

Vibrational Dephasing of Electronic Excitations in Semiconducting Carbon Nanotubes

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Carbon nanotubes (CNT) are one of the most intriguing and robust elements of the emerging nanotechnology field. Their potential in numerous applications has led to the exertion of great effort in the scientific community to elucidate their electronic, chemical, vibrational and optical properties. Of particular interest for incorporation into nanoscale applications is the understanding of a CNTs response to optical simulation. Synthesis and purification is one of the greatest challenges faced by the community studying nanotubes. The electronic structure of CNTs is intimately linked to the twist (or chiral angle) the carbon atoms take as they build these nanoscale cylinders. The extreme conditions during synthesis and large distribution of possible chiral angles and diameters make it extremely difficult to separate and isolate single CNT. Optical measurements on bundles or ropes of CNTs lose much of the fine spectral structure. However, in the last few years great strides have been made. Among the most important gains to the spectroscopic area was the separation of individual tubes in solution. This was quickly followed by a mapping of the optical structure of individual tubes. This separation of individual nanotubes from bundles has also allowed for photoluminescence studies and probing the intrinsic CNT excitations by interaction with light. Owing to improvement in the processing and production of CNTs, applications in molecular and quantum information technology are moving forward. Electron-phonon interaction and phonon-induced electronic dephasing play key roles in many applications.

Phonon-induced dephasing of electronic transitions in semiconducting single-wall carbon nanotubes (CNT) is investigated by *ab initio* molecular dynamics. Three ideal geometry tubes, (6,4), (7,0) and (8,4) and two common defects, 7-5-5-7 and Stone-Wales, are studied. The two defects and their transition densities are shown (Figure 1). The SW defect corresponds to a rotation of one of the C-C bonds, creating two five-membered rings and two seven-membered rings. The 7557 defect occurs by insertion of a C-C dimer into the middle of one of the benzene rings on a CNT cylinder. The 7557 defect also creates two pentagon-shaped rings and two heptagon-shaped rings, although with different orientations to one another than those imposed by the SW defect. The 7557 defect distorts the CNT geometry more strongly than the SW defect, protruding from the surface of the tube. The

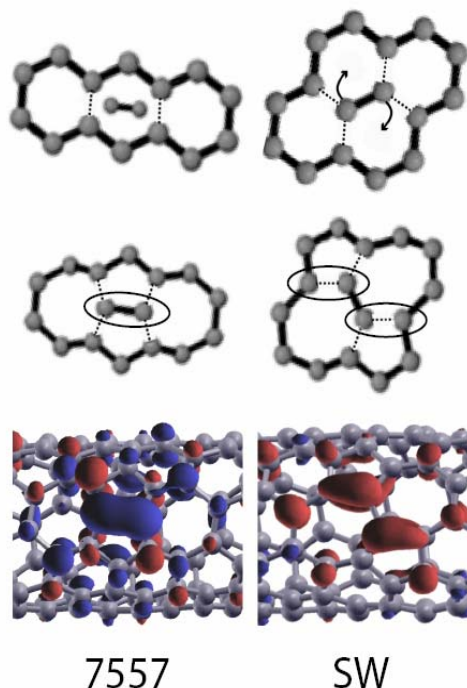


Figure 1. Schematic of 7557 (left) and SW (right) defects. Top two figures show how the defects form from an ideal hexagonal lattice. Bottom pictures show density difference of the electronic transition.

influence of the 7557 defect on the electronic structure of the (6,4) tube is much more localized. The excitation localized on the 7557 defect removes electron density from the inserted C-C bond and spreads it to the nearby carbon atoms. The 7557 localizes the density on the HOMO, while the SW defect localizes it on the LUMO.

The results of our simulation are summarized in Table 1. The dephasing function was fit by the equation

$$f(t) = \exp\left(\frac{-t}{T}\right) \frac{1 + A \cos(\omega t)}{1 + A}$$

Here, τ represents the dephasing time (T_2) in the table. A accounts for the oscillatory component of the dephasing function and ω represents the frequency of the oscillations. Omega values near 0.30 fs^{-1} correspond to carbon-carbon stretches, or the G-mode. Γ represents the theoretical calculation of the experimentally observed linewidths.

In ideal tubes, the dephasing is found to occur by coupling to optical phonons. The dephasing proceeds notably faster in the presence of some defects due to stronger coupling to local modes, suggesting that the defects can be identified in CNTs by broadened optical bands. We were able to reproduce the ultrathin linewidths observed at low temperatures, as well[1]. The (7,0) tube has a very small diameter, which greatly increases the effects of curvature and strain. This is the cause of the deviations in both the calculated dephasing time and linewidths from the (6,4) and (8,4) nanotubes. Schematics of the possible local modes are shown in Figure 2. Our results are in good agreement with recent experiments on CNTs suspended across silicon pillars (table) [2] and pure dephasing is shown to be the source of the photoluminescence linewidths observed experimentally in isolated CNTs at low and room temperatures. The simulation predicts that CNT defects that strongly perturbed the nanotube structure, such as the 7557 defect studied here or oxygen and other species chemically adsorbed onto nanotubes, create electronic states with significantly broader transition lines. This fact is attributed to stronger electron-phonon interaction involving localized electronic states. The phonon-induced dephasing of the electronic transitions in the ideal tubes occurs by coupling to the high-frequency optical phonons. The dephasing of the defect states proceeds via local disorder and RBM modes. The theoretically predicted broader optical bands can be used to identify defect states in CNTs.

Tube	T_2^* [fs]	A	ω [fs^{-1}]	Γ [meV]
(8,4)	51.2	0.061	0.30	12.8
(7,0)	24.5	0	---	26.9
(6,4)	59.6	0.086	0.32	11.0
7557	18.4	0.88	0.12	35.8
SW	48.0	0.062	0.25	13.7
50K	955	0.0056	0.30	0.69

Table 1 Results of the simulation of vibration dephasing in carbon nanotubes. The table shows data fit using the equation shown to the left.

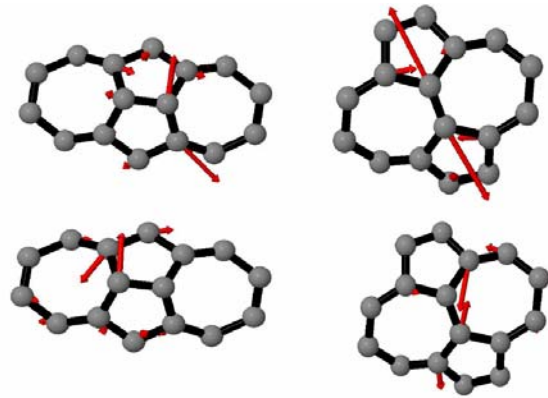


Figure 2. Local vibrational modes induced by the 7557 (left) and SW (right) defects. These modes promote faster dephasing times and broaden optical linewidths

References

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