Ultra-low frequency Raman spectroscopy of SWNTs under high pressure

Y. Shen^a, N. Quirke^b, and D. Zerulla^a

^aSchool of Physics, University College Dublin, Belfield, Dublin 4, Ireland

^bDepartment of Chemistry, Imperial College London, London, SW7 2AZ, UK

ABSTRACT

Radial deformation phenomena of carbon nanotubes (CNTs) are attracting increased attention because even minimal changes of the CNT's cross section can result in significant changes of their electronic and optical properties. It is therefore important to have the ability to sensitively probe and characterize this radial deformation. High pressure Raman spectroscopy offers a general and powerful method to study such effects in SWNTs. In this experimental work, we focus in particular on one theoretically predicted Raman vibrational mode, the so-called "Squash Mode" (SM), named after its vibrational mode pattern, which has an E_{2g} symmetry representation and exists at shifts below the radial breathing mode (RBM) region. The Squash mode was predicted to be more sensitive to environmental changes than the RBM.

Here we report on a detailed, experimental detection of SMs of aligned SWNT arrays with peaks as close as 18 cm^{-1} to the laser excitation energy. Furthermore, we investigate how the SM of aligned CNT arrays reacts when exposed to a high pressure environment of up to 9 GPa. The results confirm the theoretical predictions regarding the angular and polarization dependent variations of the SM's intensity with respect to their excitation. Furthermore, clear Raman upshifts of SM under pressures of up to 9 GPa are presented. The relative changes of these upshifts, and hence the sensitivity, are much higher than that of RBMs because of larger radial displacement of some of the participating carbon atoms during the SM vibration.

These novel ultra-sensitive Raman SM shifts of SWNTs provide enhanced sensitivity and demonstrate new opportunities for nano-optical sensors applications.

Keywords: Single walled carbon nanotubes, Raman spectroscopy, squash mode, high pressure

1. INTRODUCTION

Single walled carbon nanotubes (SWNTs) are promising one-dimensional nanomaterials because of their unique electronic and optical properties. Since their identification by Iijima in 1991,¹ the novel electronic,² mechanical,³ fluidic,⁴ and chemical⁵ properties of carbon nanotubes (CNTs) have been subject to an intense research effort. Depending on their chirality and diameter, SWNTs can be metallic or semiconducting. The former are of interest as nanowires and effective heat transporters,⁶ while the latter can be used as transistors⁷ and bio-sensors.^{8,9}

Many CNT properties are sensitive to environmental change, especially vibrational modes,^{10,11} so that exciting applications in nano-sensors and nano-medicine are envisaged.¹² One particularly important probe of nano-tube behavior is Raman scattering, indeed SWNT materials are usually characterised using the linear diameter dependence of the low frequency ($100\text{--}400\text{ cm}^{-1}$) radial breathing mode (RBM).¹³ The frequencies of RBMs are predicted to be inverse functions of their diameter d , $\omega_{\text{RBM}} = C_1/d + C_2$, where C_1 and C_2 are empirical parameters which are also depending on the CNT environment. The G band, in the region $1580\text{--}1600\text{ cm}^{-1}$, corresponds to in plane vibrations of carbon atoms presenting in most graphite-like materials.

In addition to the G-band and RBM that enable e.g. the determination of tube diameter and chirality, another vibrational mode has been theoretically predicted, the so-called "Squash Mode" (SM), named after its vibrational mode pattern (see Fig. 1 (a)), which has an E_{2g} symmetry representation and exists below the RBM

Figure 1. (a) Illustration of animated Squash Mode vibrational behavior, taken from a modified MM2 force field simulation of a (10,0) nanotube. (b) AFM image of our sample demonstrating high density vertically aligned SWNTs with varying lengths. Shorter tubes close to the protruding long tubes are not displayed because of the physical aspect ratio of the AFM tip. In addition, the sketch of the excitation and detection geometry are presented.

region ($<100 \text{ cm}^{-1}$).¹⁴ Note that symmetric and asymmetric squash modes are energetically degenerate for our long CNTs.^{15,16}

From non-resonant bond-polarization theory, the frequency of SMs is predicted to be proportional to $r^{-1.95 \pm 0.03}$ with an intensity of the same magnitude as the G-band, the most intense feature of the SWNT spectrum.^{14,17} The mode is also predicted to be highly sensitive to the effects of bundling, showing a theoretical upshift of 25 cm^{-1} compared to an upshift of 6 cm^{-1} of the RBM for an identical system.¹⁸ Thus we expect the SM to be even more sensitive to environmental changes than the RBM and therefore a more sensitive probe.

The first experimental evidence of the existence of this mode using surface enhanced Raman spectroscopy (SERS) was reported in the work by Alexander A. Puretzky *et al.*¹⁹ In their investigation SERS was chosen to amplify the SM signal due to the severe experimental challenges faced in making measurements very close to the elastic scattered laser light. While SERS is an ideal tool to boost the sensitivity of Raman signals, its inherent molecule specific sensitivity and the fact that its directionality is linked to the electromagnetic field distribution at the SERS active interface makes it less attractive for our angle dependent studies as illustrated below.

High pressure Raman spectroscopy offers a powerful method to study the vibrational and deformation related properties of SWNTs. Ruoff *et al.* observed the van der Waals (vdWs) interaction induced radial deformation of two adjunct SWNTs using transmission electronic microscope (TEM) in 1993.²⁰ Since then, the radial deformation of carbon nanotubes (CNTs) has attracted an ever increasing attention both experimentally and theoretically.^{21–24} As an extreme sensitive radial vibration, high pressure SM analyses are of great significance to understand the radial deformation of CNTs.

Further author information: (Send correspondence to Dr. D. Zerulla)

Dr. D. Zerulla: E-mail: dominic.zerulla@ucd.ie, Telephone: +353 1 716 2507

In this paper, we report clear experimental evidence using polarisation angular resolved Raman spectroscopy of the existence of the squash modes which were originally predicted, using zone-folding and force-constant models, by Saito *et al.*¹⁴ Additionally, we have been able to fully assign all low frequency modes to the correct chirality/diameter parameters using the theoretical predictions in conjunction with cross correlations to simultaneously recorded RBMs.²⁵ Furthermore, clear Raman upshifts of SM under pressure up to 9 GPa are presented.

2. EXPERIMENTS

Because of the extreme closeness of the SM related vibrational modes in respect to the laser line, the experiments are challenging. Our apparatus employs a stabilized single frequency laser (associated bandwidth of <1 MHz) at 532 nm (Torus, Laser Quantum) which has been additionally filtered for spontaneous emission (ASE filter), in conjunction with an ultrasharp line-rejection filter consisting of an eXtreme Low-frequency Filter with OD8 suppression (XLF, ONDAX, realized via a volume Bragg grating combination). Finally, the collimated light is dispersed by a high throughput HoloSpecTM f 1.8 spectrometer (Kaiser Optical) utilising a volume-phase holographic (VPHTM) transmission grating and mapped onto a cooled Andor Newton EMCCD camera. Unlike most commercially available systems, this combination delivers unmatched rejection of the laser line, permitting spectral features to be recorded that are <8 cm⁻¹ away from the laser energy, but retains a very high throughput and thus sensitivity.

According to Saito's theoretical predictions, the intensity of the SM of SWNTs is highly orientation and polarisation dependent with respect to both the incoming laser direction (must be along the SWNT main axis for maximum intensity) and the detection direction (X) which should be perpendicular to the incoming direction (Z). Such a configuration can only be reached when the SWNTs are oriented with respect to a fixed framework, e.g. being aligned on a flat substrate. Here, we have chosen to align our SWNTs vertically on a smooth aluminium substrate as sketched in Fig. 1 (b). The incident angle θ of the laser light is 6.3° of normal within the plane of excitation which itself is perpendicular to the sample substrate and the plane of detection. Please note that p and s are the notations of the light polarisation in the reference frame of the plane of detection, where p-polarisation means the wave vector of the beam is parallel to the plane (0°, or Y for incidence and Z for detection) and s-polarisation means it is perpendicular (90°, or X for incidence and Y for detection). The angle of detection ϕ is 86.6° against the vertically aligned SWNTs which are normal to the sample plane. These angles are chosen to maximise the Raman excitation and effective detection cone. Moreover, maintaining θ close to 0° and ϕ close to 90°, the polarisation data is virtually unperturbed.

Aluminium has been chosen, because unlike gold and silver it does not generate strong, and here unwanted, surface enhanced Raman scattering. High quality, non-capped SWNTs which exhibit a very small size distribution centred around a diameter of 0.8 nm (>50 % population (6,5) chirality) have been used in the array.^{26,27} The resulting vertically aligned configuration was independently confirmed using atomic force microscopy as demonstrated in Fig. 1 (b).

For the high pressure detection, the aligned samples are placed inside a diamond anvil cell (*Diacell*[®] μ ScopeDAC-HT(G)), which is capable of generating uniform (isotropic) high hydrostatic pressures. The sample is immersed into a 4:1 mixture of methanol and ethanol which is commonly used as the pressure transmission medium (PTM) of choice. The DAC has an internal gasket heater that operates up to 600 °C.

3. RESULTS

Complete Raman spectra have been recorded from the arrays with the laser beam at normal incidence to the sample. Furthermore, a polariser was inserted into the path on the detection side and the emitted Raman scattering was analysed in 15° steps from p-polarisation (Z) to s-polarization (Y) as depicted in Fig. 2. Besides the presence of the G-band and its polarisation dependent intensity which is widely accepted as proof of the presence of nanotubes,²⁸ Fig. 2 also shows the RBM in the 200-400 cm⁻¹ region and its polarisation dependent variations. The polarisation dependent results are consistent with vertically aligned SWNTs. Both modes will be further analysed at the end of this proceeding. The low vibrational region of the Raman spectrum is magnified

Figure 2. Raman spectra of SM, RBM and G-mode regions of vertically aligned SWNTs for differing polarisation angles of detection. See Fig. 1 for setup geometry.

Figure 3. (a) Enlarged extreme low frequency Raman region revealing distinctive squash modes of vertically aligned SWNTs with polarisation angle equal to 90° . (b) Raman spectrum and peak fitting results of the RBM region of vertically aligned SWNTs.

by three times, which additionally probes the anisotropic behavior of Raman intensity in this region by analysing the polarisation angle of the scattered light.

A detailed analysis of the low frequency region presented in Fig. 3 (a) reveals four peaks (a, b, c, and d) in the SM region between 17 cm^{-1} and 43 cm^{-1} . An additional peak (e) at $86\text{--}90\text{ cm}^{-1}$ represents bundled SWNTs as confirmed by Kahn and Lu.¹⁸ All found peaks have been fully assigned in Table 1 as detailed below.

Fig. 3 (b) shows an enlarged high quality spectrum of the RBM region including peak fitting data which will be used to analyse the chirality composition of the SWNT arrays in conjunction with the results of the SM region. Extreme care needs to be taken in the assignment of the SWNT chiralities because the Raman intensity of similar tube diameters can vary by orders of magnitude.²⁹ The chiralities assigned based on SM peaks at the excitation wavelength 532 nm are the major components of our sample, which is additionally confirmed by the analysis provided by the manufacture.²⁶ More chiralities can be detected using different excitation energies. The assignments of the modes are consistent with those of Dresselhaus *et al.*³⁰

As predicted by zone-folding and force-constant models,¹⁷ the intensity of the SMs is suppressed at s-polarisation but reaches a maximum for p-polarised light and thus has the inverse behavior of the RBM, which is shown in Fig. 2 and more clearly demonstrated in Fig. 5. The relative intensity of all three regions (G-mode, RBM, SM) will be further analysed below as a function of scattering polarisation angle.

Before the completion of the polarisation analysis, this work focuses firstly on the minutiae of the SM. Fig. 3 (a) shows the SM region in more detail. Five clearly distinguishable peaks can be identified and are listed in Table 1. Additionally, Fig. 4 shows our experimental results (squares) in comparison to a diameter dependent

Figure 4. Resonant frequency of SM dependent on diameter. The peaks a, b, c, and d are marked in Fig. 3 (a) See Table 1 for detailed assignments.

Table 1. Assignments of Squash Modes to SWNT chiralities based on diameter and RBM

ω_{SM} (cm ⁻¹)	Linewidth (FWHM) (cm ⁻¹)	Diameter range (Å)	Chirality	RI of RBM	ω_{RBM} (cm ⁻¹)
a 18.29	9.59	12.53- 13.31	(10,9)	< 0.001	185*
b 38.31	5.96	8.14-9.40	(7,6)	0.008	261*
c 42.10	8.41	8.14-9.40	(8,4)	3.402	278
d 55.47	9.20	7.05-8.14	(6,5) (10,0)	0.065 4.637	315 295
e 88.79	8.12	<<7.05/ bundle			

*were not found experimentally in the RBM region because of their extremely low relative intensity.

SM model defined as $y = ax^b$ where $b = -1.91 \pm 0.36$ (red line), which matches closely the theoretical prediction that the frequency of the squash mode is proportional to $r^{-1.95 \pm 0.03}$.¹⁷ As a result, this relation has been used as an additional model to assign Raman peaks to different SWNT diameters in Table 1.

Comparing the RBM data with the theoretical predictions for the mainly diameter dependent SM frequencies and the measured SM modes allows for a complete identification of the chirality distribution within the aligned sample.

Only two peaks have solely been assigned using tight-binding theory.^{18,31,32} However, their low Raman intensity (RI) and as a consequence their invisibility in the RBM region has been predicted^{18,31,32} and therefore fits the model perfectly. Moreover, it demonstrates the utility of the SM region which can track certain SWNT species which are not traceable in the RBM region.

Furthermore, we compare the polarisation dependent anisotropy of the aligned samples (array) in the G-mode (A_{1g} representation), RBM, and SM regions with the theoretical predictions. The polarisation dependent Raman scattering intensity is plotted against the analyser angle (0° = p-polarization (Z), 90° = s-polarization (Y)) in Fig. 5 providing further evidence that the found ultra-low frequency modes are indeed the sought after SMs of SWNTs. Their polarisation dependent intensity is inverse to the RBM and G-mode behavior as predicted by Saito. Recording both regions makes it possible to choose the stronger signal depending on the analyser setting. Finally, the relative wavelength-shift upon changing chirality/diameter of the CNTs (a measure of the mode's sensitivity with respect to environmental changes) is larger for the SM region as the shifts scale as:

$$\frac{\Delta\omega_{SM}}{\omega_{SM}} = \frac{87.79 - 18.29}{87.79} = 0.7917 \quad (1)$$

$$\frac{\Delta\omega_{RBM}}{\omega_{RBM}} = \frac{315 - 185}{315} = 0.4127 \quad (2)$$

Figure 5. Polarization dependent Raman intensity (RI) of the (a) SM, (b) and RBM and (c) G-mode.

4. HIGH PRESSURE ANALYSIS

Additionally, low frequency region Raman spectra of SWNT arrays exposed to high pressure environments (up to 9 GPa) are shown in the following. Figure 6 displays the full set of spectra for the RBM region on the left and for the SM region on the right.

Figure 6. Raman spectra of RBM and SM regions of vertically aligned SWNTs under different pressure conditions.

In general, the RBM peak intensity of all different types of CNTs (with differing chiralities/diameters) within our sample is continuously decreasing when the pressure is increasing. The RBM peaks almost disappear at a pressure of 9 GPa. Likewise, the intensity of SM peaks is reduced at higher pressures.

This is because of the fact that the pressure induced changes in energy difference between the singularities in the valence and conduction bands in the 1D density of electronic states will reduce the resonance enhancement

in the Raman cross section. Furthermore, the enhanced inter-tube interactions at higher pressures resulting in increased density of electronic states near the Fermi level can also contribute to reduced Raman intensity.³³ In brief, under high external compression, resonance in the radial direction is suppressed.

Furthermore, both modes experience frequency upshifts. In a simplified model, the relative shifts for squash modes are high because selected atoms have a comparably large radial displacement in their vibrational pattern. Because of interactions with neighboring tubes this is energy intensive.

5. CONCLUSION

In summary, we report an experimental direct polarisation dependent detection of SWNT Squash Modes (E_{2g}) in the ultra-low frequency Raman region 18-100 cm^{-1} . We have assigned different chiralities of our SWNT samples by peak fitting the highly resolved Raman spectra and cross-correlating the experiment results with the theoretical relative Raman intensities of the SM and RBM region. The sensitivity of the SM frequency against changes of diameter/chirality was analysed and it was confirmed that its sensitivity is higher than the sensitivity of the RBM frequency shift. Finally the polarisation dependent anisotropies of the G-mode, RBM, and SM-regions has been measured and we show that the SM polarisation dependent Raman scattering indeed shows inverse intensity dependence compared to other Raman regions.

Furthermore, clear Raman peaks of SM under pressure up to 9 GPa are presented. The SM upshifts are much higher than that of the RBM because of greater radial displacement of selected carbon atoms during the SM vibrational pattern. Further analysis including the Raman shifts and the nanotube cross section changes are under study.

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REFERENCES

- [1] Iijima, S., "Helical microtubules of graphitic carbon," *Nature* **354**(6348), 56–58 (1991).
- [2] Ouyang, M., Huang, J.-L., and Lieber, C. M., "Fundamental electronic properties and applications of single-walled carbon nanotubes," *Acc. Chem. Res.* **35**(12), 1018–1025 (2002).
- [3] Sears, A. and Batra, R. C., "Macroscopic properties of carbon nanotubes from molecular-mechanics simulations," *Phys. Rev. B* **69**(23), 235406 (2004).
- [4] Whitby, M. and Quirke, N., "Fluid flow in carbon nanotubes and nanopipes," *Nature Nanotech.* **2**(2), 87–94 (2007).
- [5] Dai, H., "Carbon nanotubes: synthesis, integration, and properties," *Acc. Chem. Res.* **35**(12), 1035–1044 (2002).
- [6] Yao, Z., Kane, C. L., and Dekker, C., "High-field electrical transport in single-wall carbon nanotubes," *Phys. Rev. Lett.* **84**(13), 2941 (2000).
- [7] Tans, S. J., Verschueren, A. R., and Dekker, C., "Room-temperature transistor based on a single carbon nanotube," *Nature* **393**(6680), 49–52 (1998).
- [8] Kong, J., Franklin, N. R., Zhou, C., Chapline, M. G., Peng, S., Cho, K., and Dai, H., "Nanotube molecular wires as chemical sensors," *Science* **287**(5453), 622–625 (2000).
- [9] Li, J., Lu, Y., Ye, Q., Cinke, M., Han, J., and Meyyappan, M., "Carbon nanotube sensors for gas and organic vapor detection," *Nano Lett.* **3**(7), 929–933 (2003).
- [10] Henrard, L., Hernandez, E., Bernier, P., and Rubio, A., "van der waals interaction in nanotube bundles: consequences on vibrational modes," *Phys. Rev. B* **60**(12), R8521 (1999).
- [11] Rao, A. M., Chen, J., Richter, E., Schlecht, U., Eklund, P. C., Haddon, R. C., Venkateswaran, U. D., Kwon, Y. K., and Tomanek, D., "Effect of van der waals interactions on the raman modes in single walled carbon nanotubes," *Phys. Rev. Lett.* **86**(17), 3895 (2001).

- [12] Kostarelos, K., Bianco, A., and Prato, M., "Promises, facts and challenges for carbon nanotubes in imaging and therapeutics," *Nature Nanotech* **4**(10), 627–633 (2009).
- [13] Strano, M. S., Doorn, S. K., Haroz, E. H., Kittrell, C., Hauge, R. H., and Smalley, R. E., "Assignment of (n, m) raman and optical features of metallic single-walled carbon nanotubes," *Nano Lett.* **3**(8), 1091–1096 (2003).
- [14] Saito, R., Dresselhaus, G., and Dresselhaus, M. S., [*Physical properties of carbon nanotubes*], vol. 4, World Scientific (1998).
- [15] de Frin, C., Quirke, N., and Zerulla, D., "Finite length and solvent analysis effects on the squash mode of single walled carbon nanotubes," *Appl. Phys. Lett.* **103**(15), 153109 (2013).
- [16] de Frin, C., Lestini, E., Quirke, N., and Zerulla, D., "Environmental effects on the raman spectra of single walled carbon nanotubes," *Physica Status Solidi (b)* **250**(12), 2635–2638 (2013).
- [17] Saito, R., Takeya, T., Kimura, T., Dresselhaus, G., and Dresselhaus, M. S., "Raman intensity of single-wall carbon nanotubes," *Phys. Rev. B* **57**(7), 4145 (1998).
- [18] Kahn, D. and Lu, J. P., "Vibrational modes of carbon nanotubes and nanoropes," *Phys. Rev. B* **60**(9), 6535 (1999).
- [19] Puretzky, A. A., Geohegan, D. B., and Rouleau, C. M., "Narrow and intense resonances in the low-frequency region of surface-enhanced raman spectra of single-wall carbon nanotubes," *Phys. Rev. B* **82**(24), 245402 (2010).
- [20] Ruoff, R. S., Tersoff, J., Lorents, D. C., Subramoney, S., and Chan, B., "Radial deformation of carbon nanotubes by van der waals forces," *Nature* **364**, 514 (1993).
- [21] Sharma, S. M., Karmakar, S., Sikka, S., Teredesai, P. V., Sood, A., Govindaraj, A., and Rao, C., "Pressure-induced phase transformation and structural resilience of single-wall carbon nanotube bundles," *Phys. Rev. B* **63**(20), 205417 (2001).
- [22] Lopez, M., Rubio, A., Alonso, J., Qin, L.-C., and Iijima, S., "Novel polygonized single-wall carbon nanotube bundles," *Phys. Rev. Lett.* **86**(14), 3056 (2001).
- [23] Elliott, J. A., Sandler, J. K., Windle, A. H., Young, R. J., and Shaffer, M. S., "Collapse of single-wall carbon nanotubes is diameter dependent," *Phys. Rev. Lett.* **92**(9), 095501 (2004).
- [24] Hasegawa, M. and Nishidate, K., "Radial deformation and stability of single-wall carbon nanotubes under hydrostatic pressure," *Phys. Rev. B* **74**(11), 115401 (2006).
- [25] Shen, Y., Quirke, N., and Zerulla, D., "Polarisation dependence of the squash mode in the extreme low frequency vibrational region of single walled carbon nanotubes," *Appl. Phys. Lett.* **106**(20), 201902 (2015).
- [26] Source: SOUTH WEST NANOTECHNOLOGIES produced via the CoMoCAT method SG 65, Length 450-2000 nm, Carbon content 90 % - 99 %, Chirality distribution >50 % (6,5) .
- [27] Source: purchased from PICOWORX .
- [28] Costa, S., Borowiak-Palen, E., Kruszynska, M., Bachmatiuk, A., and Kalenczuk, R., "Characterization of carbon nanotubes by raman spectroscopy," *Mater. Sci-Poland* **26**(2), 433–441 (2008).
- [29] Sato, K., Saito, R., Nugraha, A. R., and Maruyama, S., "Excitonic effects on radial breathing mode intensity of single wall carbon nanotubes," *Chem. Phys. Lett.* **497**(1), 94–98 (2010).
- [30] Dresselhaus, M. S., Dresselhaus, G., Saito, R., and Jorio, A., "Raman spectroscopy of carbon nanotubes," *Phys. Rep.* **409**(2), 47–99 (2005).
- [31] Li, X. P., Nunes, R. W., and Vanderbilt, D., "Density-matrix electronic-structure method with linear system-size scaling," *Phys. Rev. B* **47**(16), 10891 (1993).
- [32] Xu, C., Wang, C., Chan, C., and Ho, K., "A transferable tight-binding potential for carbon," *J. Phys.: Condens. Matter* **4**(28), 6047 (1992).
- [33] Teredesai, P., Sood, A., Muthu, D., Sen, R., Govindaraj, A., and Rao, C., "Pressure-induced reversible transformation in single-wall carbon nanotube bundles studied by raman spectroscopy," *Chem. Phys. Lett.* **319**(3), 296–302 (2000).