exhibits a degree of orientational disorder due to the rotational movement of the C_{60} clusters.[6,7]

The electronic structure of solid C_{60} differs in several important and fundamental ways from that of the isolated C_{60} cluster. While transitions between the highest-occupied molecular orbital (HOMO) and the lowest-unoccupied molecular orbital (LUMO) are dipole forbidden in the isolated cluster,[8] they are weakly allowed in condensed phases; in solution, via vibronic coupling, and in the solid, where solid-state effects uniformly enhance the oscillator strength over a broad region, down to approximately 1.4 eV. Band-structure calculations for the fcc geometry[9] characterize solid C_{60} as a direct-gap semiconductor where the (HOMO-derived) valence-band maximum and the (LUMO-derived) conduction-band minimum lie at the X point of the Brillouin zone. Photoemission and inverse photoemission spectra of the HOMO-derived and LUMO-derived bands show unusually narrow linewidths, characteristic of the photoemission spectra of isolated molecules.[3,10,4] Optical absorption and luminescence measurements have indicated the presence of a HOMO-LUMO gap at 1.6–1.9 eV.[11–13] Both the exponential leading edge and the spectral structure observed in the band-edge absorption are highly reminiscent of the optical absorption properties of amorphous semiconductors.[11]

In this paper, we report the initial studies of carrier relaxation in solid C_{60}, using time-resolved optical transmission measurements. To date, these types of measurements have been of fundamental importance in elucidating the carrier relaxation mechanisms in both crystalline and amorphous semiconductors.[14–16] Our observations of carrier relaxation in solid C_{60} show that the relaxation process follows a nonexponential decay, described by the stretched-exponential form:

$$F(t) = \exp[-(t/\tau)^{\beta}], \tag{1}$$

where $0 < \beta < 1$. This type of decay, often termed Williams-Watts[17] or Kohlrausch[18] relaxation, is observed in a wide class of dynamical phenomena in disordered systems. Examples include spin correlations in Cu-Mn and Ag-Mn spin glasses,[19] specific heat in magnetic glasses,[20] dielectric relaxation in charge-density-wave systems,[21] neutron spin-echo measurements of ionic glasses,[22] and carrier relaxation in amorphous semiconductors, such as hydrogenated amorphous silicon.[23] This type of nonexponential relaxation is frequently seen in systems also exhibiting dispersive transport.[24] Both nonexponential relaxation and dispersive transport are associated with the presence of localized electronic states in the solid.

The synthesis and purification of C_{60} was accomplished using the method of Kratschmer *et al.*[2] The samples were grown in parallel with reported photoemission and inverse photoemission spectroscopic measurements, using the same raw material and under the same preparation conditions.[3–5] Films were evaporated from Ta boats at 550 °C, in a UHV chamber with typical background pressure of $< 10^{-10}$ Torr. Based on scanning tunneling microscopy results for multilayers grown under equivalent conditions, we expect the surface to exhibit close-packed molecular arrays but with crystalline disorder at grain boundaries.[25] X-ray scattering studies of C_{60} thin films grown under similar deposition conditions report the existence of small crystalline domains and short-range order (60 Å coherence length).[13] Sapphire flats of 0.25 mm thickness were used as the substrate material. The films were optically thick, exhibiting 67% transmission at 633 nm wavelength. This corresponds to a film thickness of approximately 1000 Å.[13] An absorption spectrum of the films grown in this manner is shown in Fig. 1. The major features of this absorption spectrum

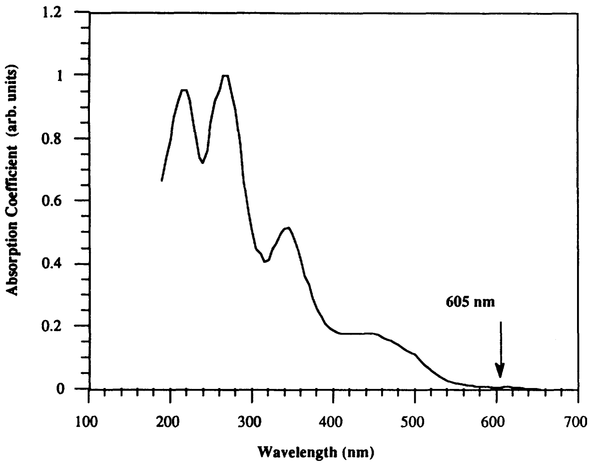

FIG. 1. Absorption of C_{60} thin film on sapphire substrate. Arrow corresponds to the excitation and probe wavelength (605 nm). Structural features in the high-resolution band edge spectrum assigned in Ref. 11 are not resolved.

agree well with the more detailed absorption measurements reported on films grown by other workers.[11-13] The strongest peaks in this absorption spectrum, at 345, 270, and 220 nm, correspond to dipole-allowed transitions in the isolated cluster.[8] Additionally, there is a weaker, very broad absorption with a maximum at 450 nm that extends to approximately 700 nm, corresponding to the dipole-forbidden transitions in the 2.6–2.8-eV range for the isolated cluster. The arrow in the figure indicates the laser wavelength used in the time-resolved absorption measurements described below.

The optical source for this experiment was a colliding-pulse mode (CPM) locked dye laser, which produces an output pulse energy of 0.2 nJ at a repetition rate of 100 MHz. Although a typical CPM laser operates at a center wavelength near 620 nm, the transient absorption signal of C_{60} fulleride is very weak at this wavelength. The CPM laser center operating wavelength was therefore shifted to 605 ± 2 nm by lowering the saturable absorber concentration and adjusting the laser cavity such that the beam waist was smaller in the absorber jet. This wavelength shifting was done at a sacrifice of pulsewidth from the nominal 100 fsec to approximately 300 fsec, and long-term stability of the laser output was also reduced.

The experimental setup was a standard pump-to-probe geometry with pump-to-probe intensity of approximately 20:1. A 5-mW pump beam was incident on the sample at approximately 20° from the sample normal, and focused to a 20 μm spot size. Differential phase-sensitive detection yielded a sensitivity to transmission changes of 10^{-6}, with multiple-scan averaging used to enhance detection sensitivity.

The time-resolved measurement of the change in optical transmission upon photoexcitation of solid C_{60} is shown in Fig. 2. We observe a photoinduced increase in absorption that is usually characteristic of amorphous semiconductors.[23] This photoinduced absorption results from the relaxation of k-vector conservation for optical transitions in or out of localized states. The stretched-exponential fit of the time-resolved absorption is also shown in Fig. 2. These data were taken at room temperature, with $\beta = 0.42$ and $\tau = 43$ psec. The error to this fit is $< 0.2\%$, indicating exceptional agreement with the stretched-exponential functional form.

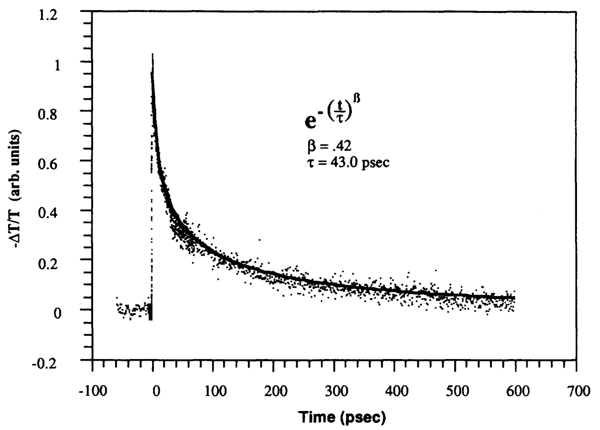

FIG. 2. Time-dependent transmission (normalized) of C_{60} thin film on sapphire, taken at room temperature. Both the pump and probe wavelengths were 605 nm. A calculated stretched exponential curve with $\beta = 0.42$ and $\tau = 43$ psec is also shown.

Since more than one relaxation mechanism can give rise to nonexponential decay, a characterization of the temperature dependence of this relaxation is necessary to elucidate the possible microscopic mechanism or mechanisms controlling carrier relaxation in solid C_{60}. The two processes relevant for understanding carrier relaxation are (1) carrier trapping, where recombination occurs via an exponential distribution of localized states in the band tail, and (2) carrier hopping, where carriers in localized states tunnel between states. In carrier trapping, as described by the multiple trapping model,[26,27] carriers in localized states will be excited via quasiparticle interactions to extended states above a mobility edge, and subsequently retrapped into lower energy states. This mechanism, which is operative in amorphous semiconductors, is characterized by a linear temperature dependence of β and an Arrhenius-like temperature behavior of τ. In contrast, there is little or no temperature dependence associated with a hopping mechanism, since tunneling probabilities are related only to the barrier thickness. Temperature-independent behavior may occur in systems where the localized states are energetically far below a mobility edge,[28] or where the density of localized states is large, such that the tunneling probability is significantly larger than the trapping probability.[29]

We have performed time-resolved carrier relaxation measurements over a broad range of temperatures, between 150 and 400 K. These data are shown in Fig. 3. It is evident from this figure that within our error there is no temperature dependence in either β or τ for this relaxation. If relaxation occurred via trapping by an exponential distribution of states in the band tail,[24,30] β would increase linearly with increasing temperature. Scaled to our room-temperature data, we would have been able to see a change in β of approximately 83% over this temper-

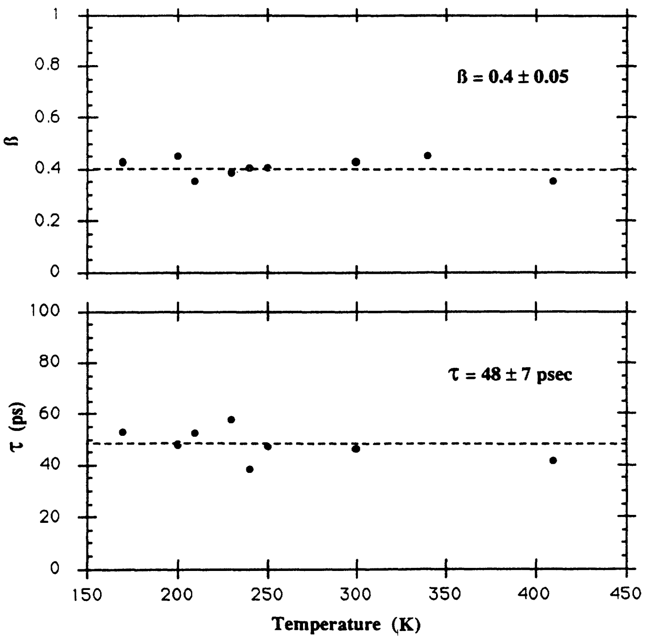

FIG. 3. (a) Demonstrated temperature independence of the exponent β obtained in the stretched exponential fit of Fig. 2. (b) Temperature independence of the relaxation time τ.

ature range. In the case of C_{60}, both electronic structure calculations and inverse photoemission spectra indicate that a transition from unoccupied "molecularlike" states to "delocalized" states occurs at about 4 eV above the LUMO state.[10] Since this barrier height is much greater than kT, it is consistent with our measurement of a temperature-independent τ. These measurements essentially rule out the role of trapping as the predominant relaxation mechanism. A hopping model where carriers tunnel between localized states seems to be a more appropriate interpretation for carrier relaxation in solid C_{60}.

In conclusion, we report initial measurements of the carrier relaxation in solid C_{60}, using time-resolved optical pump-probe techniques. The relaxation can be characterized by a stretched exponential time dependence, and shows no significant temperature-dependent variation across the temperature range 150–400 K. All of our observations, i.e., photoinduced absorption, nonexponential relaxation, and temperature-independent relaxation, are consistent with the interpretation of localized states corresponding to the HOMO-LUMO transition in solid C_{60}. This interpretation is consistent with the photoemission data of solid C_{60} where exceptionally narrow peaks were observed for the HOMO-derived and LUMO-derived states, similar in character to the photoemission spectra of isolated molecules.

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