

Stability of High-Density One-Dimensional Excitons in Carbon Nanotubes under High Laser Excitation

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(Received 30 August 2004; published 8 March 2005)

Through ultrafast pump-probe spectroscopy with intense pump pulses and a wide continuum probe, we show that interband exciton peaks in single-walled carbon nanotubes (SWNTs) are extremely stable under high laser excitations. Estimates of the initial densities of excitons from the excitation conditions, combined with recent theoretical calculations of exciton Bohr radii for SWNTs, suggest that their positions do not change at all even near the Mott density. In addition, we found that the presence of lowest-subband excitons broadens all absorption peaks, including those in the second-subband range, which provides a consistent explanation for the complex spectral dependence of pump-probe signals reported for SWNTs.

DOI: 10.1103/PhysRevLett.94.097401

PACS numbers: 78.47.+p, 73.22.-f, 78.67.Ch

Optically excited electron-hole (e - h) pairs in a semiconductor provide a rich system for the study of carrier interaction effects. Depending on the density, they exhibit qualitatively different spectral features of bound and unbound carriers. Excitons (or bound e - h pairs) are stable when the Bohr radius is much smaller than the interexciton distance. As the former approaches the latter, the Mott transition [1] is expected to occur, transforming the insulating excitonic gas into a metallic e - h plasma. This scenario is complicated in real systems by other interaction effects, such as band gap renormalization (BGR) and biexcitonic correlations. In addition, optical gain develops and coherent processes can dominate the emission spectra. There have been a number of studies on highly excited 3D and 2D semiconductor systems [2,3].

1D excitons are expected to be different: the exciton binding energy in an ideal 1D system is infinite [4], the 1D Sommerfeld factor is less than 1 [5], and radiative lifetimes are intrinsically longer [6]. High-density excitons in semiconductor quantum wires [7–11] have exhibited a range of novel (and conflicting) results regarding gain, BGR, and Mott transitions. The magnitude of 1D BGR is still under debate, but it appears to be a common observation that 1D excitons are stable up to very high densities [8–10]. This stability, while good for device applications, is not fully understood, and the density at which gain should appear is a subject of controversy [12].

Excitons in carbon nanotubes can provide new insight into these long-standing issues. With much smaller diameters (and thus larger subband separations and binding energies), these excitons should allow one to study high-density regimes without having to take into account the population of higher subbands. Since the success of preparing individually suspended single-walled carbon nano-

tubes (SWNTs) [13,14], their optical properties have been intensively studied. While theoretical understanding of linear optical properties is progressing [15–20], their non-linear optical properties, especially under high excitations, remain unexplored. Recent time-resolved studies on bundled [21,22] and unbundled [23–27] SWNTs have raised an array of questions on the origin of nonradiative recombination and the values of intrinsic radiative lifetimes. In particular, strongly wavelength-dependent non-degenerate pump-probe data [21,22,24] have produced differing interpretations.

In this Letter, we report results of nondegenerate pump-probe spectroscopy with a strong pump beam and a white-light continuum probe. From excitation conditions we estimated the initial pair density to be $\sim 5 \times 10^6 \text{ cm}^{-1}$. This, combined with recent calculations of the Bohr radius (2–5 nm) [17–19], indicates that the initial density is comparable to the Mott density. However, the band edge absorption peaks were very stable, their positions showing no variation with time (i.e., density), similar to the observations in quantum wires [8–10]. Furthermore, we found that there are long lived (up to ~ 100 ps) pump-probe signals in the second-subband transition range, even though there are no real carriers left in the second subband. Through spectral analysis we concluded that the absorption peaks are broadened by the excitons present in the first subbands. This result provides a new and consistent scenario for the complex pump-probe dynamics.

The samples used in our experiments were micelle suspended in D_2O , which showed a number of chirality-dependent peaks in photoluminescence (PL) and absorption [13]. The first (E_{11}) and second (E_{22}) subband transition energies were determined through PL excitation spectroscopy. They possess long pump-probe decay times,

especially when excited resonantly [23]. Similar lifetimes have been reported using time-resolved PL measurements [24–26], indicating that these long lifetimes are related to radiative interband recombination.

We used an optical parametric amplifier (OPA) pumped by a chirped-pulse amplifier (CPA-2010, Clark-MXR, Inc.) that produced 150-fs pulses at 1 kHz. As a pump, either the OPA beam covering 0.07–2.5 eV or the CPA beam (1.6 eV or 775 nm) was used. Pump fluences up to ~ 1 mJ/cm² were used. As a probe, we used a white-light continuum generated by focusing a small portion of the CPA beam onto a sapphire crystal, covering wavelengths from the visible to the infrared. Both beams were focused onto a 5-mm thick sample cell with pump and probe diameters of 1 and 0.8 mm, respectively. After passing through the sample, the probe was spectrally resolved with a monochromator and detected by an InGaAs photodiode. Chirp in the probe was measured through a second harmonic generation technique, and it was taken into account in all data analysis. The pulse width of the probe (i.e., the temporal resolution of the setup) was 270 fs. To detect the small change in probe transmission ΔT , we synchronously chopped the pump beam at 500 Hz, which blocked every other pump pulses. The probe pulse train was then sampled in a box car integrator that electronically inverted every other signals. A computer then collected the pulses and separated them to extract pump influenced (T) and non-influenced transmission (T_0).

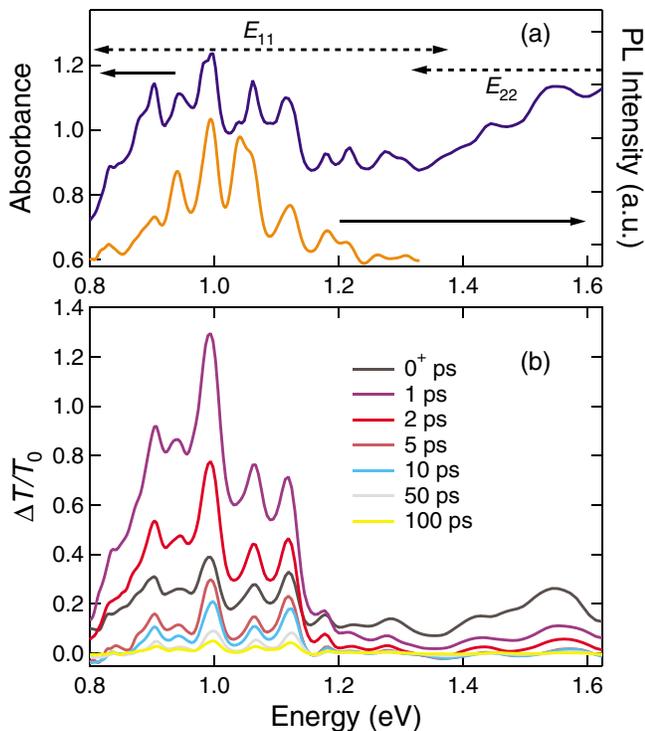


FIG. 1 (color). (a) Linear absorption (blue line, left axis) and PL (red line, right axis) spectra. The PL was taken with cw 1.6 eV (775 nm) excitation. (b) Chirp corrected differential transmission spectra for various time delays.

Absorption and PL spectra are shown in Fig. 1(a). The PL was excited by cw 775 nm radiation. Differential transmission spectra with a 775 nm pump are shown in Fig. 1(b) for different time delays. At 0 ps, positive ΔT exists both in the E_{11} and E_{22} ranges. However, during the first 1 ps, the signal in the E_{11} range rapidly increases at the expense of the signal in the E_{22} range, indicating a fast intraband (i.e., intersubband) carrier decay. At subsequent time delays, the overall shape of the spectra remains the same, and the amplitude decays slowly.

The evolution of absorbance, obtained from differential transmission, is shown in Fig. 2(a). Absorbance quenching up to $\sim 30\%$ is seen at 1 ps, but it recovers as time progresses. At 100 ps, the absorbance spectrum coincides with that taken at negative time delays, indicating that a majority of carriers have already recombined. The inset shows the estimated pair density versus time, normalized to the value at 1 ps. The density at each time delay was deduced from the amount of spectrally integrated absorp-

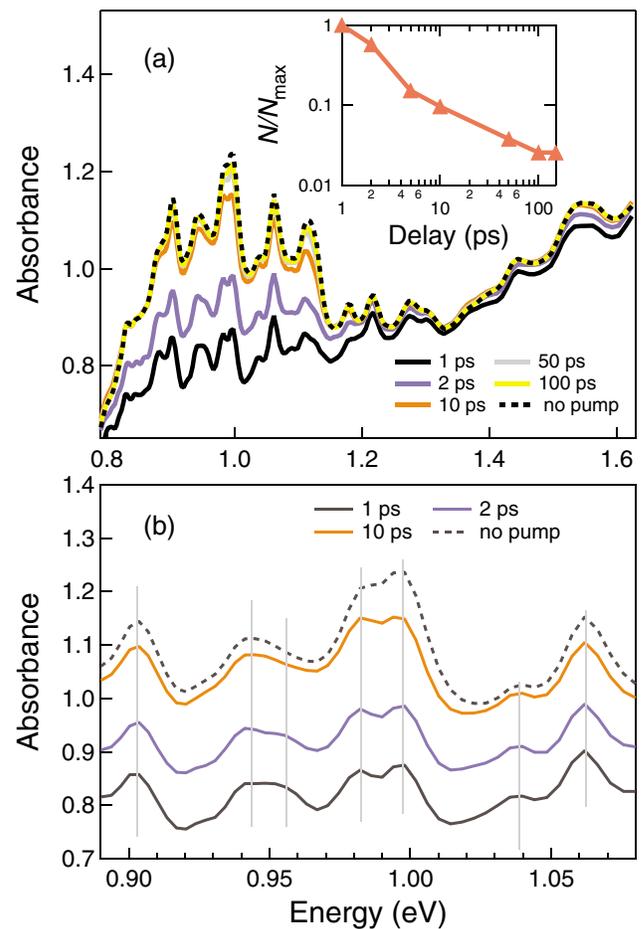


FIG. 2 (color). (a) Absorbance spectra at different time delays, reconstructed from the differential transmission data in Fig. 1. The inset shows the time decay of the normalized $e-h$ pair density, obtained by spectrally integrating the absorbance change at each time delay. (b) Absorbance spectra within the first subband range at different time delays, showing that exciton peaks do not shift.

tion change. Figure 2(b) shows an expanded view in the 0.9–1.1 eV range. It is seen that the *absorption peak positions do not change at all with time, i.e., with density.*

We also found that the presence of first subband excitons modifies the absorption in the second subband. Figure 3(a) shows $\Delta T/T_0$ as a function of probe energy, mostly in the second-subband range. This continuous probing reveals previously unobserved *oscillatory behavior.* Especially after 1 ps, when all carriers have decayed into the first subband, the *sign of ΔT sensitively depends on the probe energy.* Positive ΔT (i.e., absorption bleaching) is located mostly around absorption peaks, while negative ΔT (i.e., photoinduced absorption) exists in the vicinity of absorption dips. Examples of $\Delta T/T_0$ versus time delay for selected probe energies are shown in Fig. 3(b).

The density of photoexcited *e-h* pairs (n_X) was estimated as follows. For typical 1-nm-diameter nanotubes that are abundant in the sample [say, (8, 7) tubes], the linear mass density is calculated to be 2.4×10^{-11} mg/cm. This, combined with the mass density (52.4 mg/l from linear absorption with Beer's law) and the average tube length

(150 nm from atomic force microscopy), provides 5.7×10^{11} as the total number of tubes within the pump-excited volume (3.9 mm^3). The number of absorbed photons (and thus created *e-h* pairs) in the same volume is estimated to be 4.26×10^{13} from the nonlinear absorbance (1.043 at 0 ps for 1.6 eV) and the pump energy ($12 \mu\text{J}$). These numbers yield $n_X \approx 5 \times 10^6 \text{ cm}^{-1}$ (or an average separation of ~ 2 nm). [Note that the average length (150 nm) cancels out and does not affect n_X .] A possible source of uncertainty in n_X is the existence of residual bundles, which can absorb the pump and make the estimated n_X larger. However, the clear appearance of peaks in absorption indicates that absorption from unbundled SWNTs is dominant. A possible error may also come from the neglect of scattering, but a recent study [28] indicates that scattering is of small importance for low repetition-rate femto-second pulses. Finally, we did not take into account any contribution of two-photon absorption, which should lead to the creation of *e-h* pairs at 3.2 eV, mostly in metallic nanotubes, and thus reduce the pair density in semiconductor nanotubes.

Recent theoretical calculations using different methods [17–19] have reported 2–5 nm for the Bohr radii (a_B^*) of excitons in SWNTs with a ~ 1 nm diameter. This suggests that $r_s = n_X a_B^* \sim 1$. Namely, right after they are created by the pump pulse, the exciton density is similar to the 1D Mott density. Since the photoinduced carrier density decays to almost zero in ~ 200 ps, this translates that we are monitoring the behavior of exciton peaks in a widely varying density range, going from the initial high-density regime to the final dilute limit. Nonetheless, the observed absorption peaks are very stable in position. This stability is similar to what has been observed in high-quality GaAs quantum wires [8–10], implying a unique nature of excitons in 1D systems.

Previous pump-probe spectroscopy studies on bundled nanotubes [21,22] exhibited similar probe-energy-dependent bleaching and absorption behaviors, but different mechanisms were proposed. Lauret *et al.* [21] created carriers in the first subband and observed increased absorption at selected probe energies, which was interpreted as a redshift of the “plasmon” absorption peak. Korovyanko *et al.* [22] explored various probe energies and concluded that a global redshift is not a consistent picture to explain their data; instead they attributed the photoinduced absorption observed at some probe energies to excitonic intersubband transitions. Neither of the proposed mechanisms can explain our data. Since our sample consists of unbundled SWNTs that exhibit chirality-dependent peaks, we can readily see that we have no global redshift or photoinduced absorption peaks corresponding to intersubbandlike transitions.

We believe that the probe-energy-dependent sign of differential transmission can be consistently explained in terms of carrier-induced peak broadenings. Figure 4(a) depicts the idea, which is a simulation result based on three Lorentzian peaks. All three tube types are assumed

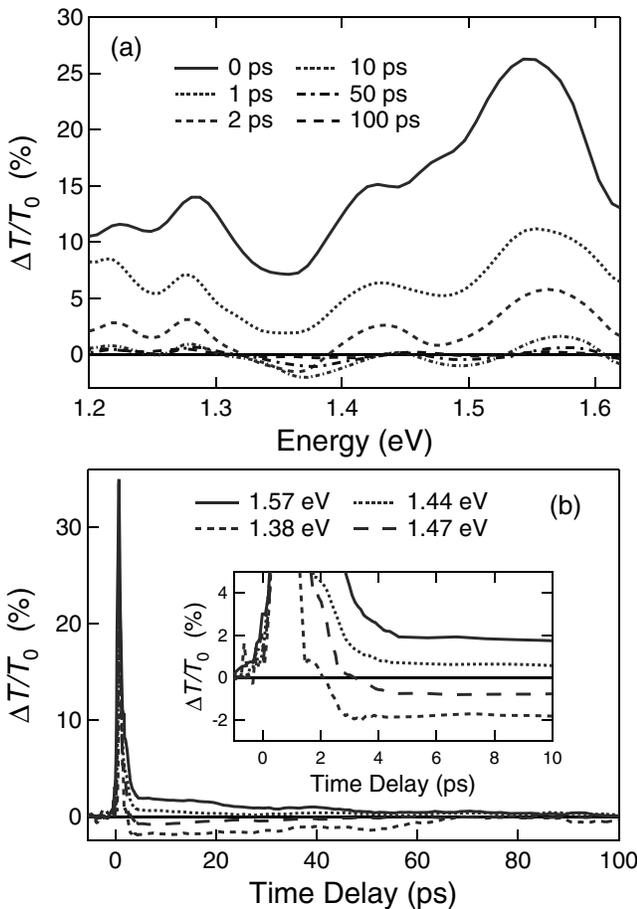


FIG. 3. (a) Differential transmission spectra at different time delays in the second-subband range. (b) Differential transmission dynamics at four different probe photon energies. At some probe photon energies the signal becomes negative (corresponding to absorption increase).

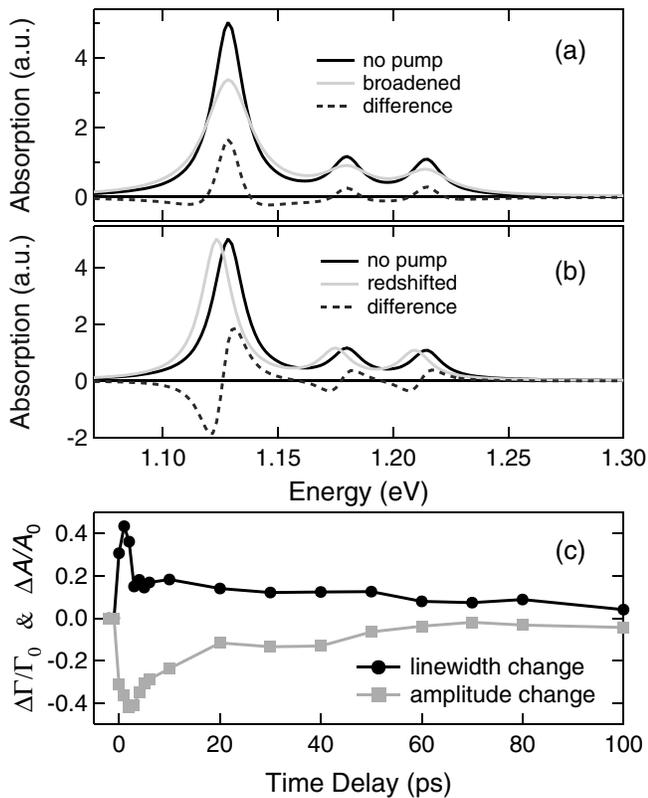


FIG. 4. Simulated differential absorption spectra for three closely lying lines with different amplitudes based on (a) line broadening and (b) a rigid redshift. (c) Obtained best fit Lorentzian parameters for the 1.17 eV absorption peak of (10, 2) nanotubes.

to have a half width at half maximum of 8 meV, and one of them is assumed to have a larger amplitude. It can be seen that the sign of pump-probe signal should show the observed oscillatory behavior. It can also be seen that the change of a small peak can be significantly influenced by a neighboring large peak. Figure 4(b) is a simulation result based on a global redshift; this model fails to explain any of the observed features.

To analyze the photoinduced broadening in more detail, we concentrated on (10, 2) tubes, which have an E_{11} peak reasonably separated from other tubes and is relatively weakly populated (i.e., the positive band filling signal is small). The evolution of the extracted Lorentzian parameters (peak amplitude $\Delta A/A_0$ and linewidth $\Delta\Gamma/\Gamma_0$) normalized to the negative delay values are shown in Fig. 4(c). Broadening and amplitude change basically follow the dynamics seen in $\Delta T/T_0$. The fact that the E_{22} peaks are broader implies that the lifetime or dephasing time is reduced for probe-created carriers in the second subband when carriers (or excitons) exist in the first subband. The most likely mechanism for the increased scattering rate is scattering between carriers in different subbands. This process is known to be important in quantum confined systems in general, and it has been shown that a carrier

in the second-subband and a carrier in the first subband can efficiently exchange momenta through this process [29].

In conclusion, we have performed nondegenerate pump-probe spectroscopy on micelle-suspended SWNTs and found (i) that interband exciton peaks are very stable even at very high densities and (ii) that second-subband absorption peaks are broadened by the excitons present in the first subbands, which provides a new and consistent explanation for the complex behavior of pump-probe signals reported for bundled and unbundled SWNTs.

We gratefully acknowledge support from the Robert A. Welch Foundation (Grant No. C-1509), the Texas Advanced Technology Program (Project No. 003604-0001-2001), and the National Science Foundation (Grants No. DMR-0134058 and No. DMR-0325474).

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