RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 46, NUMBER 11 15 SEPTEMBER 1992-I

Femtosecond pump-probe investigation of electron dynamics in solid C_{60} films

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(Received 11 May 1992)

We present an investigation of electron dynamics occurring on a femtosecond time scale in thin films of undoped and Rb-doped C_{60}. We have studied the dependence of the observed dynamics on laser intensity as well as temperature. We find strong absorption induced by laser pumping. Electron-density-dependent dynamics are observed on a $<$ 1-ps time scale. A discussion of the various scattering mechanisms at work is presented.

The femtosecond dynamics of optically excited electrons in C_{60} merits study for (at least) two reasons. First, recent experiments[1,2] have indicated that C_{60} may be a useful material because of its nonlinear optical properties; accordingly, the ultimate speed of its nonlinear optical response is of great practical interest. Second, understanding the scattering dynamics of hot electrons in a material is key to understanding its electron transport properties. For example, it has been demonstrated both theoretically[3] as well as experimentally[4] that the relaxation rate of a hot electron gas in a metal on a femtosecond time scale is governed by the electron-phonon interaction, and can be directly related to the electron-phonon coupling parameter λ important in superconductivity theory.[5] Since superconductivity has also been discovered in doped samples of C_{60},[6] study of femtosecond relaxation in this material may reveal clues about the scattering processes important for superconductivity.

Here, we present results obtained from a pump-probe study of solid films of C_{60}. We use 100-fs pulses of laser light obtained from a colliding-pulse mode-locked (CPM) laser–copper-vapor-laser (CVL) pumped amplifier system. The fast dynamics of undoped as well as Rb-doped films have been investigated as a function of pump intensity and sample temperature in the range $T =$ 300 K–10 K. Also, degenerate four-wave mixing experiments on one of the films have been performed to measure the dephasing time. We find that the effect of femtosecond laser pumping in both doped and undoped samples is to cause transient *induced absorption*, observable by measuring the change in transmitted probe (ΔT). The induced absorption decays via a two-step process: a fast relaxation process lasting on the order of 1 ps, followed by a slow decay of ΔT back to zero lasting hundreds of ps. In the undoped samples the size of the fast relaxation signal relative to that of the slow signal increases with the pump energy, whereas in the doped samples it remains constant. For the undoped samples, the fast relaxation time τ decreases with increasing pump energy, while in the doped samples it remains constant up to a threshold value, after which it also decreases. We find that the induced absorption can be explained using a multilevel model for the electronic states in solid C_{60} which is consistent with other experimental measurements. Further, we discuss the relation of the observed fast decay signals to intraband electron dynamics in the context of the multilevel picture.

The experiments were performed using a conventional pump-probe setup. The laser source was a dispersion compensated CPM laser[7] producing 80-fs pulses at $\lambda \approx$ 620 nm. The pulses were amplified in a six-pass "bow tie" amplifier[8] pumped with a CVL. The repetition rate of the CVL was 7.0 kHz. At the output of this system the pulses were measured to have a width of 100 fs and an energy of 12 μJ/pulse. Pump and probe beams were generated in the usual way.[9] The pump beam was chopped at 110 Hz to facilitate lock-in detection, and its delay with respect to the probe pulse was varied using a computer-controlled stepping motor. The polarization of the probe beam was rotated by 90° with a $\lambda/2$ plate so that the pump and probe beam polarizations were perpendicular. The two beams were focused onto the sample using a 150-mm camera lens. The laser spot diameter at the focus was measured to be 35 μm. After striking the sample, the transmitted probe beam was passed through a polarizer to block any residual pump beam scattering, and was monitored with a photodiode. The pump-probe signal was detected with a lock-in amplifier, and the measured values were transferred to a computer for storage.

Samples were made by evaporating C_{60} powder[10] from a Ta boat onto transparent quartz substrates. The powder still contained about 10% C_{70} which was then further reduced by the slow evaporation process due to the higher vapor pressure of C_{60}. The films were generally about 5000 Å thick. After deposition, the samples were transferred to a vacuum cryostat fitted with optical ports for measurement. In the experiments performed on Rb-doped samples, the samples were doped under vacuum by exposing the films to a current-driven Rb source made by SAES Corp. and run at 5.5 A for 30 min. The average doping level has been previously determined to be $\approx$ 2 Rb atoms/C_{60} molecule for this doping prescription by ellipsometric measurement and comparison to published spectra.[11] After doping, the samples remained under vacuum for the duration of the experiment.

Sample pump-probe data are given in Fig. 1, which

shows ΔT vs t for both an undoped (a), and a doped sample (b). The different curves correspond to different amounts of energy deposited by the pump pulse (E_{pu}). We find that ΔT is negative for all cases. This information coupled with the measured optical constants of C_{60} (Ref. 11) allows us to conclude that induced absorption is occuring as a result of laser pumping. Induced absorption by optical pumping in C_{60} has been previously reported by Cheville and Halas,[12] as well as Tutt and Kost.[2]

As can be seen in Fig. 1, a fast relaxation is evident for times on the order of ≈ 1 ps. This fast relaxation signal is superimposed upon a slower signal, which seems to relax on a time scale of the order of hundreds of ps. In the undoped samples the magnitude of the fast decay signal relative to the slow decay signal becomes more pronounced as the pump energy is increased. In the doped samples it remains constant for increasing pump energy, increasing only at the very highest pump power. This slow signal has been attributed to relaxation via carrier hopping by Cheville and Halas,[12] who performed pump-probe measurements on an undoped sample with low pump energy.

The time constant of the fast decay signal was derived in the usual way:[13] the slowly decaying component of the signal was subtracted from the data, and the remaining fast-decay component was fit with an exponential decay function using a least-squares fitting algorithm on a computer. The results are shown in Fig. 2, where we plot τ vs E_{pu}, the energy density of the pump laser pulse. As can be seen, for the undoped samples, τ decreases with increasing E_{pu} for all pump intensities measured, whereas in the doped samples τ remains constant at about 0.6 ps up to $E_{pu} \approx 40$–70 mJ/cm^2 and then also decreases.

Typical measured values of $\Delta T/T$ were on the order of several percent. In both doped and undoped samples, the magnitude of $\Delta T/T$ was found to increase slowly with increasing E_{pu}, although the increase was slower in the doped samples than in the undoped ones. For $E_{pu} > 50$ mJ/cm^2, we noticed that irreversible changes occurred in the sample during the course of a run. This energy density is of the same order of magnitude as that reported to be the threshold of femtosecond laser-induced melting in crystalline Si.[14] Therefore, although data taken with $E_{pu} > 50$ mJ/cm^2 seem to follow the same trend as those for which $E_{pu} \leq 50$ mJ/cm^2, these data must be regarded with some suspicion.

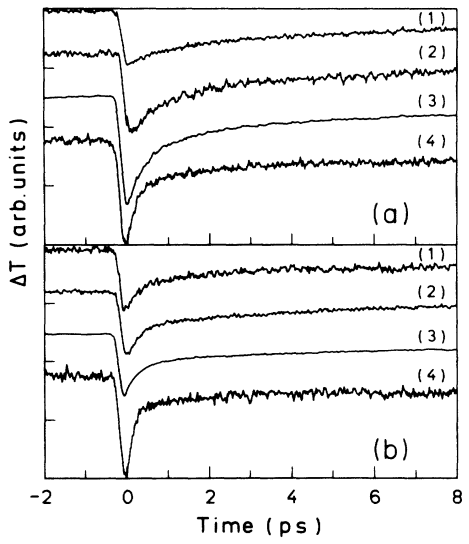

FIG. 1. Representative pump-probe data. Shown in (a) is ΔT vs t for undoped C_{60} for E_{pu} = (1) 1.4, (2) 7.2, (3) 29, and (4) 90 mJ/cm^2. In (b), E_{pu}=(1) 4.4, (2) 11, (3) 44, and (4) 73 mJ/cm^2.

In order to understand more about the physical processes at work causing the relaxation, we performed a pump-probe measurement on a doped sample at liquid-helium temperature. Upon cooling, the temperature of the cold finger to which the sample was attached was measured to be ≈ 10 K. Relaxation curves were measured before and after cooling for pump fluences of 23 and 2.4 mJ/cm^2. The measured relaxation curves are shown in Fig. 3. As can be seen, the relaxation data were identical at 300 and 10 K for both pump fluences. Thus, we conclude that the relaxation time of the fast signal is temperature independent, at least for temperatures down to a few tens of kelvin.

Finally, we have also performed a time-resolved degenerate four-wave mixing (DFWM) experiment[15] on a film of undoped C_{60}. The experiment was performed using the two-beam (self-diffraction) forward geometry. The beams were polarized parallel to one another. A very strong diffraction signal was observed—the diffracted beam was easily visible to the eye for a peak intensity of 8×10^{10} W/cm^2. The magnitude of the diffracted signal versus time is shown in Fig. 4. The diffracted signal shows no obvious decay, indicating that the dephasing time (T_2) is shorter than the laser pulse (100 fs). Decreasing the intensity in each beam by a factor of 14 failed to change the time profile of the diffracted signal, indicating that T_2 remained less than 100 fs. Since the signal is so fast, we varied the frequency of the chopper between 110 Hz and 3.5 kHz to ensure that the signal was not due to a thermal artifact.[15] The diffracted intensity remained unchanged for all chop rates, consistent with fast electronic dephasing.

A consistent explanation of the dynamics occurring in C_{60} must account for the following experimental facts.

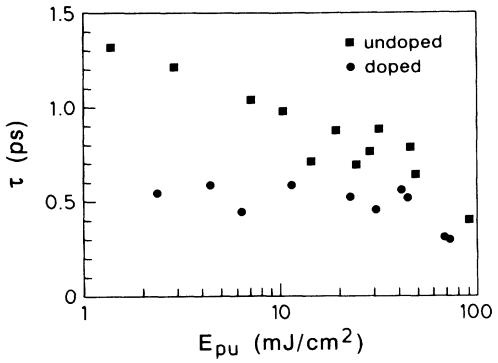

FIG. 2. Measured time constant of the fast signal τ vs E_{pu} for doped and undoped C_{60}.

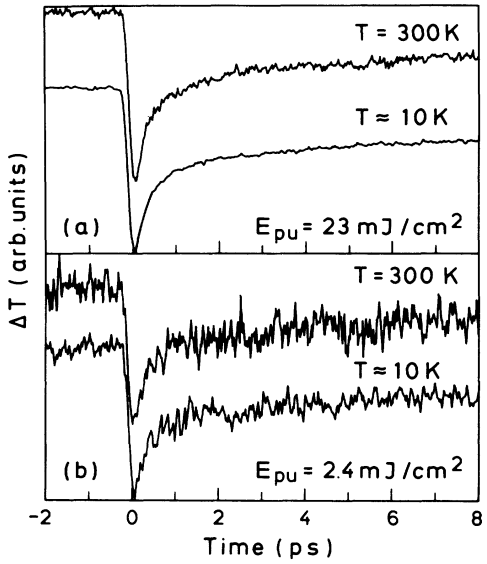

FIG. 3. ΔT vs t data for doped C_{60} at T=300 K and ≈10 K. In (a), E_{pu}=23 mJ/cm^2; in (b), E_{pu}=2.4 mJ/cm^2.

(1) Induced absorption occurs in the sample after laser pumping. Its presence is not altered by temperature, doping, or pump energy variations.

(2) The time-resolved DFWM experiment shows that the dephasing time T_2 is much less than our measured relaxation time τ.

(3) In undoped samples, τ decreases with increasing E_{pu} whereas in doped samples τ is constant with increasing E_{pu}, at least up to 50 mJ/cm^2.

(4) Finally, in a doped sample, τ remains constant upon cooling from 300 K down to ≈ 10 K. Further, at both temperatures τ remains independent of E_{pu}.

The occurrence of induced absorption [point (1)] can be explained by appealing to the level structure of C_{60} determined by previous optical,[11] photoemission,[16] and electron-energy-loss spectroscopy[17] studies, as well as molecular[18] and band-structure[19] calculations. In molecular C_{60}, the lowest-unoccupied molecular orbital (LUMO) (t_{1u} in the figure) lies ≈1.6–2.0 eV above the highest-occupied molecular orbital (HOMO) (h_u). Optical transitions between the HOMO and the LUMO are symmetry forbidden. There are a pair of occupied molecular orbitals (g_g, h_g) which are ≈1.5–2.0 eV below the HOMO; there are also a pair of empty orbitals (t_{2u}, h_g) roughly 2.0 eV above the LUMO. (See Fig. 5.) Both the (g_g, h_g) → HOMO and LUMO → h_g transitions are symmetry allowed, as indicated in the figure. [There is also a state with t_{1g} symmetry between the LUMO and (t_{2u}, h_g) orbitals. Its presence is immaterial for the discussion here.] In the solid state, these orbitals broaden into narrow bands of width ≈ 0.5 eV, and the strictly forbidden HOMO → LUMO transition becomes weakly allowed.

In undoped samples, before the arrival of the pump pulse, only the forbidden HOMO → LUMO transition can occur at 2 eV, since the higher (LUMO → h_g) and lower [(g_g, h_g) → HOMO] lying transitions are blocked. When the pump pulse arrives, it promotes electrons from the HOMO into the LUMO, thereby opening up initial and final states for the strongly allowed higher- and lower-lying transitions (see Fig. 5). After the arrival of the pump pulse, the sample is then left more absorbing for 2-eV photons, which is the effect registered by the probe pulse.

The physical origin of the fast relaxation process can be understood by considering the dependence of the relevant scattering mechanisms on pump energy, doping, and temperature. First, in accordance with point (2) above, the fact that T_2 is much shorter than the observed dynamics (≈ 1 ps) indicates that the fast signal is not related to scattering of electrons out of their initial optically coupled states. That is to say, we are in the regime where we are observing the time evolution of the carriers's nonequilibrium energy distribution which has been created by the pump pulse.

The usual picture of fast electron dynamics in metals holds that the electron and lattice systems are in equilibrium with themselves in a time shorter than the laser pulse width, and can be described via temperatures T_e and T_l, respectively. With this ansatz, Allen[3] derived an equation governing exchange of heat between the hot electrons and the lattice:

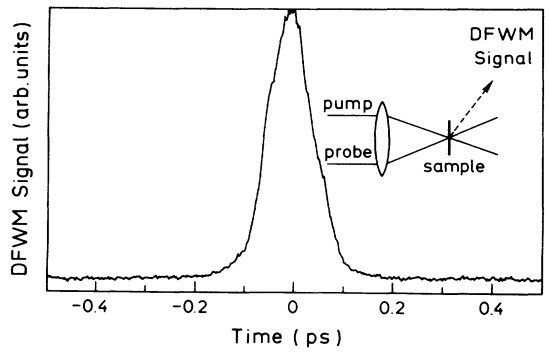

FIG. 4. Time-dependent degenerate four-wave mixing (DFWM) signal observed in undoped C_{60} in the two-beam self-diffraction geometry (see inset).

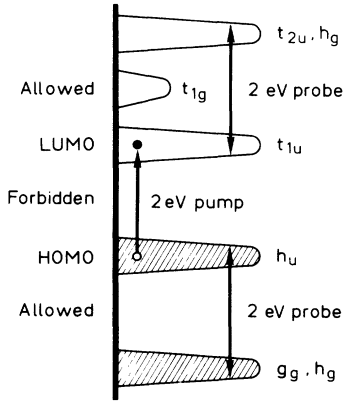

FIG. 5. Simplified picture of the energy level structure around the HOMO and LUMO levels in undoped C_{60}.

$$T_e \frac{\partial T_e}{\partial t} = -\frac{6}{\pi k_B^2} \int_0^\infty d\omega (\hbar\omega)^2 \alpha^2 F(\omega) \times \{n(\omega, T_e) - n(\omega, T_l)\}, \quad (1)$$

where $\alpha^2 F(\omega)$ is the "electron-phonon spectral function"[5] which is proportional to the phonon density of states, and $n(\omega, T) = \{\exp(\hbar\omega/k_B T) - 1\}^{-1}$ is the Bose-Einstein function. We have numerically integrated (1) assuming a model electron-phonon spectral function which successfully explains the superconducting properties of doped C_{60}.[20] At 300 K, we obtain a relaxation time of ≈ 0.8 ps, independent of E_{pu}, in agreement with our measurements on doped samples. However, at 30 K, the calculated relaxation times depend upon E_{pu}, in contrast to our experimental results [observation (4) above].

Indeed, the observed independence of τ from temperature is more reminescent of a scattering process mediated by Coulomb interactions than carrier-phonon scattering. Assuming that the effect of pumping a sample is to place electrons into the LUMO band, then observation (3) above is qualitatively consistent with a density-dependent interaction in the LUMO band: In the undoped sample the relaxation time decreases with increasing carrier density in the LUMO, whereas in the doped sample a constant number of electrons has already been doped into the LUMO, thereby resulting in the independence of τ from E_{pu}. This observation is difficult to explain with a carrier-phonon mechanism, but is consistent with a Coulomb-mediated interaction.

There are several Coulombic interactions which might give rise to the relaxation signal observed in our samples. The simplest is electron-electron scattering. Assuming a one-component plasma, a crude estimate of the shortest time (a "speed limit") in which this process can take place is given by the plasma frequency of the carriers,

$$\tau_{\rm el}^{-1} \sim \omega_p = (4\pi N e^2/m^*)^{1/2}, \quad (2)$$

where N is the carrier density, and m^* is the effective mass. From (2), it is apparent that (at least to first order) the characteristic time $\tau_{\rm el}$ decreases with increasing N, but is independent of the temperature of the system, qualitatively consistent with points (3) and (4) above. More sophisticated analysis is consistent with these simplistic observations.[21] In doped C_{60}, ω_p has been calculated[22] to be ≈ 1.2 eV, yielding $\tau_{\rm el} \approx 1$ fs. Although this number represents a lower limit on the possible interaction time, it still seems rather fast to credibly explain our results.

Another possibility involves the formation or decay of excitons in the C_{60}. Kobayashi *et al.* have reported temperature-independent exciton decay times on the order of 0.8–3.0 ps in several different polydiacetylene compounds.[23] The electronic dynamics occuring in these materials may correspond to those in C_{60} since this time scale is the same as we observe, and C_{60} is also a conjugated carbon bond system. Experiments designed to further illuminate the different ultrafast processes at work in C_{60} are currently under way.

We would like to thank I. I. Mazin and R. I. Devlen for helpful discussions, C. Thomsen for a critical reading of the manuscript, and W. Krätschmer for kindly supplying us with C_{60} powder. S.D.B. gratefully acknowledges financial support from the A. von Humboldt Foundation.

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