Femtosecond Photon Echo Spectroscopy of Semiconducting Single-Walled Carbon Nanotubes

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ABSTRACT

Three-pulse photon echo peak shift measurements were performed on semiconducting single-walled carbon nanotubes embedded in polymer matrix at room temperature. Simultaneous modeling of the peak shift data in the limit of zero-intensity and the linear absorption spectrum enable us to extract an intrinsic homogeneous line width of 178 cm⁻¹, an inhomogeneous width of 698 cm⁻¹, and a Huang–Rhys factor of 0.04 for the radial breathing mode vibration. The peak shift data when combined with two-pulse photon echo and pump–probe measurements allows us to determine a pure exciton dephasing time scale of 78 fs at room temperature.

Semiconducting single-walled carbon nanotubes (SWNTs) are one of most intriguing nanomaterials due to their large aspect ratios, size-tunable properties, and recent progress in fabrication and purification techniques.¹⁻³ The scope of optoelectronic applications for SWNTs depends critically on a detailed understanding of their underlying physical mechanisms, spectral features, and excited-state dynamics.⁴ Recent advances in the optical spectroscopy of semiconducting SWNTs have revealed specific spectral characteristics of structurally distinct tube species,⁵ the excitonic nature and binding energy of elementary excitations,⁶,⁷ and ultrafast dynamics at both the single tube and ensemble levels.⁸

One of the greatest challenges in the spectroscopic studies is the substantial heterogeneity in the samples currently available, which contain a variety of tube species with different indexes \((n, m)\). Besides metallic tubes, the samples typically contain variable amounts of semiconducting species with diameter distribution depending critically on the synthetic conditions.⁵,⁹⁻¹¹ Even for the same tube type, the length, curvature, defect, and surfactant wrapping can vary substantially from one tube to another. As a result, the frequency of a given excitonic transition varies accordingly, giving rise to significant inhomogeneous broadening of spectral lines. Assessment of the intrinsic, homogeneous line width is not possible from linear spectroscopic measurements of nanotube ensembles due to their inherent limitation in differentiating fast fluctuations of the transition frequencies (homogeneous broadening) from the static distributions (inhomogeneous broadening). Although such information should in principle be accessible by single tube spectroscopy, the reported results so far differ remarkably even for the same tube type, owing presumably to occurrence of defects,¹²,¹³ unintentional doping,¹⁴ and/or differences in tube environments.¹²,¹³

In this paper, we report an experimental study of the spectral line broadening of the lowest allowed excitonic transitions of semiconducting SWNTs by exploiting two femtosecond four-wave mixing (FWM) techniques. Application of three-pulse stimulated photon echo peak shift (3PEPS) spectroscopy¹⁵,¹⁶ enables a clear separation of the homogeneous and inhomogeneous broadening of the selected spectral line directly through measurements on nanotube ensembles and provides estimates of the strength and timescales electron–phonon coupling. A complimentary technique employing degenerate two-pulse FWM spectroscopy or two-pulse photon echo (2PE) allows for quantification of the time scale of exciton dephasing and independent determination of the corresponding homogeneous line width. Furthermore, transient grating (TG) and pump–probe (PP) spectroscopy permit measurement of exciton population relaxation dynamics under the excitation intensities used for 3PEPS and 2PE experiments, respectively.

The sample used for this study is a nanotube–polymer composite film of \(~200\ \mu m\) thickness. Use of such a sample greatly suppresses scattering arising from slow tube motion in an aqueous solution and enables measurement of photon echo signals at low excitation powers and long population times with a high signal-to-noise ratio. The starting material is a commercial D₂O suspension of the CoMoCAT nanotubes dispersed individually with surfactant sodium dodecyben-
Figure 1. (a) Linear absorption spectra of the SWNT/PVP composite film (solid line) and the D$_2$O solution of the NaDDBS dispersed SWNTs (dashed line), which was used to fabricate the SWNT/PVP film. The dotted line is the laser pulse spectrum. Both absorption spectra are normalized at the peaks of the $E_{11}$ transitions, and the laser pulse spectrum is scaled to match the $E_{11}$ peaks. (b) Steady-state fluorescence emission spectra measured for the SWNT/PVP film upon resonant excitation of the $E_{22}$ transitions of the (6, 5) and (7, 5) tubes at 572 and 655 nm, respectively.

Figure 2. Normalized integrated photon echo profiles collected in the two phase matching directions $k_1 - k_2 + k_3$ (open circles) and $-k_1 + k_2 + k_3$ (filled circles) for the population times $T = 0$ (a), 50 (b), 500 (c), and 900 fs (d), respectively. The solid lines are the fits to Gaussian functions.

The 3PEPS technique employed here has been described extensively elsewhere,$^{15,16,19,20}$ In short, the light source was a 250 kHz Ti:sapphire regenerative amplifier pumped optical parametric amplifier that generates 62 fs pulses with a central wavelength of 1018 nm. The laser pulse spectrum is indicated by the dotted line in Figure 1a. This excitation wavelength was chosen to resonantly excite the lowest transition-allowed excitonic states ($E_{11}$) of the (6, 5) as well as the (7, 5) nanotubes, with the majority of absorption coming from the (6, 5) tubes. The laser beam was split into three replicas of equal intensity with wave vectors $k_1, k_2,$ and $k_3$ and focused on the sample with a 15 cm singlet lens. Time-integrated photon echo signals at the two phase-matching directions $k_1 - k_2 + k_3$ and $-k_1 + k_2 + k_3$ were detected simultaneously with two InGaAs photodiodes connected to separate lock-in amplifiers. The intensity of the incident light was controlled with a waveplate and polarizer combination and monitored with a reference photodiode. TG signals were measured using the same setup by setting the time delay between the $k_1$ and $k_3$ pulses to zero.

Separate 3PEPS measurements were also performed at selected excitation intensities on an aqueous suspension of individualized SWNTs. A quartz cell with a path length of 100 μm was employed in order to minimize laser light scattering and thermal lensing effects. As the measurements on the aqueous solution produced similar results to those obtained from the polymer film at similar intensities, we will focus on the data collected using the film which is of higher signal-to-noise ratio. All measurements were performed at room temperature (294 K).

The same setup was used for the two-pulse FWM experiment by blocking the third beam ($k_3$), and the diffracted signal was detected at the phase-matching direction $2k_2 - k_1$. To directly time resolve the exciton dephasing process from the diffracted signal, a shorter laser pulse with duration of 45 fs was employed. Simultaneous detection of the $k_1$ beam after passing through the sample enabled concurrent measurement of the PP signals.

Representative time-integrated photon echo profiles collected in the two phase matching directions $k_1 - k_2 + k_3$ (open circles) and $-k_1 + k_2 + k_3$ (filled circles) are shown in Figure 2 for the population times $T = 0, 50, 500,$ and 900 fs. The echo signals are symmetric along the axis of coherence time ($\tau$). The peak shift ($\tau^*$) at each population time $T$ is obtained by fitting each of the echo signals to a Gaussian function and then calculating half the difference in response to electronic dephasing induced by nuclear motions.$^{21,22}$ As discussed extensively in previous studies on molecular systems and...
dependence of peak shift on excitation intensity. As shown substantial tube aggregation in the polymer film samples. provides further additional support for the absence of from the aqueous suspension. Moreover, this similarity measured on the SWNT/PVP films.

Figure 3. (a) Three-pulse echo peak shifts measured on the SWNT/ PVP film at four different excitation intensities (see (b) for color scale in µJ/cm²). The inset shows that the 3PEPS profile collected at different intensities can all be superimposed by means of a linear shift in peak shift. The open squares depict the data collected from the aqueous solution at an excitation intensity of 27.8 µJ/cm². Because of pronounced scattering, measurement was possible only for a limited range of population times. (b) Transient grating signals measured on the SWNT/PVP films.

quantum dots,19,21,23 the echo peak shift (τ*) plotted as a function of the population time is related to the time correlation function of the electronic transition frequencies $M(t)$,16,22

$$M(t) = \frac{\langle \delta \omega_{eg}(0) \delta \omega_{eg}(t) \rangle}{\langle \delta \omega_{eg}^2 \rangle}$$

where δωeg is the transition frequency from the ground to the $E_{11}$ state.

Measurements on aqueous SWNT suspensions produced essentially identical 3PEPS results (see Figure 3a, open squares) to those obtained using the PVP polymer film at the same excitation intensities. This similarity indicates that the dynamics detected using 3PEPS spectroscopy are highly insensitive to the environment outside the nanotube and thus are in stark contrast to the dynamics of exciton population relaxation.24–26 More importantly, the similarity between the results measured from the aqueous solution and the PVP films confirms that embedding SWNT into PVP polymer films does not induce additional broadening of the spectral linewidth. Otherwise, the residual peak shift at long population time ($T > 300$ fs) would be larger than that observed from the aqueous suspension. Moreover, this similarity provides further additional support for the absence of substantial tube aggregation in the polymer film samples.

One surprising finding of our 3PEPS studies is the strong dependence of peak shift on excitation intensity. As shown in Figure 3a, the peak shift at a given population time increases sharply with decreasing excitation intensity. When the intensity is decreased 27 times, the peak shift increases at all population times by ~25 fs. A related peak shift intensity-dependence has been recently reported for zinc-blende structured CdSe nanocrystals,27 but to the best of our knowledge, such a strong dependence has not been observed for any other molecular system or nanoscale material. While the observed peak shifts depend strongly on excitation intensity (see Figure 3a), the decay time scale of the 3PEPS profiles themselves are largely invariant to intensity effects. This invariance is best illustrated by overlaying the peak shift profiles (Figure 3a, inset) onto the curve collected at the lowest intensity. Each of the 3PEPS profiles can be satisfactorily described by a monoeXponential decay with a 60 fs decay constant and a time-independent nonzero offset. This time constant is very different from the time scales of exciton population relaxation, which were determined through TG measurements at the corresponding excitation intensities (see Figure 3b). The TG signals measured at different intensities exhibit essentially identical kinetics, with their peak amplitudes linearly proportional to the excitation intensity. This behavior is fully consistent with the results of previous PP measurements.28 To extract the time scales of population relaxation from the TG data, we performed deconvolution fitting by explicitly considering the finite laser pulse width and the $E$-field squared nature of the TG signal. This fitting gives two time scales of 130 and 790 fs, both are much longer than the 60 fs decay time of the 3PEPS profiles. The decay profiles and the time scales differ from those reported in ref 29 for HiPCO nanotubes suspended in an aqueous solution, with no rise component detectable in our data.

The intensity dependence of peak shifts arises from exciton–exciton scattering and annihilation and its analysis will be described elsewhere. Instead, we focus our analysis on extracting absorption line shape information from the 3PEPS profile in the limit of zero-intensity, where complications from exciton–exciton interactions can be neglected. The invariance in the decay behavior of the 3PEPS profiles with excitation intensity (see Figure 3b, inset) enables us to construct a zero-intensity 3PEPS profile. This construction involves measuring the peak shifts under different excitation intensities at selected population times and then extrapolating the experimental data to the limit of zero-intensity. This extrapolation gives a $r^*(T = 0) = 52$ fs, which is only marginally higher than the $r^*(T = 0) = 50$ fs measured at the lowest experimental excitation energy (0.60 µJ/cm² for all three beams). The constructed zero-intensity profile shown in Figure 4 is obtained by shifting the entire 3PEPS profile measured at the lowest excitation intensity by a 2 fs increment in peak shift. The resulting 3PEPS profile can then be modeled by conventional methods because all the effects from the exciton–exciton interactions that dominate at higher intensities become negligible.

Our data simulation involves constructing an $M(t)$ that is capable of reproducing both the peak shift curve and the experimental linear absorption spectrum in the high-temperature limit ($2k_BT \gg \hbar \omega$, $\omega$ is the frequency of vibra-
The extracted frequency of 245 cm$^{-1}$ is fairly close to the frequency of the radial breathing mode (RBM) of 282 cm$^{-1}$ observed from a resonant Raman measurement on the PVP film sample (data not shown). The remaining vibrational parameters extracted from our simulations are $A_c = 10$ cm$^{-1}$, $\tau_c = 120$ fs, and a phase factor $\phi_c = 4.5$ rad.

To verify that the simulation parameters used are physically reasonable, we simulated the linear absorption spectrum via the relation

$$
\sigma(\omega) = \frac{1}{\pi} \text{Re} \int_0^\infty \text{d}t \exp[i(\omega - \omega_{eg})t - g(t)]
$$

where $\omega_{eg}$ is the transition frequency of the system and $g(t)$ is the line-broadening function that is obtained from $M(t)$. As shown in Figure 4b, the simulated spectrum fits rather well to the experimental absorption spectrum, with an overall full width of half-maximum (fwhm) of 720 cm$^{-1}$. The corresponding homogeneous line width is calculated by setting $\sigma_0$ to zero in eq 2, resulting in a value of 178 cm$^{-1}$. These results give a ratio of overall to homogeneous widths of 4.1. Note that the total width is an overestimate of the $E_{11}$ band associated with the $(6, 5)$ tube because of the contribution from the $(7, 5)$ tube and others. On the basis of Gaussian decomposition of the broad featureless absorption band of the PVP sample in the $E_{11}$ region, we estimate that the contribution from the $(7, 5)$ and other tubes should not be greater than 25% of the total width. The homogeneous width may be also overestimated by a similar amount.

From the frequency and coupling strength of the vibrational contribution, we can further calculate the Huang–Rhys factor $S = \Delta^2/2 = A_c/\hbar \omega_c = 0.04$, where $\Delta$ is the dimensionless displacement between potential minima of the ground-state and the resonant electronic state. This value is fully consistent with the results of recent ab initio calculations and Raman experiments, and provides further evidence for weak exciton–phonon coupling in semiconducting SWNTs. Our simulations further provide one of the first experimental estimates for the time scale ($\tau_c = 120$ fs) for the damping of the RBM. The damping time is significantly shorter than the overall exciton population relaxation times but is similar to the time scale obtained for pure dephasing (see below).

The exceptionally large values of the initial peak shift $\tau^\ast$ ($T = 0$ fs) make semiconducting SWNTs distinct from all previously studied molecular systems studied with similar pulse durations. At the lowest excitation intensity possible (0.60 $\mu$m/cm$^2$), we measured a initial peak shift of 50 fs. A slightly larger value of 52 fs is obtained by extrapolating the experimental data to the limit of zero intensity. Generally, large initial peak shift values are indicative of weak electron–phonon coupling. This is fully consistent with the small Huang–Rhys factor calculated using the simulation parameters. It is also in line with the rather small Stokes shift and reorganization energy, the latter was required for simulating our 3PEPS results. Further work is required, however, to determine the influence of the delocalization length of the coherent excitons on the effective exciton–phonon coupling. The extent to which exchange narrowing related effects, such as seen in molecular ag-
gregates,\textsuperscript{36} reduces the apparent exciton phonon coupling strength is not yet clear.

As an independent verification of the homogeneous line width extracted from the simulation, we performed two-pulse FWM measurements on the same film sample. Figure 5a shows the time-integrated FWM signal measured at an excitation intensity of 4.2 \( \mu \text{J/cm}^2 \), along with the autocorrelation profile of the two laser pulses (dotted line) and the fitting result (solid line). The FWM signal exhibits an essentially instantaneous rise for the negative delay times and reaches a maximum at a positive delay of +37 fs. This shift from the zero delay time corresponds well to the peak shift at \( T = 0 \) determined at a similar intensity. The decay of the FWM signal is best characterized by a time scale of \( \tau_d = 19.5 \text{ fs} \), obtained through a least-squares fit with explicit consideration of the finite temporal response. From the extracted time scale \( \tau_d \), we calculate the fwhm homogeneous line width \( \Gamma_1 \) through a simple relaxation \( \Gamma_1 = 2\hbar / \tau_2 \), where the dephasing time \( \tau_2 \) is obtained from \( \tau_d \) by \( \tau_2 = 4\tau_d \).\textsuperscript{37} Although the latter relation is strictly valid only for a strongly inhomogeneously broadened, independent two-level system, our recent study on a sample that is highly enriched in a single tube species shows that the homogeneous linewidths obtained with this expression at different temperatures agree very well with the results of a single tube photoluminescence experiment.\textsuperscript{38} Calculation based on the same relation gives an homogeneous line width of 136 cm\(^{-1} \) at room temperature, which is fairly close to the value (178 cm\(^{-1} \)) determined from our 3PEPS simulation.

A simultaneously measured PP signal has a much slower decay (see Figure 5b) and excludes any significant contribution from exciton population relaxation to the observed FWM signal decay. On the basis of the well-known relation between the dephasing time \( \tau_2 \), pure dephasing time \( \tau_d \), and the population relaxation time \( \tau_1 \) for a two-level system

\[
\frac{1}{\tau_2} = \frac{1}{\tau_d} + \frac{1}{2\tau_1}
\]

we can deduce a \( \tau_1 \) value, corresponding to pure exciton dephasing, of 78 fs at room temperature. This result suggests that a proper description of ultrafast exciton dynamics in semiconducting SWNTs should take exciton coherence into account even at room temperature.

In summary, we have demonstrated that photon echo spectroscopy is an incisive technique for elucidating spectral line shape information through ensemble measurements of semiconducting SWNTs. We observed a strong dependence of the peak shift on excitation intensity owing to simultaneous creation of multiple excitons and their mutual interactions. To overcome these multie exciton complications, and to extract absorption line shape information, we simulate the 3PEPS profile obtained in the limit of zero-excitation intensity. We find that the linear absorption spectrum associated with the transitions from the ground-states to the \( E_1 \) excitonic states of the abundant tube species is dominated by inhomogeneous broadening with a fwhm of 698 cm\(^{-1} \) and a narrow 178 cm\(^{-1} \) homogeneous width. The total width (720 cm\(^{-1} \)) is overestimated for the spectral band of the (6,5) tube because of the contribution from the (7,5) and other tubes, which amount to no greater than 25% of the total line width. Determination of the very short decay time of the two-pulse FWM signal compared with the exciton population relaxation further enables us to conclude that the obtained finite homogeneous width arises primarily from a pure exciton dephasing process. Moreover, the exceptionally large initial peak shift observed at \( T = 0 \) suggests weak exciton–phonon coupling. This is further supported by the small RBM Huang–Rhys factor and the weak phonon bath coupling strengths needed to model the Gaussian and exponential components in the peak shift profile decay.

Future study employing laser pulses of <20 fs should enable assessment of the coupling strengths of high-frequency vibrational modes and excitons.

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**References**


