Electronic Excitations and Dynamics in Carbon Nanotubes Induced by Femtosecond Pump-Probe LASER Pulses

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We have continued our efforts in the J. R. Macdonald Laboratory directed toward the study of electronic excitations and dynamics in carbon nanotubes excited by femtosecond pump-probe laser pulses generated by the ultra-fast Ti:Sapphire Kansas Light Source, KLS. We use time-of-flight of electrons emitted from carbon nanotubes to deduce the energy and temporal behavior of the electronic states of the nanotubes. Experiments have been performed on multiwalled carbon nanotubes, MWNT, and more recently on both double walled carbon nanotubes, DWNT, and single walled carbon nanotubes, SWNT.

MWNT: Quasi-ballistic transport of charge carriers in multi walled carbon nanotubes. *M. Zamkov, A. Alnaser, N. Woody, S. Bing, Z. Chang, and P. Richard*

Our initial motivation for studying carbon nanotubes was to search for the Rydberg-like tubular image potential states in carbon SWNT predicted by the Harvard group of Granger, Kral and Sadgepour (PRL **89**, 135506 (2002)). These interesting and unique states have a tubular presence surrounding the nanotube cylinder. The term "tubular image states" are reserved for the high angular momentum states that are bound at large distances from the surface in a shallow well formed by the combination of the image attraction and the angular momentum barrier. Following the ideas of Granger et al, we calculated the energy spectra of circular image potential states as well as tubular image potential states for both SWNT and MWNT. The "circular image states" are the more tightly bound low angular momentum states which have similar spatial profiles to the tubular states Our predictions (Publication #1) demonstrated that the energetics of electron emission were more favorable for observing circular image potential states in MWNT than for tubular states in SWNT. We observed the excitation energies and lifetimes of the circular states produced around MWNT (Publication#2) and reported the results last year in the AMOS research meeting - **Time–resolved photo imaging of image–potential states in carbon nanotubes** *Experimental Group: M. Zamkov, N. Woody, B Shan, Z. Chang, and P. Richard Theory Group: H.S. Chakraborty and U. Thumm.*

The second phase of the research on MWNT involves the study of the charge carriers in MWNT. The image potential states are formed by pumping the MWNT with the third harmonic (4.71 eV) of the KLS laser beam and probing the states with the primary beam (1.57 eV), see top schematic in Fig. 1. We are able to study the charge carriers in the nanotubes by reversing the role of the pump and probe. The excited image potential states can be seen in the upper end of the electron time of flight spectrum in Fig. 1b whereas the excitation of the charge carriers can be seen at the lower end of the spectrum. The image potential spectrum is the difference between the pump-probe and pump spectra whereas

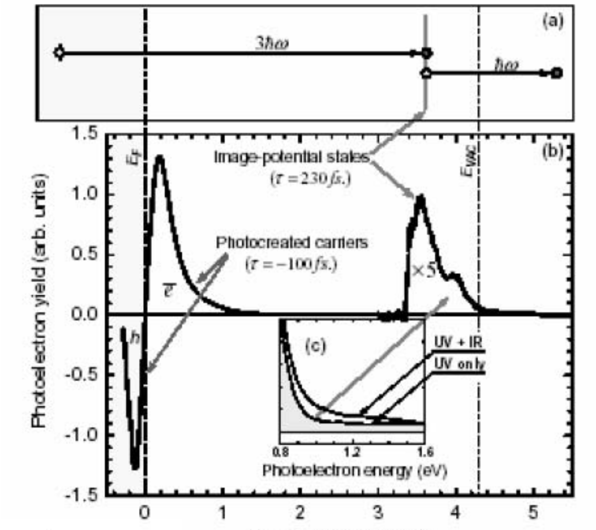

Figure 1

the carrier spectrum is the difference between the pump-probe and probe spectra. The bipolar shape of the charge carrier difference spectrum is characteristic of the hole and the promoted electron as seen by the probe pulse. The lifetimes of the excited electrons is probed by the delay between the pump and probe just as in the case of the study of the image potential states. Lifetime plots show a two component curve. The fast part of the decay curve is due to the e-e interactions and the slow decay is due to e-phonon interactions, as published (Publication #3) and reported last year in the AMOS research meeting **-Lifetime of Charge Carriers in Multi-walled Nanotubes** *M. Zamkov, N. Woody, B Shan, Z. Chang, and P. Richard*. We observed that the e-e decay curves were in the range of 200 to 700 fs and followed a $(E\text{-}E_F)^{-n}$ with $n \approx 2.07\pm0.1$ behavior which is consistent with a two or three dimensional Fermi-liquid behavior as opposed to a one-dimensional Luttinger Liquid behavior as was observed for SWNT.

The final phase of our study of MWNT is the investigation of the long lived e-ph interaction, which brings us to the subject of quasi-ballistic transport of charge carriers in multi-walled carbon nanotubes. The basic idea in this experiment is that the time of flight difference spectra can be fit to the difference in a Fermi-Dirac, FD, distribution at some intermediate cooling temperature to that at room temperature. The effect of the laser pump-pulse is to promote the electrons into the conduction band and thus increase the thermal energy of the electronic system. In this case the thermal equilibrium between the unperturbed lattice and the excited carriers will be realized by the energy exchange through e-ph coupling. By fitting the data to

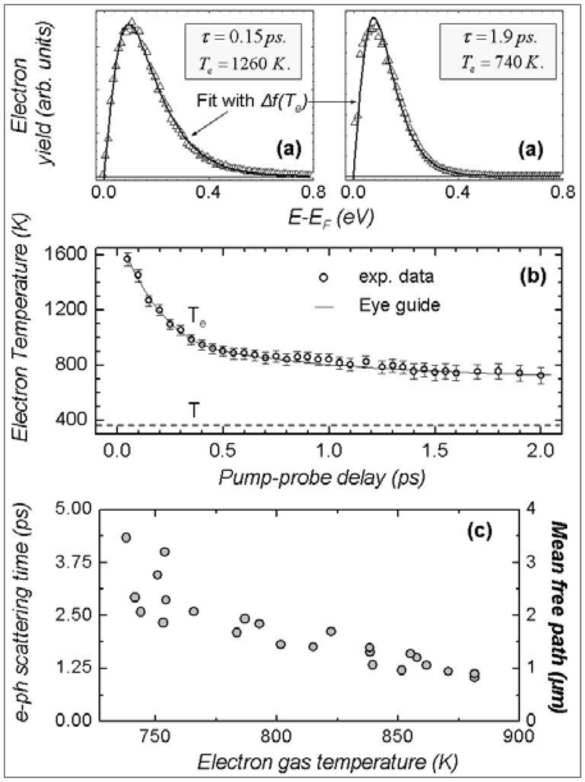

Figure 2

the non equilibrium minus the equilibrium FD calculation, we can determine the temperature T_e of the system for every delay τ (see upper panel in Fig. 2). We then use the two temperature model (TTM) adapted to the case of carbon nanotubes by Hertel and Moos PRL **84**, 5002(2000) to the e-ph decay rate $\tau_{e-ph}(T_e) = \tau_E(T_e) \times A \times \frac{1-(T/T_e)^2}{1-(T/T_e)^5}$, where A = 0.9534. The resulting e-ph scattering times, obtained within the thermalization approach, are shown in Figure 2(c) along with the associated electron mean-free paths. The latter is found to be within 0.8 and 4 μm, which agrees well with the range of *l* inferred from the direct measurements of τ_{e-ph}. This agreement provides additional support to the fact that a collision-free distance for an electron in a MWNT is comparable to the nanotube length. In particular, close to the Fermi level, where the electron mean-free path extends up to 3-4 μm, the charge transport is believed to be ballistic. The result of this work has recently been submitted for publication (see Publication # 4).

DWNT: Do the charge carriers in DWNT behave as a Fermi-Liquid as observed in MWNT or as a Luttinger Liquid as reported for SWNT? *I. Chatzakis, A. Habib, M. Zamkov, and P. Richard*

We have undertaken the task of measuring the lifetimes of the charge carries (Fermi-Dirac type?) and the electron mean free path (ballistic motion?) in DWNT. The first efforts in this project were to use DWNT formed on a plastic backing. These targets are known to form nanotubes in ropes, which is not ideal for this experiment. We have, however, recently obtained isolated DWNT in the form of "bucky" paper from NanoLab Inc, Newton, MA. These are isolated nanotubes of a similar form to those used in our MWNT work reported above. The apparatus for this experiment is presently being moved out of the KLS lab into an isolated laser hutch serviced by a laser beam transport. This move is necessitated due to the interference of this experiment with the work on development and use of the carrier envelope phase locking. Preliminary results have been obtained using the original targets, but we have no results using the new targets. We anticipate that our apparatus move to the new hutch will be complete at the end of August and that the experiment will be running during the fall 2007.

SWNT: Exciton Dynamics in Bundles of Single Walled Carbon Nanotubes. *Mikhail Zamkov, Ali S. Alnaser, Bing Shan, Zenghu Chang, and Patrick Richard*

Systems exhibiting one-dimensional (1D) electron confinement have long fascinated scientists due to their unusual electrical and optical properties. The microscopic origin underlying this behavior is the significant enhancement in the Coulomb interaction that only permits collective multi-particle excitations, which leads to the formation of strongly correlated electron-hole (*e-h*) pairs, known as excitons. Semiconductive SWNT are one of the most interesting representations of such systems where the excitonic nature of optical excitations was manifested by the emission of fluorescence (FL) arising from the recombination of bound *e-h* pairs. FL emission in SWNT, however, can be observed only when a nanotube is isolated from its environment by encapsulating in a SDS micelle. On the other hand, when their natural surroundings are not chemically suppressed, smooth-sided SWNT readily aggregate into bundles, in which case no FL signal is detected. The quenching of optical emission poses considerable experimental challenges for studying the dynamics of excitons in interacting SWNT, raising a question if strongly bound *e-h* pairs even exist in nanotube bundles. According to several experimental reports the intertube interaction in aggregated SWNT unlocks the carrier tunneling ability and, could, in principal, wipe out the reduced dimensionality of *e-h* excitations. In this case, some basic photoelectrical properties of bundled SWNT such as the carrier photogeneration and the spatial separation of opposite charges would be substantially different from those of isolated nanotubes. Resolving these issues, for the most part, depends on our ability to probe the character of optical excitations in non-fluorescing bundles, favoring an experimental approach that does not rely on FL emission.

Therefore in this work we have turned our attention to SWNT. Sample production of nanotubes, at best, isolates single wall, double wall and sets of multi-wall nanotubes. In each of these types of samples a distribution of nanotubes diameters is produced as well as a mixture of semi-conductive (***S***) and metallic (***M***) nanotubes. In some processes the nanotube samples are free standing, some form bundles of nanotubes , and in some processes they are created in a dielectric environment such as in a micelle-suspension or in an aqueous solution.

In this study time-resolved photoemission was used to differentiate between excitons and free carriers in non-fluorescing bundles of SWNT. In summary, by monitoring the electron emission from non-fluorescing nanotube bundles, we have demonstrated that the primary excitations in aggregated *S* SWNTs are strongly bound excitons. In particular, our findings indicate that the van-der-Waal forces between the interacting nanotubes do not destroy the 1D character of optical excitations. We also show that the excitonic stability against non-radiative annihilation in bundles could be weakened due to robust tunneling of carriers from *M* into *S* nanotubes. This intertube charge exchange may play a decisive role in lowering the quantum efficiency for fluorescence emission in aggregated SWNTs and will merit further investigation. First results of this work are being submitted for publication.

Publication # 1**: Image Potential States of single- and multi-walled Carbon Nanotubes**, M. Zamkov, N. Woody, B. Shan, H. S. Chakraborty, Z. Chang, U. Thumm, and P. Richard, Phys. Rev. B **70,** 115419 (2004).

Publication # 2**: Time-Resolved Photoemission of Image-Potential States in Carbon Nanotubes**, M. Zamkov, N. Woody, B. Shan, H. Chakraborty, Z. Chang, U. Thumm, and P. Richard, Phys. Rev. Lett. **93,** 156803 (2004).

Publication # 3**: Lifetime of Charge Carriers in Multi-walled Nanotubes** M. Zamkov, N. Woody, B. Shan, Z. Chang and P. Richard, Phys. Rev. Lett. **94,** 056803 (2005).

Publication # 4: **Quasi-ballistic transport of charge carriers in multi walled carbon nanotubes.** M. Zamkov, A. Alnaser, N. Woody, S. Bing, Z. Chang, and P. Richard, submitted for publication.

Publication # 5: **Exciton Dynamics in Bundles of Single Walled Carbon Nanotubes**.*Mikhail Zamkov, Ali S. Alnaser, Bing Shan, Zenghu Chang, and Patrick Richard* submitted for publication.