

Disorder-induced electron-phonon interactions and gap states in carbon nanotubes

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Single-walled carbon nanotubes (SWNTs) have infrared-allowed phonon modes, but the associated, purely vibrational, transition moments are very weak. The mid-infrared (MIR) spectra, however, present sizable, stronger than expected, asymmetric bands at the energies of the phonon modes (tangential mode at $\sim 1600\text{ cm}^{-1}$, radial mode at $\sim 870\text{ cm}^{-1}$ and a defect mode at $\sim 1250\text{ cm}^{-1}$).

We have recently shown that the SWNT vibrations become observable in MIR spectroscopy because the phonon modes induce variations in the optical density of the electronic background, which is a large absorption band in the far-infrared (FIR) due to interband transitions of small bandgap metallic SWNTs and intraband free carrier excitations, through electron-phonon interactions. [1] We used chemical doping to modulate the charge carrier density, which increases the amplitude of the FIR band, and observed a stronger signal from the phonon modes along with an anti-resonance line shape. The findings were successfully interpreted in the framework of the Fano resonance, which appears whenever a coupling exists between a discrete state and a continuum. [2]

Using the diazonium reaction, bromophenyl addends were attached to the SWNT sidewall, thus inducing defects. We observed that the effective cross-section of the Fano resonance is enhanced with an increasing disorder. Moreover, the resonance is suppressed for pristine and undoped SWNTs. We concluded that the phonon modes couple to intraband free carrier excitations, not interband transitions. The electronic bands of SWNTs are thus broadened by the grafts, entering the so-called 'dirty regime' known to happen in other semiconductors. [3]

Herein, we present the results of a further study on the effect of grafting addends to SWNTs on the FIR and MIR optical conductivity. Mats of laser ablation SWNTs were subjected to the diazonium reaction with different reaction times and different concentrations, thus grafting varying amounts of bromophenyls to the sidewall. At a constant doping level, we observe that a broad absorption band is displaced from the FIR to higher energies with increasing amount of defects (see Figure 1), as asserted by Raman spectroscopy and X-ray photoelectron spectroscopy. Also, the transition oscillator strength is

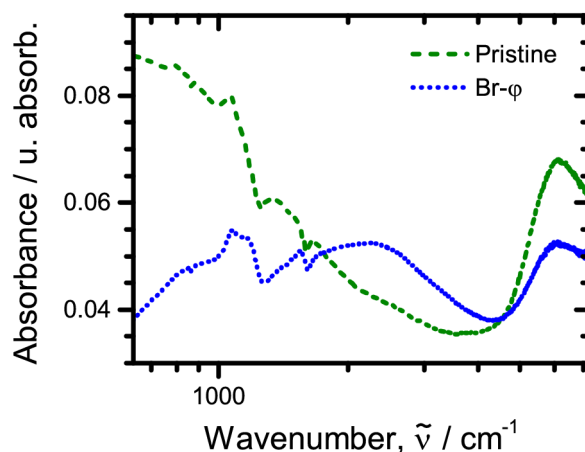


Figure 1. Comparison of the MIR spectra of SWNT mats in the pristine state and functionalized with bromophenyl (Br-φ) moieties. The x axis is a logarithmic scale.

smearing out. Moreover, as the defect-induced absorption band is shifted through the MIR region, the Fano resonance amplitude is greatly increased and becomes a true anti-resonance, which indicates that electron-phonon coupling is enhanced.

We tentatively relate this behavior to gap states created by the bromophenyl addends. The evidences of disorder-induced electron-phonon interactions and gap states in the MIR spectra are supported by transport experiments on individual SWNT transistors. These measurements show an increase of the leak current of semiconducting SWNT devices functionalized with monovalent moieties, attributed to graft-induced gap states. [4] Both optical and electrical experiments thus agree with the general view that strong disorder leads to gap states and enhances the electron-phonon interactions. [5,6]

References

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