Femtosecond time-resolved photoemission as a probe of electronic transport in single wall carbon nanotubes

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Femtosecond Time–Resolved Photoemission as a Probe of Electronic Transport in Single Wall Carbon Nanotubes

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Abstract. We have performed the first time–domain measurements of the electron-electron (*e–e*) and electron-phonon (*e–ph*) dynamics in single-wall carbon nanotube samples (bucky paper) using time–resolved two-photon photoemission. In these room temperature experiments the absorption of a visible femtosecond pump pulse creates a non–equilibrium electron distribution whose evolution in time can be probed by a second UV-pulse. The decay of the excited electron distribution is characterized by a fast channel on the subpicosecond time–scale — associated with thermalization of the non–equilibrium distribution — and a slower channel which can be attributed to *e–ph* interaction. Once thermalized the electron distribution cools down to the lattice temperature as determined by the electron–phonon coupling constant g which was found to be $1\times10^{15}\,\mathrm{Wm^{-3}K^{-1}}$.

INTRODUCTION

The interaction of electrons with other charge–carriers, phonons and lattice inhomogenieties is crucial to the mean characteristic lengths for electron momentum and phase relaxation L_m and L_φ. The magnitude of these lengths with respect to the Fermi wavelength and the size of the sample determines if electronic transport in a certain experimental arrangement is ballistic, diffusive or classic and if localization effects or universal conductance fluctuations may be observed [1]. Knowledge of L_m and L_φ would, therefore, help to understand electronic transport through carbon nanotubes better. Femtosecond time–resolved photoemission has previously been used to study charge–carrier dynamics in metals and semiconductors [2,3]. Here we apply this technique to study the dynamics in single wall carbon nanotubes at room temperature.

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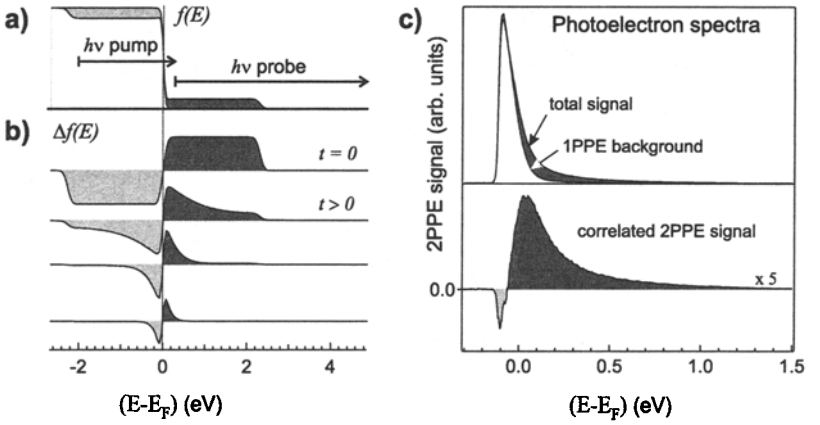

FIGURE 1. a) Perturbation of the Fermi–Dirac distribution by the femtosecond pump pulse. b) Change of the difference of the non–equilibrium with respect to the equilibrium distribution as a function of time. c) Uncorrected and background corrected photoelectron spectra

RESULTS AND DISCUSSION

Single wall carbon nanotube (bucky paper) samples were produced from commercial nanotube suspension (tubes@rice, Houston, Texas) following the procedure described by Rinzler *et al.* [4]. Samples obtained in this manner were attached to a tantalum block which could be resistively heated to 1200° C. The nanotube sample was outgassed thoroughly by repeated heating and annealing cycles under UHV conditions. Two–photon photoelectron (2PPE) spectra where obtained by means of the time–of–flight technique with an improved energy resolution of 10 meV [5]. The visible pump pulses with a duration of less than 90 fs were focused nearly collinearly onto the sample together with the frequency doubled probe pulses. The pump pulse fluence was kept below $10^9\,\mathrm{Wcm}^{-2}$.

In order to study charge carrier dynamics in the vicinity of the Fermi level we used a probe photon energy $h\nu_{probe}$ of 4.60 eV, slightly above the work function of the nanotube samples $e\Phi$ of 4.5 eV. The pump photon energy was 2.30 eV. Fig. 1a) and b) shows a schematic illustration of the experiment together with a typical photoelectron spectra in Fig. 1c). The intermediate state energy of the electrons $(E - E_F)$ is calculated from the electron kinetic energy E_{kin} via the relation $(E - E_F) = E_{kin} + e\Phi - h\nu_{probe}$. 2PPE spectra from these samples show no sign of Van Hove type singularities. Such features are probably broadened and smeared out due to tube–tube interactions and averaging effects.

To obtain the correlated 2PPE signal which reflects the changes induced in the electron distribution by the pump pulse, we have to subtract the time independent one–photon photoemission background from the UV probe pulse. The resulting correlated 2PPE signal at zero pump–probe delay is shown in Fig. 1c). This spectrum reflects the excitation–induced depletion of charge carriers below the Fermi

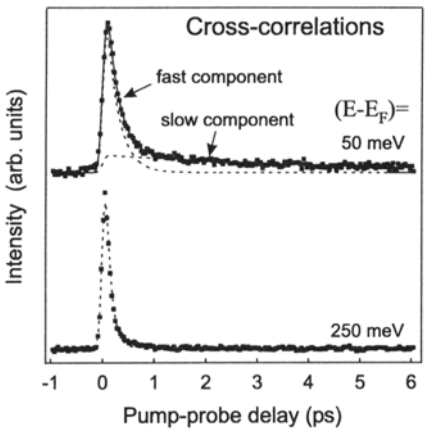

FIGURE 2. Cross-correlations at two different intermediate state energies. The upper trace was recorded at an energy of 50 meV and the lower one was recorded at 250 meV above the Fermi level.

level (negative signal) and the increase in the electron population at energies above the Fermi level (positive signal).

If the intensity at a particular energy in these spectra is recorded as a function of the pump–probe delay we obtain cross–correlations like the ones shown in Fig. 2. The upper cross–correlation in Fig. 2 shows that the electron dynamics is characterized by a slow and a fast component. In analogy to our results obtained on highly oriented pyrolytic graphite the fast component can be attributed to carrier–carrier interactions which lead to a rapid thermalization of the non–equilibrium electron distribution [6,7]. This thermalization can be observed directly from the time dependence of 2PPE spectra which can be described by a thermal Fermi–Dirac distribution after about 500 fs [7]. For the fast channel the characteristic time for relaxation of the electron or hole population at 50 meV above or below the Fermi level is found to be (250 ± 50) fs. Using a Fermi velocity v_F of 8 Å fs^{-1} this yields an *e–e* mean free path of 200 nm. Due to the contribution of secondary electron cascades to the 2PPE signal this decay–time should be considered as an upper limit of the actual *e–e* scattering time. At higher electron energies the relaxation time decreases continuously to less than 20 fs at 2 eV above the Fermi level.

For the pump pulse fluence used in these experiments the temperature of the electronic system has equilibrated after 500 fs at about 850 K. The slow component in the cross-correlations and the dynamics of the 2PPE spectra can then be used to follow the cooling of the electronic system down to the lattice temperature T_l via *e–ph* interaction. If approximated by an exponential decay $\frac{dT_e}{dt} = -\tilde{c}(T_e - T_l)$ the characteristic rate $\tilde{c}$ at which the electronic temperature T_e decreases is found to be $\sim(2\,\mathrm{ps})^{-1}$.

Such a coupling of the electronic system to the lattice is frequently discussed in the framework of the two–temperature model introduced by Anisimov *et al.* [8]. This model has been used extensively to study *e–ph* coupling in metals using transient reflectivity measurements (see for example ref. [9]). According to Anisimov *et*

al. the flow of energy between the electronic system and the lattice can be described by the two coupled heat equations:

$$C_e(T_e)\frac{\partial T_e}{\partial t} = \nabla(\kappa\nabla T_e) - g(T_e - T_l) \quad (1)$$

$$C_l(T_l)\frac{\partial T_l}{\partial t} = g(T_e - T_l). \quad (2)$$

Here C_e and C_l are the specific electron and lattice heat capacities respectively. Since C_l is much greater than C_e in graphite (and nanotubes) we can neglect the heating of the lattice and use equation 1 alone to determine the coupling constant g. In the absence of diffusive transport ($\nabla(\kappa\nabla T_e) \approx 0$) a fit of equation 1 to the experimental temperature evolution yields a coupling constant g of 1×10^{15} $\mathrm{Wm^{-3}K^{-1}}$. Here we have used the electronic heat capacity of graphite γ of $2.4\,\mathrm{J\,m^{-3}\,K^{-1}}$. Using the formalism originally developed for *e–ph* dynamics in metals the coupling constant g can be related to the electron–phonon coupling parameter λ from the BCS theory of superconductivity via $g = (3\gamma\hbar\lambda\langle\omega^2\rangle)/(\pi k_B)$ [10] which is also related to the characteristic time for emission of a phonon by $\tau_{e-ph} = (\pi\lambda\langle\omega\rangle)^{-1}$ ($\langle\omega\rangle$ being the mean phonon frequency) [11]. Using the fit to equation 1 we obtain a value of $\lambda = 0.0025$ which is about 2 orders of magnitude smaller than values typically found in metals [9]. The corresponding *e–ph* scattering time is 0.85 ps and the *e–ph* mean free path becomes $0.7\,\mu$m.

Assuming that electron momentum and phase relaxation lengths L_m and L_φ are dominated by *e–ph* and *e–e* interactions respectively [1] these results yield a momentum relaxation length $L_m = [3^{-1/2}\, v_F\, \tau_{e-ph}]$ of $0.4\,\mu$m and a phase relaxation length L_φ of 115 nm. In the presence of other momentum or phase changing scattering events these relaxation lengths give an upper limit for the respective processes.

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