

Advances in single nanotube spectroscopy: Raman spectra from cross-polarized light and chirality dependence of Raman frequencies

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Abstract

This work discusses new results obtained from analysis of Raman signal from isolated single wall carbon nanotubes. (1) Study of tangential (G band) modes frequency dependence on tube diameter and lineshape dependence on scattering polarization geometry shows clear observation of symmetry selection rules at the single nanotube level. Observation of E_2 phonon modes indicates Raman spectra coming from cross-polarized light, i.e. from $E_\mu^v \rightarrow E_{\mu\pm 1}^c$ electronic transitions. (2) Study of the disorder induced (D) band and other small intensity features show strong dependence of Raman frequencies of nanotube chiral angle.

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1. Introduction

Raman spectroscopy has been widely used to study and characterize the different forms of carbon [1]. In the case of carbon nanotubes, specially, this technique has been very successful on providing information from both electronic and structural properties, mostly due to the resonance nature of the Raman scattering process involving the so-called one-dimensional (1D) van Hove singularities (vHSs) [2,3]. The presence of the vHSs is responsible for a huge optical response of carbon nanotubes, making it possible to measure the Raman spectra from a single isolated single wall carbon nanotube (SWNT) [3,4].

So far, most of the work on nanotube Raman spectroscopy in SWNTs has been devoted to three features, (i) radial breathing mode (RBM) feature, that exhibits

strong frequency (ω_{RBM}) dependence on tube diameter (d_t), i.e. $\omega_{\text{RBM}} \propto 1/d_t$; (ii) the tangential (G band) modes, that provides information about selection rules and phonon symmetries; (iii) the disorder induced (D) band, that appear in the Raman spectra of carbon nanotubes through a multiple resonance mechanism.

This work discusses experimental results on single nanotube Raman spectroscopy. Polarization analysis of the G band and study of the selection rules indicate Raman spectra at the single nanotube level involving optical transitions between electronic states at the valence and conduction bands with different symmetries, i.e. $E_\mu^v \leftrightarrow E_{\mu+1}^c$. Study of the D band shows strong frequency dependence on SWNT chirality.

2. Experimental

Isolated SWNTs were grown on an oxidized Si wafer by the chemical vapor deposition (CVD) method using Fe nanoparticles as catalytic material. Raman spectra

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from isolated SWNTs were acquired using a micro-Raman Renishaw 1000B spectrometer equipped with a CCD detector. Three laser lines were used to excite the sample, $E_{\text{laser}} = 2.54$ eV (488 nm), 2.41 eV (514 nm) from an Ar⁺ laser and 1.98 eV (633 nm) from a He–Ne laser.

3. Results and discussion

3.1. G band measurements—observation of $E_{\mu}^v \leftrightarrow E_{\mu\pm 1}^c$ electronic transitions

Fig. 1 shows two Raman spectra from the G band of one isolated SWNT with the incident and scattered light polarized crossed with nanotube axis (XX) and parallel to nanotube axis (ZZ). The polarization assignment is based on the extinction of the E_2 modes at the (ZZ) scattering geometry, as expected according to the Raman selection rules [5]:

$$\begin{aligned} E_{\mu}^v &\xrightarrow{Z} E_{\mu}^c \xrightarrow{A} E_{\mu}^c \xrightarrow{Z} E_{\mu}^v \\ E_{\mu}^v &\xrightarrow{X} E_{\mu\pm 1}^c \xrightarrow{A} E_{\mu\pm 1}^c \xrightarrow{X} E_{\mu}^v \\ E_{\mu}^v &\xrightarrow{Z} E_{\mu}^c \xrightarrow{E_1} E_{\mu\pm 1}^c \xrightarrow{X} E_{\mu}^v \\ E_{\mu}^v &\xrightarrow{X} E_{\mu\pm 1}^c \xrightarrow{E_1} E_{\mu}^c \xrightarrow{Z} E_{\mu}^v \\ E_{\mu}^v &\xrightarrow{X} E_{\mu\pm 1}^c \xrightarrow{E_2} E_{\mu\mp 1}^c \xrightarrow{X} E_{\mu}^v \end{aligned} \quad (1)$$

Since the observation for E_2 modes can only be achieved by cross-polarized light, the (XX) spectrum in Fig. 2 indicates the observation of Raman spectra from an isolated SWNT involving transition between E_{μ}^v and $E_{\mu\pm 1}^c$ electronic states.

3.2. D band measurements—chirality dependence of Raman mode frequencies

RBM and G band features from isolated SWNTs above 1 nm diameter have been measured and do not

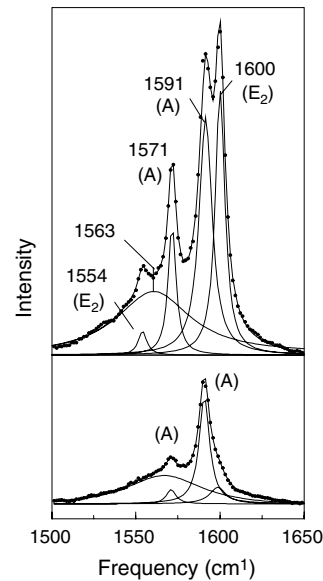


Fig. 1. G-band Raman spectra from a resonant SWNT obtained at the same spot in the Si/SiO₂ substrate. The two spectra differ on light polarization (90°). Since E_2 modes are observed in the top spectrum, we assign it as a (XX) polarized scattering geometry, which means incident and scattered light polarized crossed with nanotube axis. Note that the (XX) Raman intensity is higher than the (ZZ) intensity—incident and scattered light polarized along nanotube axis—in disagreement with the expected depolarization effect.

exhibit chirality dependence, but only diameter dependence for their frequencies. However, this is not the case for other Raman features that originates from the center of the two-dimensional (2D) graphite Brillouin zone (BZ), such as the D band feature. In such cases, the anisotropy of the 2D BZ leads to chirality dependence of the Raman frequencies for the (n, m) nanotubes. Fig. 2(a) shows a trigonal warped equienergy contour around the K point of the 2D BZ. Also shown are the cutting lines for the allowed k vectors from two SWNTs,

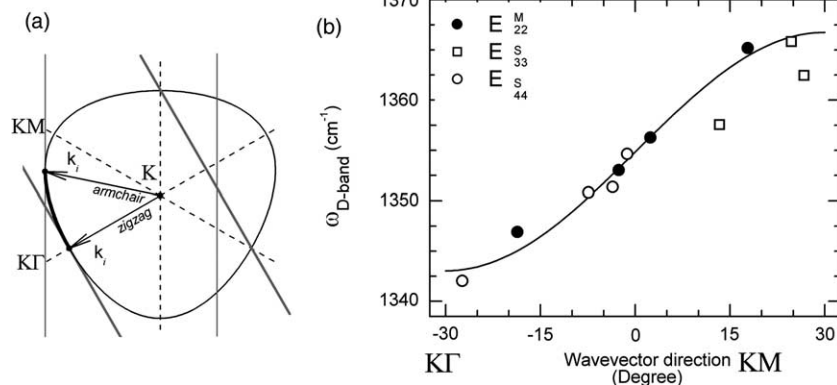


Fig. 2. (a) Schematic picture of the trigonally warped equienergy close to the K point in the 2D graphite Brillouin zone. The 1D nanotube Brillouin zone is composed by 1D parallel cutting lines, as shown for two nanotubes, a zigzag and an armchair. The two points indicated by the k_i wavevectors exhibit the same energies but different $|k_i|$. Similarly, nanotubes with same $|k_i|$ but different wavevector direction (different chiral angles) will exhibit different energies, as shown in (b).

an armchair and a zigzag. The wavevector for the equi-energy vHSs k_i is shown, and they exhibit different values due to the trigonal warping effect [6]. The phonon structure also exhibits trigonal warping effect around the K point, thus leading to chirality dependence of phonon frequencies. Fig. 2(b) shows the angular dependence of the phonon frequencies around the K point, for a given q value ($|q| = 0.24KI$). Therefore, 24 cm^{-1} difference has been measured between $0^\circ < \theta < 30^\circ$.

4. Summary

In summary, we presented resonance Raman spectra on several isolated SWNTs, focusing on the G band and D band features:

- (i) Polarization analysis of the G band feature shows clear observation of E_2 phonon modes within the single nanotube level. According to the Raman scattering selection rules, observation of E_2 phonon modes must be related to optical electronic transitions between $E_\mu^v \rightarrow E_{\mu\pm 1}^c$ electronic states. These transitions are supposed to be suppressed by the depolarization effect. Suppression of cross-polarized spectra has been observed experimentally, thus making this a controversial result that must be clarified.
- (ii) Using the (n, m) assignment we are able to identify the chirality dependence of the D band mode frequency. This chirality dependence can be used for nanotube chiral angle characterization and should be observed not only for the D band, but also for any Raman feature appearing in the spectra coming from the interior of the anisotropic 2D graphite Brillouin zone.

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