

# INFLUENCE OF VAN DER WAALS INTERACTIONS ON THE RAMAN MODES IN SINGLE WALLED CARBON NANOTUBES

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Raman spectroscopy has been used extensively to characterize SWNT bundles that are synthesized by the pulsed laser vaporization (PLV) or the electric arc (EA) methods [1-4]. A typical SWNT bundle contains on the order of 100 well-aligned SWNTs that are held together by the van der Waals (vdW) forces in a closed-packed triangular lattice. The room temperature Raman spectrum of the EA- derived SWNT bundles obtained using the 1064 nm excitation wavelength exhibits two prominent features at  $\omega_R \sim 160 \text{ cm}^{-1}$  (radial band) and  $\omega_T \sim 1590 \text{ cm}^{-1}$  (tangential band) (see Fig. 1). Three modes, previously identified with  $A_{1g}$ ,  $E_{1g}$  and  $E_{2g}$  symmetries and frequencies that are nearly independent of the tube diameter, are expected near the  $1590 \text{ cm}^{-1}$  band for achiral tubes [5]. For the chiral tubes, six modes are Raman-active with  $A_1$ ,  $E_1$  and  $E_2$  symmetries [5]. In contrast to the high frequency band at  $1590 \text{ cm}^{-1}$ , the low frequency band centered  $\sim 160 \text{ cm}^{-1}$  is identified with  $A_{1g}$  radial breathing modes whose frequency is strongly dependent on the tube diameter [5]. Consistent with the calculated mode frequencies and intensities, other weak Raman-active features have been observed in the intermediate phonon frequency region between  $\omega_R$  and  $\omega_T$  [1]. The position and the lineshape of these bands have been used extensively to determine the SWNT diameter distribution [3] and semiconducting/metallic nature of SWNTs [6]. In this

paper, we present a Raman study of bundled and isolated SWNTs, and discuss the influence of vdW interaction on the vibrational and electronic properties of SWNT bundles as they are separated into isolated SWNTs.

Recently, Chen et al. [4] reported the synthesis of soluble shortened and full-length single-walled carbon nanotubes. Details of the preparation and characterization of the solubilized tubes (S-SWNTs) are described in Ref. 4. Atomic force microscope (AFM) images showed that the majority of the bundled SWNTs were separated into small bundles (2-5 nm in diameter) and isolated tubes during the solubilization process [4]. In Fig. 1, the Raman spectrum of S-SWNTs in  $\text{CS}_2$  is compared to that obtained for bundled SWNTs, the latter in powder form. The S-SWNTs and bundled SWNTs referred to in Fig. 1 are from the same as-prepared EA material.

For an isolated SWNT, theoretical calculations have shown that the radial mode frequency  $\omega_R$  exhibits a particularly simple dependence on the tube diameter  $d$  as [3],

$$\omega_R \sim 224 \text{ cm}^{-1} \cdot \text{nm} / d. \quad (1)$$

(Henceforth, primed and unprimed notation correspond, respectively, to isolated and bundled SWNTs). Based on a high pressure Raman study of SWNT bundles and a generalized tight binding calculation which included the effects of the externally applied pressure, the simple  $\omega_R' \sim 224 \text{ cm}^{-1}\cdot\text{nm} / d'$  relation for isolated tubes was generalized to nanotubes inside a bundle by the addition of a nearly constant upshift of  $\sim 7\%$  for tubes in the diameter range  $0.7 \text{ nm} < d < 1.5 \text{ nm}$  [7]. Thus, in the case of bundled SWNTs, Eq. (1) is modified as

$$\omega_R \sim (224 \text{ cm}^{-1}\cdot\text{nm} / d) + \Delta\omega_R, \quad (2)$$

where  $\Delta\omega_R$  is the anticipated upshift due to vdW interactions.

According to Eq. 2, the observed upshift in  $\omega_R$  from bundled to S-SWNTs in Fig. 1 is anomalous, since the loss of inter-tube interactions in S-SWNTs would be expected to soften  $\omega_R$  relative to its frequency of  $160 \text{ cm}^{-1}$  observed in the Raman spectrum of bundled SWNTs. Shifts in  $\omega_R$  or  $\omega_T$  have also been observed in doped nanotube bundles, where they have been related to the charge-transfer between the nanotubes and the alkali metal (downshift) or halogen dopants (upshift) [8]. However, charge transfers induced by doping were found to affect *both* the radial and tangential mode frequencies by large amounts [8] unlike the tube-tube coupling which affects mainly  $\omega_R$  and not  $\omega_T$  (see for example Fig. 1).

It is also of interest to note from the right hand inset to Fig. 1 that the loss of inter-tube interactions in the S-SWNTs in  $\text{CS}_2$  leads to narrower line widths for the tangential band relative to those observed in bundled SWNTs. A Lorentzian lineshape analysis reveals at least four narrow sub-bands for the bundled SWNTs and a single narrow mode for S-SWNTs in  $\text{CS}_2$ . Similarly, from the left hand inset in Fig. 1 for the radial band, a reduced number of Lorentzians is observed in the spectrum of S-SWNT sample when compared to that of the bundled SWNTs.

The spectra in Fig. 2 suggest that similar upshift in  $\omega_R$  is observed in PLV synthesized bundled SWNTs and *solid* full length PLV synthesized S-SWNTs (i.e., solubilized full length SWNTs obtained by evaporating the organic solvents) using visible excitation wavelengths (514.5 and 647.1 nm). Unfortunately, the Raman spectra of S-SWNT dissolved in organic solvents ( $\text{CS}_2$  or THF) obtained using visible laser excitations showed strong luminescence, and prevented us from detecting the radial or the tangential bands. The origin of this luminescence is not

understood at present and warrants an independent study. The radial bands in solid S-SWNTs are consistently upshifted relative to those of bundles SWNTs in all spectra depicted in Fig. 2 (left figure). On the other hand, narrowing of the tangential band seen in S-SWNTs in  $\text{CS}_2$  (see right hand inset in Fig. 1) is absent in the tangential bands in solid S-SWNTs (Fig. 2 right figure). At least two important conclusions can be drawn from the Raman data presented in Fig. 2:

- (i) Both semiconducting and metallic tubes exhibit  $\sim 10 \text{ cm}^{-1}$  upshift as bundled tubes are solubilized. [Pimenta *et al.* [6] have argued that the 647.1 nm excitation couples predominantly to metallic tubes in the sample.]
- (ii) The relatively broader tangential band in solid S-SWNTs compared to that of S-SWNT in  $\text{CS}_2$ , suggests that the organic solvent - nanotube interactions have a smaller influence on the tangential mode lifetime than the tube-tube interactions in solid S-SWNTs.

We now discuss the anomalous upshift in  $\omega_R$  in the context of our calculations of the electronic density of states (DOS) for isolated and bundled nanotubes with a diameter distribution representative of the sample. A density functional formalism within the local density approximation (LDA) was used [9]. Our results indicate that inter-tube coupling causes an additional band dispersion of  $\sim 0.2 \text{ eV}$  which not only opens up a pseudo-gap at Fermi level ( $E_F$ ), but also broadens the van Hove singularities by  $0.2 \text{ eV}$  and the positions of the peaks in DOS shift away from  $E_F$ . This leads to a net increase of the energy spacing  $\Delta_1$  between the first, and  $\Delta_2$  between the second, pair of van Hove singularities in the electronic DOS for bundled nanotubes (Table 1).

The combined scanning tunneling spectroscopy studies on PLV synthesized SWNTs [10,11] and optical transmission spectra taken from SWNTs synthesized using Ni:Y catalyst in the EA method [12] yield the approximate relations for semiconducting and metallic nanotubes, respectively:

$$\Delta_1' = \alpha / d' \quad (3a).$$

In the above relation between  $\Delta_1'$  and the tube diameter  $d'$ , tight binding theory shows that  $\alpha = 2\gamma_0 d_{C-C}$  for semiconducting tubes and  $\alpha = 6\gamma_0 d_{C-C}$  in metallic tubes where  $\gamma_0$  is the nearest neighbor overlap energy (or the transfer integral of a tight binding model) and  $d_{C-C}$  is the nearest neighbor distance in the hexagonal network. Amending this equation for intertube interactions, we have

$$\Delta_1 = \alpha / d + \delta\Delta_1 \quad (3b).$$

The  $\sim 10 \text{ cm}^{-1}$  upshift can be understood and estimated numerically via Eqs. (1) - (3). Using the calculated value for  $\Delta\omega_R \sim 14 \text{ cm}^{-1}$  in bundled tubes in Ref. 7, Eq. (2) can be re-written as

$$\omega_R \sim 224 \text{ cm}^{-1}\cdot\text{nm} / d + 14 \text{ cm}^{-1} \quad (4).$$

Because of the resonant Raman scattering process in SWNTs, at a fixed excitation laser energy ( $E_{\text{laser}} = \Delta_1$ ), it follows from Eqs. (3a) and (3b) that the following equality should be satisfied as the bundles are processed into isolated tubes,

$$\alpha / d' = \alpha / d + 0.2 \text{ eV} \quad (5).$$

For  $\gamma_0 \sim 2.9 \text{ eV}$  [13],  $d_{C-C} \sim 1.42 \text{ \AA}$  and  $\omega_R \sim 224 \text{ cm}^{-1}\cdot\text{nm} / d'$  it follows from Eqs. 2, 4 and 5 that  $\omega_R' - \omega_R \sim 40 \text{ cm}^{-1}$  for semiconducting tubes, and  $\sim 4 \text{ cm}^{-1}$  for metallic tubes. Furthermore, for fixed laser frequency, we see that the laser couples preferentially to isolated tubes with diameter  $d'$  and bundled tubes with diameter  $d$ , where  $\Delta d = d' - d \cong -0.2 d^2 / \alpha$ . Regardless of the tube type (semiconducting or metallic), the net result of de-bundling is an apparent upshift in the Raman active radial breathing mode frequency for the S-SWNTs using the same excitation frequency.

In conclusion, we have measured the Raman spectrum of nearly isolated SWNTs in solution and compared it to that obtained from the same starting material where the tubes are present in ordered bundles or ropes. Interestingly, the radial mode frequencies for the tubes in solution are found to be  $\sim 10 \text{ cm}^{-1}$  higher than those observed for tubes in a rope, in apparent contradiction to lattice dynamics predictions. We suggest that there is no such contradiction, and propose that the upshift is due rather to a decreased energy spacing of the van Hove singularities in isolated tubes over the spacings in a rope, thereby allowing the same

laser excitation to excite different diameter tubes in these two samples.

## Acknowledgements

AMR and RCH acknowledge financial support from the NSF MRSEC grant No. 9809686 and PCE through the NSF MRSEC grant No. 9809686 and ONR grant # N00014-99-1-0619). UDV acknowledges partial support of this research by the Donors of The Petroleum Research Fund, administered by the American Chemical Society. YKK and DT acknowledge financial support by the Office of Naval Research and DARPA under Grant Number N00014-99-1-0252. US acknowledges a scholarship from the Fulbright-Commission.

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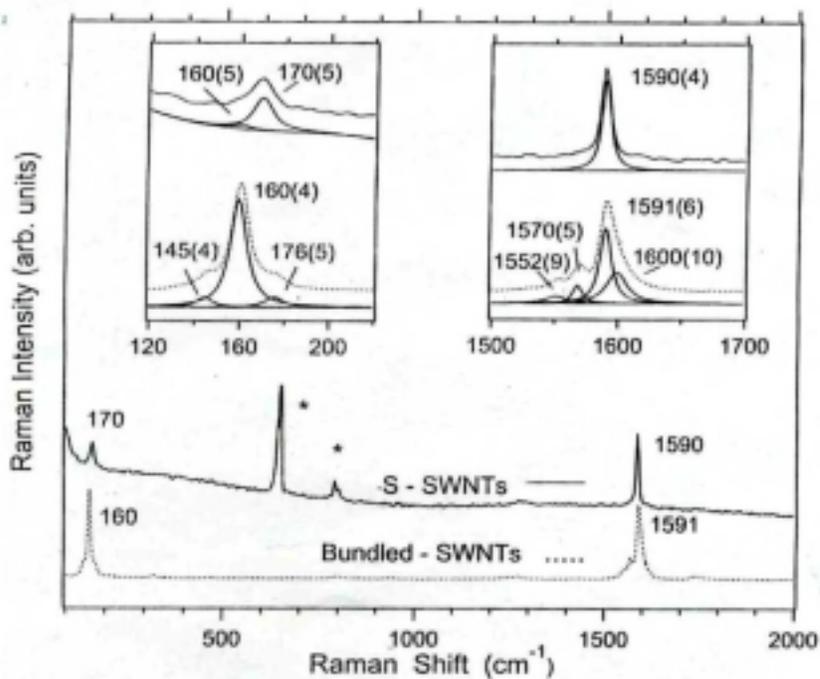


Fig. 1 : Room temperature Raman spectrum of arc synthesized bundled SWNTs and solubilized SWNTs (S-SWNTs) in CS<sub>2</sub> (excitation wavelength = 1064 nm). The peaks identified by \* are attributed to CS<sub>2</sub>. The tangential band intensity is set to a constant peak intensity value so that the radial band intensities in the two spectra can be compared. Left and right hand insets show, respectively, the deconvolution of the radial and tangential bands in bundled and S-SWNTs. The vertical and horizontal axes for the two insets correspond, respectively, to the Raman intensity and shift. The numbers within parentheses refer to the full width at half maximum (FWHM) intensity of the Raman lines.

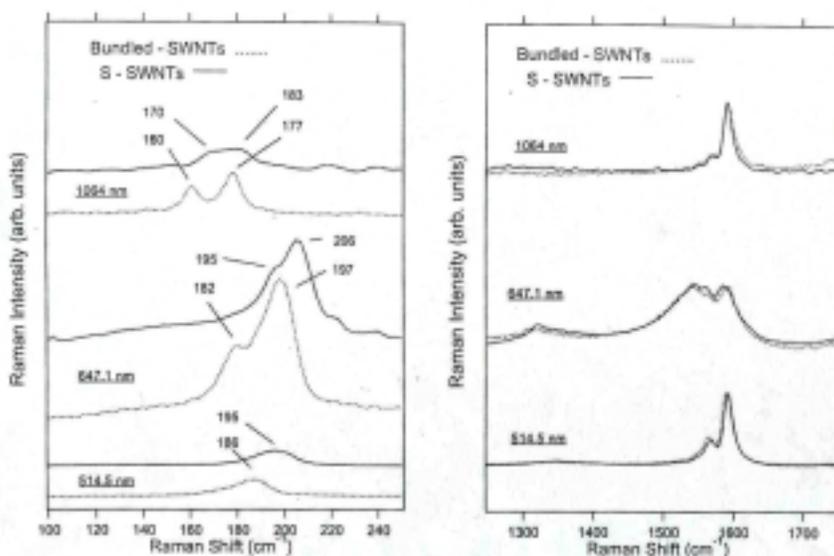


Fig. 2 : Comparison of the radial (left figure) and tangential bands (right figure) in the PLV synthesized bundled and S-SWNTs for three laser excitation energies. The tangential bands for the bundled and S-SWNTs are superimposed for comparison of the linewidths.

Table 1 : Calculated energy difference  $\Delta_1$  between the first and  $\Delta_2$  between the second pairs of van Hove singularities in the electronic density of states for isolated tubes and weakly interacting tubes in a bundle. The difference between the tube and bundle values is denoted by  $\delta\Delta$ . All energy values are in eV units.

$(n, n)$	$\Delta_1(\text{tube})$	$\Delta_1(\text{rope})$	$\delta\Delta_1$	$\Delta_2(\text{tube})$	$\Delta_2(\text{rope})$	$\delta\Delta_2$
(8,8)	2.03	2.23	0.20	3.69	3.89	0.20
(9,9)	1.83	1.99	0.16	3.39	3.55	0.16
(10,10)	1.64	1.84	0.20	3.12	3.29	0.17
(11,11)	1.49	1.63	0.14	2.87	2.98	0.11