

## Non-Markovian Decoherence of Localized Nanotube Excitons by Acoustic Phonons

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We demonstrate that electron-phonon interaction in quantum dots embedded in one-dimensional systems leads to pronounced, non-Markovian decoherence of optical transitions. The experiments that we present focus on the line shape of photoluminescence from low-temperature axially localized carbon nanotube excitons. The independent boson model that we use to model the phonon interactions reproduces with very high accuracy the broad and asymmetric emission lines and the weak red-detuned radial breathing mode replicas observed in the experiments. The intrinsic phonon-induced pure dephasing of the zero-phonon line is 2 orders of magnitude larger than the lifetime broadening and is a hallmark of the reduced dimensionality of the phonon bath. The non-Markovian nature of this decoherence mechanism may have adverse consequences for applications of one-dimensional systems in quantum information processing.

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In single-wall carbon nanotubes (SWNTs), the 1D nature of electronic states results in an enhancement of Coulomb interactions and has led to the observation of remarkable effects such as Luttinger-liquid states in transport experiments [1]. On the other hand, a common feature of the small diameter semiconducting SWNTs is the unintentional confinement of the electronic or excitonic states along the nanotube axis; this leads to the formation of zero-dimensional (0D) quantum dot (QD)-like states, manifesting themselves through Coulomb blockade in transport experiments [2,3] or through localized emission [4] and strong antibunching in photoluminescence (PL) [5]. Spatial confinement of electrons or excitons in SWNTs is, in fact, desirable for applications in single photonics or quantum information processing (QIP), which in turn motivates theoretical and experimental investigations of elementary physical properties of optically active QDs in SWNTs.

Electron coupling to Raman-active phonon modes such as the radial breathing mode (RBM) and the  $G$  mode has been an invaluable tool for characterizing SWNTs. Interest in long-wavelength acoustic phonons of SWNTs primarily stems from their potential use as nanomechanical resonators. A question that is of interest from a QIP perspective is the decoherence induced by interactions between QD electrons or excitons and 1D acoustic phonons: While this problem has been addressed theoretically for QD excitons in quasi-1D III–V nanowires in the high-temperature limit [6], experimental confirmation of predicted features has not been obtained.

In this Letter, we analyze the influence of exciton-phonon interactions on the PL line shape of SWNT QDs. We show that the experimental PL spectra consisting of broad and strongly asymmetric lines can be fit with remarkable accuracy using an analytical solution to the independent boson model, over a dynamical range spanning 2 orders of magnitude and a temperature range varying from 5 to 35 K. In our model, we assume that the lowest bright SWNT excitons, formed out of bound electron-hole

pairs from the first band-to-band transition  $E_{11}$  [7], are confined to form QD-like states; this assumption is justified since PL has been shown to exhibit strong photon antibunching [5]. The principal result of our work is the demonstration that the 1D nature of acoustic phonons and the resulting Ohmic exciton-phonon coupling give rise to strong pure dephasing of spatially localized optical excitations even as we approach the zero-temperature limit. Even though we study localized SWNT excitons in our experiments, we emphasize that our conclusions are valid for localized transitions in any 1D system. Our findings also suggest that simple PL measurements can be used to determine quantities such as the localization length scale of excitons and the deformation potential coupling strength in carbon nanotubes.

We measured the PL from isolated SWNTs at cryogenic temperatures. Details on the experimental setup and sample preparation are given in Ref. [5]. Briefly, we deposited surfactant-embedded CoMoCat SWNTs directly on a functionalized solid-immersion lens and used a confocal microscope to detect PL upon excitation with a tunable Ti:sapphire laser (cw or pulsed mode). The sample is placed in a helium bath cryostat, and the temperature is controlled locally through a thermoresistor. As discussed in Ref. [5], spatially localized emission and strong photon antibunching indicate that the PL signal originates from unintentionally axially confined excitons, i.e., from SWNT QDs. Figure 1 shows typical experimental PL spectra (open circles) at  $T = 4.2$  K that we observed: The line shape is clearly asymmetric with a full width at half maximum of 3.5 meV. Time-resolved measurements indicate that the PL decay follows a biexponential law with a fastest time constant of 36 ps (Fig. 1 inset) in agreement with previous reports (see [8,9], and references therein), which implies that the measured linewidth is a factor of 100 larger than the lifetime broadening. This particular nanotube PL exhibited strong photon antibunching with a value for the normalized second-order correlation function  $g^{(2)}(0) = 0.1$  [5].

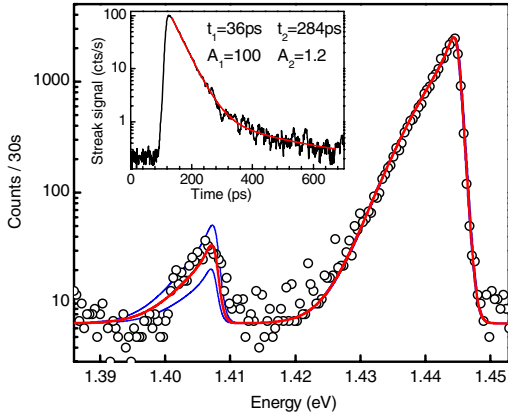


FIG. 1 (color online). Photoluminescence of a nanotube quantum dot at  $T = 4.2$  K and  $P = 300$  nW (open circles) and the calculated spectrum (solid line) plotted on a logarithmic scale. For the theoretical model, we used the parameters  $D_S = 14$  eV,  $D_{\text{RBM}} = 1.4$  eV/Å,  $\hbar\omega_{\text{RBM}} = 37.2$  meV,  $\Delta E = 44$  meV, and  $T_{\text{fit}} = 6.3$  K. The upper and lower solid blue lines are calculated spectra with identical parameters but  $D_{\text{RBM}} = 1.8$  eV/Å and  $D_{\text{RBM}} = 1.0$  eV/Å, respectively, demonstrating the precision with which the coupling strength can be determined. The inset shows a time-resolved measurement (dark line). The red line is a biexponential fit of the PL decay revealing a main fast component with characteristic time  $t_1 = 36 \pm 0.2$  ps and weight  $A_1 = 100 \pm 0.3$  and a vanishingly weak long tail ( $t_2 = 284 \pm 40$  ps,  $A_2 = 1.2 \pm 0.2$ ). From the value of  $t_1$ , we expect a lifetime-limited linewidth of  $\sim 0.036$  meV, in strong contrast to the measured and calculated width of 3.5 meV.

To explain this broad and asymmetric PL line shape, we develop a theoretical model where we assume a harmonic confinement potential for excitons along the nanotube axis. For confinement length scales that are long compared to the exciton Bohr radius, QD states are superpositions of free excitonic states with envelope wave functions determined by the 1D harmonic oscillator Hamiltonian. We further assume that the confinement is strong enough to lead to well-separated QD levels, with an energy splitting  $\Delta E \gg k_B T$ , where  $k_B$  is the Boltzmann constant and  $T$  the absolute temperature.

To account for the coupling of this QD to the acoustic phonons of the SWNT, we follow the extension of the independent boson model developed in Ref. [10]. We assume that the phonon dispersion of the bare SWNT remains unaltered by the confining potential. Since no atomic bonds are formed with the embedding surfactant, we also assume that coupling to phonons of the surrounding material is negligible. Long-wavelength acoustic phonons in nanotubes are well described by a continuum elastic model [11,12], and they couple to electrons through deformation potentials [11–13]. Because of momentum conservation, only phonon modes with zero angular momentum can couple to excitonic states within a single subband  $E_{11}$ ; the potentially relevant modes are therefore stretching, twisting, and radial breathing modes. We neglect the coupling to the twisting mode, whose strength is

expected to be 1 order of magnitude smaller than to the stretching mode [11]. The stretching mode corresponds to lattice vibrations with longitudinal displacements of the atoms along the nanotube axis [12]. It has linear dispersion  $\omega_s(q) = v_s q$  for small wave vectors [12], and the strength of its coupling to excitons is characterized by the deformation potential  $D_S$ . It would provide the dominant contribution to the broadening of the localized exciton emission, aka the zero-phonon line (ZPL). Since the RBM has an approximately flat dispersion for small wave vectors (with an energy  $\hbar\omega_{\text{RBM}}$ ), its principal contribution would be the appearance of phonon sidebands in PL that are separated from the exciton line by  $\hbar\omega_{\text{RBM}}$ .

Following Ref. [10], we obtain the exciton-phonon matrix elements:  $g_j(q) = \mathcal{G}_j(q)\mathcal{F}^{\text{exc}}(q)$ , where  $j$  stands for  $S$  (stretching mode) or RBM. The form factor  $\mathcal{F}^{\text{exc}}(q) = \int dz |\Psi^{\text{exc}}(z)|^2 e^{iqz}$  provides a cutoff for the coupling in momentum space that is inversely proportional to the spatial extension of the wave function. With our choice of a parabolic potential, we get for the QD ground state a Gaussian envelope along  $z$ :  $\Psi^{\text{exc}}(z) = \frac{1}{\pi^{1/4} \sigma^{1/2}} \exp(-\frac{z^2}{2\sigma^2})$ , where  $\sigma$  is the confinement length. This yields  $\mathcal{F}^{\text{exc}}(q) = \exp(-\frac{q^2 \sigma^2}{4})$  and the energy splitting:  $\Delta E = \frac{\hbar^2}{m_{\text{exc}}^* \sigma^2}$ , where  $m_{\text{exc}}^*$  is the effective mass of the exciton. The deformation potential couplings are  $\mathcal{G}_S(q) = D_S q / \sqrt{2\rho L \hbar \omega_s(q)}$  and  $\mathcal{G}_{\text{RBM}}(q) = D_{\text{RBM}} / \sqrt{2\rho L \hbar \omega_{\text{RBM}}}$ , where  $L$  is the length of the nanotube and  $\rho$  its linear mass density.

The linear susceptibility  $\chi(t)$  ( $t \geq 0$ ) of the QD in response to a  $\delta$ -shaped laser pulse at  $t = 0$  [10,14] can be decomposed into a temperature-dependent and a temperature-independent contribution  $\chi(t) = -ie^{-i\tilde{\Omega}t} \chi_T(t) \chi_0(t)$ , with

$$\chi_T(t) \propto i \exp\left(\sum_q |\gamma_S(q)|^2 [-n_S(q) |e^{-i\omega_S(q)t} - 1|^2]\right), \quad (1)$$

$$\chi_0(t) \propto i \exp\left(\sum_q |\gamma_S(q)|^2 [e^{-i\omega_S(q)t} - 1]\right), \quad (2)$$

where  $\gamma_j(q) = g_j(q)/\omega_j(q)$  and  $n_j(q) = (e^{\hbar\omega_j(q)/k_B T} - 1)^{-1}$  is the phonon occupation number. The polaron-shifted transition energy is  $\tilde{\Omega} = \Omega - \sum_{j,q} |\gamma_j(q)|^2 \omega_j(q)$ , where  $\hbar\Omega$  is the bare energy of the QD state. Performing the Fourier transformation of  $\chi(t)$  and taking its imaginary part gives the absorption spectrum of the QD. The PL-emission line shape that we measure experimentally is obtained by taking the mirror image of the absorption profile with respect to the ZPL [15].

The solid curve in Fig. 1 shows that this simple theoretical model describes the experimental observation remarkably well. To obtain this fit, we use SWNT parameters that were reported earlier; in particular, we take  $\rho = 1.67 \times 10^{-15}$  kg/m,  $v_s = 19.9$  km/s [11], and  $m_{\text{exc}}^* \approx 0.2m_e$  [16]. An electron-phonon deformation potential for the stretching mode [11,12] of strength  $D_S = 14$  eV has been extracted from data on low-field mobilities in

semiconducting SWNTs [13,17]. Our procedure, applied to 10 different SWNT spectra, involves varying the values of  $D_S$  and the confinement to obtain the best fit to the data. The range of  $D_S$  values we thereby obtained varied from 12 to 14 eV. The other fitting parameter is the confinement potential along the SWNT axis which determines the cutoff in momentum space or, equivalently, the level spacing  $\Delta E$ . We found values for  $\Delta E$  between 20 and 44 meV, consistent with our assumption that  $\Delta E \gg k_B T \approx 2.8$  meV (at 35 K) and corresponding to an extension of the wavefunction envelope on the order of  $\sim 10$  nm. Since this confinement length scale is bigger than the Bohr radius [7,18], our assumption of exciton center-of-mass confinement is also justified.

The PL spectrum from Fig. 1 is plotted on a logarithmic vertical scale to show the quality of the fit over two decades of counts and to emphasize the presence of a red-detuned replica that is exactly reproduced by the model. The RBM deformation potential for excitons are well documented [19–21] and expected to lie between 1 and 2 eV/Å. Here we obtained the best fit for  $D_{\text{RBM}} = 1.4 \pm 0.2$  eV/Å and a RBM energy of 37.2 meV corresponding to a SWNT diameter of about 0.7 nm, in good agreement with CoMoCat SWNTs emitting at this wavelength. The linear power dependence of the red-detuned replica for very low excitation intensities (not shown) is consistent with that of a phonon sideband and excludes an explanation based on biexciton emission.

Figure 2 shows the experimental PL lines (open circles) for two different SWNTs. In the left panel, the temperature is increased by flowing current in the thermoresistor. The very asymmetric lines at the lowest temperatures and the evolution to broader symmetric lines with increasing temperature is a general feature common to virtually all of the 30+ SWNTs that we measured. The computed spectra (solid red lines) reproduce both qualitatively and quantitatively this behavior when the coupling to the stretching mode only is taken into account. Only the considerable shifts in the transition energies are not reproduced by the model; arbitrary offsets were therefore introduced for each spectrum. This unexpected sensitivity on minor environmental changes is another evidence for localized emitting states [5]. In contrast, the transition energy of a delocalized exciton is not expected to shift so dramatically with temperature [22].

The right panel in Fig. 2 (different SWNT) shows that the effect of increasing the excitation power can be reproduced by only increasing the temperature of the phonon bath in the model and keeping all of the other parameters fixed. From this, one can conclude that the laser excitation led to a very local heating of the SWNT that was not directly measured by our thermoresistor placed about 1 mm away from the nanotubes.

We emphasize that the unusually broad lines observed in SWNT PL can be accurately and quantitatively explained by solely taking into account interaction with long-wavelength 1D acoustic phonons. The resulting Ohmic

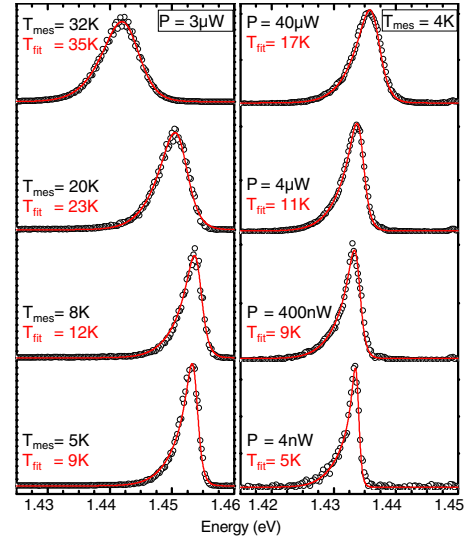


FIG. 2 (color online). Left panel: Experimental (open circles) and calculated (solid red lines) PL spectra for the same SWNT at different temperatures  $T_{\text{mes}}$  (the vertical scale is arbitrary). The excitation power was kept constant at  $P = 3 \mu\text{W}$ . The effective temperature used in the simulation is given by  $T_{\text{fit}}$ ; the other parameters are  $D_S = 12.7$  eV and  $\Delta E = 22$  meV. Right panel: Emission from another nanotube at constant sample temperature  $T = 4.2$  K. The changes induced by increasing the laser intensity from 4 nW to 40  $\mu\text{W}$  are very well reproduced by increasing the temperature  $T_{\text{fit}}$  in the model. The parameters for this SWNT are  $D_S = 13$  eV and  $\Delta E = 20$  meV.

coupling [23] gives rise to linewidths that are 2 orders of magnitude larger than the ones expected from lifetime broadening. To highlight this feature, we have plotted in Fig. 3 a comparison of the theoretical PL line shape for a QD interacting with 1D and 3D phonon reservoirs. Coupling to 2D or 3D acoustic phonons yields a super-Ohmic spectral function [23], for which the independent boson model predicts a (lifetime-broadened) ZPL accompanied by phonon sidebands (Fig. 3, upper right). This is in strong contrast to our observations from SWNTs [24].

The enhanced pure dephasing of QD transitions in 1D structures was analyzed theoretically in Ref. [6], where the finite width was attributed to the high-temperature (Markovian) limit. This part is due to the temperature-dependent contribution  $\chi_T(t)$  in Eq. (1) and vanishes linearly as  $T \rightarrow 0$ . It provides a symmetric contribution to the line shape (as illustrated in Fig. 3, lower panel, red curve). In contrast, the highly asymmetric character of the observed line shapes at low temperatures is largely due to the temperature-independent part of the susceptibility  $\chi_0(t)$  in Eq. (2). For comparison, we plot these two contributions separately, although they appear in the line shape as a convolution. The temperature-dependent term is responsible for the presence of a high-energy tail at nonzero temperature, while the broad low-energy tail that we measure constitutes a direct signature of the temperature-independent pure dephasing. Furthermore, we find that the characteristic energy of the latter quasiexponential



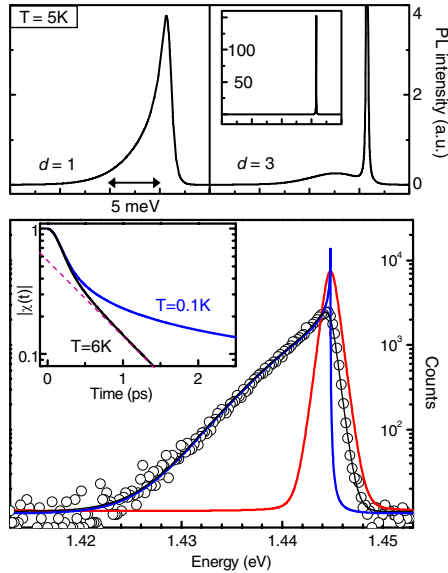


FIG. 3 (color online). Upper panel: Calculated emission line shapes at  $T = 5$  K for a QD coupled to a phonon bath of dimension  $d = 1$  (left) and  $d = 3$  (right) are shown. The coupling to a single acoustic phonon branch with linear dispersion ( $v_s = 19.9$  km/s) is considered. To extend the model to higher dimension, we assume an isotropic coupling of the QD to LA phonons described by the same deformation potential. A lifetime broadening corresponding to  $\tau_1 = 36$  ps is introduced. Lower panel: For illustration, fit of the spectrum shown in Fig. 1 (open circles) with only the temperature-dependent [Eq. (1), red line] and the temperature-independent [Eq. (2), blue line] contributions. Each curve is scaled to span the same total area. The inset shows the susceptibility ( $T = 6$  K) used to fit the data (black curve), where a deviation from an exponential decay is visible for  $t \leq 1$  ps. The blue curve of the inset shows the same function at  $T = 0.1$  K where the non-Markovian nature of dephasing becomes clearer.

tail is directly proportional to the width of the form factor in  $q$  space. This dependence is to be expected since the inverse localization length scale determines the highest phonon energies to which the QD is effectively coupled. A stronger confinement therefore leads to a faster dephasing, even at arbitrarily low temperatures.

In Fig. 3 (lower panel), the inset shows the time dependence of the calculated linear susceptibility  $\chi(t)$  used to fit the experimental spectrum: The deviation from an exponential decay that is apparent for  $t \leq 1$  ps is a hallmark of non-Markovian decoherence [25]. Our calculations indicate that this initial (Gaussian) decay crosses over to a power-law decay and finally to an exponential decay at long times. The regime where power-law decay is dominant expands as temperature is decreased; further reduction of the temperature to 0.1 K leads to the appearance of power-law decay of the susceptibility extending to 15 ps (blue curve). Observation of such a strong deviation from Markovian dynamics should be within reach.

In conclusion, we have used an extension of the independent boson model to reproduce with remarkable quan-

titative accuracy the asymmetric and broad lines that we measured on isolated SWNTs. In strong contrast to 3D systems, the reduced dimensionality of the phonon bath in SWNTs leads to Ohmic coupling of confined excitons to stretching mode phonons: In this limit, the ZPL is replaced by a power-law singularity. This conclusion remains valid at arbitrarily low temperatures, where the induced pure dephasing becomes manifestly non-Markovian, and would apply to QDs defined in any one-dimensional system. These intrinsic effects are of fundamental interest in view of applications in quantum information processing, where the non-Markovian nature of decoherence may substantially alter the attainable accuracy thresholds [26].

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