Influence of excited electron lifetimes on the electronic structure of carbon nanotubes

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We have studied the dynamics of electrons in single wall carbon nanotubes using femtosecond time-resolved photoemission. The lifetime of electrons excited to the $\pi^*$ bands is found to decrease continuously from 130 fs at 0.2 eV down to less than 20 fs at energies above 1.5 eV with respect to the Fermi level. This should lead to a significant lifetime–induced broadening of the characteristic van Hove singularities in the nanotube DOS.

1. Introduction

The unique electronic and mechanical properties of carbon nanotubes have stimulated considerable interest in these materials with their possible applications as nano–electronic devices or in new composite materials [1,2]. One of the outstanding features of individual single wall carbon nanotubes (SWNTs) is their quasi one–dimensional (1D) band–structure which can be derived by zone folding the two–dimensional band–structure of graphene onto the 1D Brillouin zone of the tubes [1]. The nanotube density of states (DOS) then exhibits a series of characteristic van Hove singularities (VHS) that diverge like $E^{-1/2}$. Recent experiments using scanning tunneling spectroscopy to study the electronic structure of SWNTs were indeed able to resolve features in the tunneling spectra that are characteristic for 1D van Hove singularities [3,4]. The width and position of these features, however, is modified with respect to the results from idealized tight binding calculations. It is generally accepted that interactions of the nanotubes with their environment, e.g. tube–tube and tube–substrate interactions, will lead to a deviation from 1D behaviour and will induce modifications in the SWNT band structure. The scattering of electrons with phonons or other electrons will also modify the 1D band structure and transport properties of SWNTs. Such scattering processes result in a finite lifetime of excited electrons which will be investigated here. The observed short electron lifetimes are expected to lead to a broadening of VHS. Other effects contributing to a shift and broadening of features in the nanotube DOS are curvature–induced $\sigma$–$\pi$ hybridization [5] and bond disorder [6]. Knowledge of the influence of different effects for changes of the electronic structure, therefore, appears to be crucial for the understanding of the spectroscopy of SWNTs.

Here we present the first time–domain study of electronic excitations in SWNTs using femtosecond time–resolved photoemission. We have studied the room temperature electron dynamics at energies between -0.1 eV and 2.3 eV with respect to the Fermi level — a region which is of considerable interest in tunneling spectroscopy but of which only a fraction is accessible by conventional transport studies. The measured electron lifetimes should contribute significantly to the broadening of VHS in the nanotube DOS. We discuss the implications of these results for the spectroscopy of SWNTs.

2. Experimental

Single–wall carbon nanotube samples used in this study are made from as–produced soot and from commercial nanotube suspension (tubes@rice, Houston, Texas) with similar results for both types of samples. The as–produced soot is pressed mildly between two glass slides with
a pressure of about 6 kg cm\(^{-2}\) to form a mat of entangled nanotube ropes. The commercial nanotube suspension, containing SWNTs whose diameter distribution is sharply peaked at 12 Å, is used to fabricate bucky paper samples according to the procedure described in reference [8]. The chiral wrapping angle which also plays a crucial role for the electronic structure was recently found to vary widely [3,4] leading to a mixture of conducting and semiconducting tubes within these samples. The samples are attached to a tantalum block which can be resistively heated up to 1200°C. They are outgassed thoroughly by repeated heating and annealing cycles under ultra high vacuum conditions. Photoelectron spectra are obtained by means of the time of flight technique with an energy resolution of \(\approx 10\) meV. The visible pump pulses with a photon energy of typically 2.32 eV are focused onto the sample nearly collinearly together with the frequency doubled UV probe pulses (pulse width 85 fs). The beam waist at the sample position is 50 μm in diameter. More details about the experimental setup can be found in reference [9]. The experiments were performed on a number of samples and on different spots on each sample to ensure reproducibility of the data.

3. Results and discussion

The visible–pump UV–probe scheme employed in our experiments is illustrated schematically in Fig. 1 (for a review of the time–resolved photoemission technique see reference [10]). The pump pulse initially excites electrons from the occupied \(\pi\) bands to some intermediate state of the unoccupied \(\pi^*\) bands above the Fermi level. The electrons then lose energy by various scattering processes and relax towards the Fermi level. After a well defined time–delay a second UV probe pulse photoemits electrons into the vacuum where they are detected energy selectively. If the photoemission signal at a certain energy is recorded as a function of the time–delay we obtain cross–correlation traces which directly reflect the electron dynamics. The intermediate state energy of the probed electrons \((E - E_F)\) is calculated from the electron kinetic energy \(E_{kin}\) via the relation \((E - E_F) = E_{kin} + e\Phi - h\nu_{probe}\), where \(e\Phi = 4.52 \pm 0.05\) eV is the sample work–function.

The 2PPE spectrum also shown in Fig. 1 does not exhibit any signs of the VHS characteristic for the band structure of SWNTs. We attribute this to a combination of effects: a) The width of the diameter distribution of nanotubes in the sample gives rise to VHS at different energetic positions in the corresponding density of states. b) Tube–tube interactions may lead to a broadening of features in the DOS. Calculations by different authors indicate that tube-tube interactions may cause a band splitting of 0.1 eV to 0.5 eV for
nanotube arrays [11–13]. c) Most importantly it needs to be considered that — unlike optical absorption [14] or EELS [15] measurements — photoemission is very sensitive to the position of the band structure with respect to the vacuum level. Shifts in the alignment of the band structure can be induced by charge transfer between different tube species (‘self–doping’). In particular the latter effect should contribute to the smearing of VHS beyond recognition in our 2PPE spectra and indicates the presence of tube–tube interactions. Here, we take advantage of one of the particular strengths of time–resolved techniques: they allow to study the dynamics in systems with inhomogeneously broadened or heavily congested spectra.

![Figure 2](image.png)

**Figure 2.** Cross–correlation traces for various intermediate state energies. The electron dynamics are obtained from the exponential decay of the correlated signal.

A typical cross-correlation trace recorded with a narrow energy pass of about 50 meV are shown in Fig. 2 for various intermediate state energies. The cross-correlations can be fit with a single exponential decay except for intermediate state energies close to the Fermi level where we also find a small contribution from a slower component which decays on the picosecond time–scale. The slow decay is attributed to the cooling of the laser heated electron gas after the initial fast electron dynamics have lead to a thermalization of the excited electron distribution and will be discussed elsewhere [16]. The decay–time of the fast component can be seen to increase continuously as the intermediate state energy approaches the Fermi–level (see Fig. 3).

![Figure 3](image.png)

**Figure 3.** Relaxation time obtained from the exponential fit to cross–correlations for various intermediate state energies. The corresponding lifetime broadening is given on the right axis. This fast decay may be attributed to electron–electron interactions and decreases continuously to less than 20 fs at energies above 1.5 eV. The dashed line is an empirical fit to the higher energy data and is used for the computation of the lifetime broadened spectra in Fig. 4.

The detailed kinetics of the electron relaxation involves the decay from a particular exited state as well as the filling of the same state by electrons which themselves decay from higher lying states. The refilling becomes more important at energies close to the Fermi level and leads to an...
overestimation of the electron lifetimes by the corresponding cross-correlation decay. However, an estimate of the influence of such secondary electron cascades on the 2PPE signal reveals that the actual lifetime at 0.2 eV above the Fermi level is at most 20% shorter than the measured decay time [17]. We, therefore, assume that the influence of secondary electron cascades on the measured decay times at energies above about 0.2 eV represents a minor correction to the actual lifetimes. Irrespective of the magnitude of the effect, however, the measured decay times used to estimate the lifetime–induced broadening of VHS should give a lower bound for the actual broadening.

A qualitatively similar behaviour is also observed in simple metals where the electron lifetime ideally increases with $(E - E_F)^{-2}$ due to phase space limitations for scattering events near the Fermi level (Fermi–liquid behavior) [10,18]. In ideal one-dimensional systems the energy dependence of the electron lifetimes is expected to be proportional to $(E - E_F)^n$ with $n = 1$ [19]. In our study the energy dependence of the cross-correlation decay $\tau$ (at energies above 0.5 eV) can best be approximated by the empirical function $\tau = [30((E - E_F)/eV)^{−1.5} + 4] \text{fs}$. We note, however, that the energy dependence of electron lifetimes should only be used to draw conclusions with respect to the character of the system — e.g. Luttinger–liquid vs Fermi–liquid — in combination with ab initio studies that account for all band structure effects including the interaction with the nanotube environment. Recent calculations of the electron dynamics in aluminum, for example, revealed that band structure effects can lead to a substantial deviation of electron lifetimes from the Fermi–liquid predictions [20,21] in spite of the fact that aluminum is generally considered to be a nearly ideal free electron gas. In addition we note that the electron lifetimes in 2-D graphite are also expected to scale with an exponent $n$ close to unity [22].

The short decay–times observed here suggest that the fast energy relaxation dynamics in nanotubes is likely due to electron–electron ($e$–$e$) scattering in analogy to recent experimental studies and calculations on $e$–$e$ interactions in graphite [22]. Electron–phonon ($e$–$ph$) scattering is expected to be much slower and would provide less efficient energy transfer for the scattering electrons [24].

These finite electron lifetimes lead to a modification of electronic spectra with respect to the spectra expected for an isolated, non–interacting system. We illustrate the effect this has on the electronic structure of carbon nanotubes by convoluting the tight binding density of states $N(E)$ with a Lorentzian of energy dependent width $\Gamma(E)$ (see Fig. 4). The energy dependence of the line–width is obtained from the empirical fit to graphite [22].

Figure 4. Influence of the electron lifetime on the calculated nanotube DOS for the metallic (13, 7) and the semiconducting (10, 8) species. The upper curve of each pair of traces gives the DOS obtained from tight binding calculations while the lower traces are obtained by a convolution of that DOS with an energy dependent Lorentzian. The van Hove singularities are seen to be increasingly broadened at higher energies due to the strong decrease of the electron lifetime with energy.
the lifetimes $\tau$ in Fig. 3 according to $\Gamma = \hbar/\tau$, where we assume identical lifetimes for electron and hole excitations. Note that the observed decrease of the lifetime to $\approx 20$ fs at an energy of 1.5 eV leads to a broadening of features in the SWNT DOS of 30 meV. At still higher energies this presents only a lower limit to the expected lifetime broadening as given by the time resolution of these experiments. In Fig. 4 we show the results of this convolution for the metallic (13,7) tube (recently identified by tunneling spectroscopy [1]) and the semiconducting (10,8) tube. The density of states for the $\pi$ and $\pi^*$ derived bands was obtained in the usual way by zone folding the 2D graphite band structure into the 1D Brillouin zone of the nanotubes with a nearest neighbor overlap integral $\gamma_0$ of 2.5 eV. It is evident that the influence of the electron lifetime on the shape of the VHS in the DOS becomes more pronounced at higher energies and may even lead to the coalescence of VHS. The magnitude of this effect is about a factor of 2–10 smaller than the band splitting calculated for nanotube arrays [13], but should still give a significant contribution to the electronic spectra in particular at higher electron energies.

Another interesting aspect of this study is that we do not observe any slow decay that can be assigned to carrier recombination processes across the band gap of semiconducting tubes, despite the abundance of such tubes in these samples. Interband recombination is generally expected to be quite slow like in C$_{60}$ films (30 ps–40 ps) [23] or in silicon where recombination occurs on the ns time-scale [24]. We take the absence of such a slow channel as further evidence that tube–tube interactions are sufficiently strong to induce charge transfer between semiconducting and metallic tubes on a time-scale comparable to or faster than the observed decay. Actually the lifetimes found here are qualitatively similar to results obtained for highly oriented pyrolytic graphite where the decay is found to be about a factor of 1.5–2 slower than in the nanotube samples [16]. Note that tube–tube interactions which lead to only 50 meV band–shift or splitting would already allow charge transfer between tubes within $\hbar/50$ meV $\approx 13$ fs. Charge transfer between different tube types may also be enhanced by scattering from static or dynamic lattice distortions. Also note that the aforementioned slow channel from the cooling dynamics cannot be assigned to the semiconducting species since it only contributes to the 2PPE signal at energies below about 0.3 eV where no significant photoemission is expected from semiconducting tubes in these samples (the average band–gap is about 0.55 eV).

Electron–electron scattering may provide an important mechanism for electron phase relaxation — in particular in low temperature transport studies. If compared with calculated $e$–$ph$ scattering times of about 1.4 ps [24] the short electron lifetimes observed in this study suggest that $e$–$e$ scattering may dominate phase relaxation even at room temperature if electron energies of a few hundred meV above the Fermi level are considered. The corresponding phase relaxation lengths can be estimated from the data of Fig. 3. This yields the energy dependence of the $e$–$e$ contribution to the phase relaxation length $L_\varphi = \left[3^{-1/2} \nu_F \tau_{e-e} \right]$ which increases from less than 10 nm at energies above 1.5 eV up to about 60 nm at an energy of 0.2 eV ($\nu_F = 8 \times 10^5$ m s$^{-1}$, [1]). We note that at energies below about 0.2 eV $e$–$e$ scattering times cannot be determined unambiguously from these experiments because a combination of $e$–$ph$ scattering and electron cascade effects makes the interpretation of the data more difficult.

In summary, we have characterized the energy dependence of the electron energy relaxation time and illustrated the consequences for the electronic structure of SWNTs. The continuous decrease of the electron lifetime to less than 20 fs at energies above 1.5 eV with respect to the Fermi level should lead to a significant broadening of the VHS in the nanotube DOS. These findings should help to analyze spectra from carbon nanotubes with respect to different contributions from various line–broadening mechanisms. In order to predict the influence of the finite electron lifetime on spectral features at higher energies it is desirable to obtain data with higher time–resolution than in the present study. Ideally, phase–controlled measurements may provide very detailed infor-
mation on electron decoherence [27]. Our studies furthermore indicate that tube–tube interactions in nanotube ropes are strong enough to lead to electron transfer between neighboring metallic and semiconducting tubes on the sub–picosecond time–scale.

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