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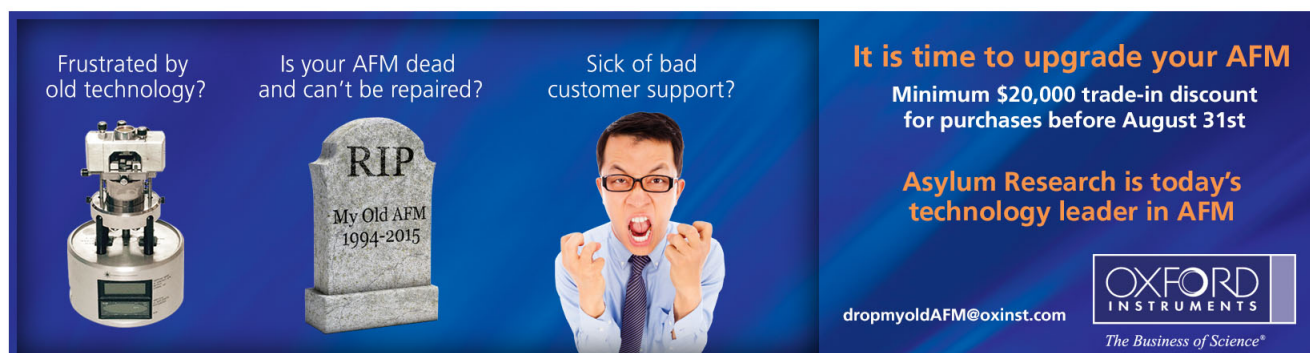
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Polarisation dependence of the squash mode in the extreme low frequency vibrational region of single walled carbon nanotubes

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There is considerable interest in the vibrational modes of carbon nanotubes as they can be used to determine interaction potentials. In particular, theory predicts the appearance of so called squash modes (SMs, with E_{2g} symmetry representation) at very low frequencies. These SMs are expected to be extremely sensitive to environmental changes and thus ideal as nanoscale probes. Here, we report clear experimental evidence for the existence of SMs of ordered, dry, single walled carbon nanotube (SWNT) arrays with peaks as close as 18 cm^{-1} to the laser excitation. Furthermore, we confirm the theoretical predictions regarding the angular and polarisation dependent variations of the SM's intensity with respect to the excitation. Additionally, using both SM and radial breathing mode data, we unambiguously assign the chirality and diameter of the SWNTs in our sample.

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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 (Ref. 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 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. These parameters have been experimentally determined via Raman spectroscopy: C_1 ranges from 204 cm^{-1} to 248 cm^{-1} while C_2 has an average value of 14 cm^{-1} as reported by Araujo *et al.* and Michel *et al.*^{14,15} Group theory selection rules indicate that there are up to 16 Raman active modes of SWNTs, including the well characterised RBM and the G mode. The G band is found in the region $1500\text{--}1600\text{ cm}^{-1}$, while the RBM is found between 100 and 400 cm^{-1} , depending on the nanotube's diameter and chirality.¹⁶

The behavior of SWNTs regarding differing environments has been studied especially in the context of solvent induced shifts of RBMs which can be used to determine SWNT/solvent interaction potentials.¹⁷ Further RBM-like modes related to radial deformation are found due to either evolution of the E_2 resonances with pressure¹⁸ or external

hydrostatic pressure,¹⁹ while molecular dynamics simulations predict mixing between SWNTs and solvation RBMs.¹⁷ Below the RBM frequencies, there are a range of interesting vibrational (and associated harmonic) modes, some of which have been reported to play a role for atom collision induced resistivity changes of CNTs.^{20,21}

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 region ($<100\text{ cm}^{-1}$).²² Note that symmetric and asymmetric squash modes are energetically degenerated for the here used long CNTs.^{23,24}

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.^{22,25} 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.²⁶ Thus, we expect the SM to be even more sensitive to environment 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 pioneering work by Poretzky *et al.*²⁷ 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.

In this letter, we report the first experimental evidence using polarisation angular resolved Raman spectroscopy of the existence of the squash modes which were originally

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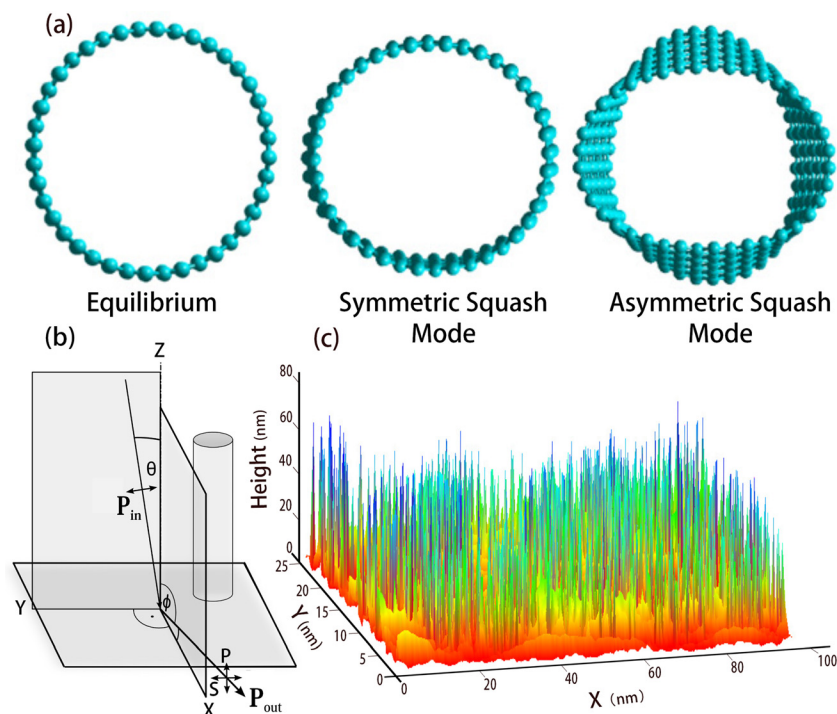


FIG. 1. (a) Illustration of animated squash mode vibrational behavior, taken from a modified MM2 force field simulation of a (10,0) nanotube. (b) Sketch of the excitation and detection geometry; (c) AFM image of the here used sample demonstrating high density vertically aligned SWNTs with varying lengths. Shorter tubes close to the protruding long tubes are not displayed because of the physical aspect ratio of the AFM tip.

predicted, using zone-folding and force-constant models, by Saito *et al.*²² 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. Furthermore, using highly ordered nano-arrays of SWNTs, we have recorded the angular dependent variations in SM peak intensity with respect to spatial orientation and polarisation and compare these results with theory.

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 $<8\text{ cm}^{-1}$ 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 are 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.^{28,29} The resulting vertically aligned configuration was independently confirmed using atomic force microscopy, as demonstrated in Fig. 1(c), and additionally by the polarisation dependent data as presented in Fig. 2 and summarised in Fig. 5.

The raw Raman spectra have been background corrected using a Gaussian broadened elastically scattered peak centred at 0 cm^{-1} , whose width is essentially determined by the apparatus function, i.e., the quality of the monochromator system. The peak fitting is performed using Lorentz peaks with initial wavenumber values as reported in the literature³⁰ and using a least square algorithm.

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

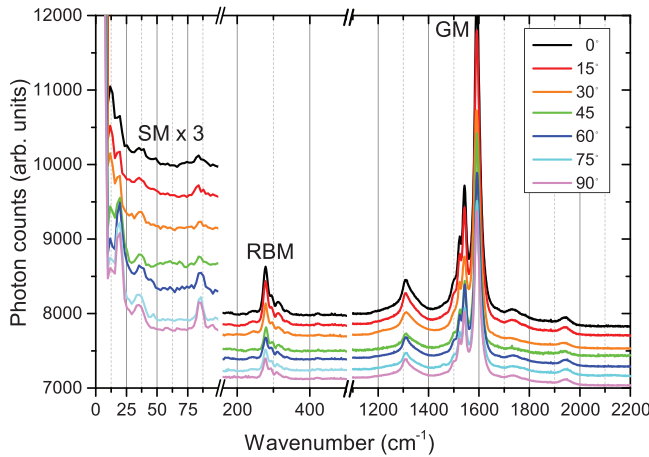


FIG. 2. Raman spectra of SM, RBM, and G-mode regions of vertically aligned SWNTs for differing polarisation angles of detection. See Fig. 1 for setup geometry.

analysed in 15° steps from p-polarisation (Z) to s-polarisation (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,³¹ 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 letter. The low vibrational region of the Raman spectrum is magnified by 3 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 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 86–90 cm⁻¹ represents bundled SWNTs as confirmed by Kahn and Lu.²⁶ All found peaks have been fully assigned in Table I, as detailed below. RBM assignment data taken from Maultzsch *et al.*³²

As predicted by zone-folding and force-constant models,²⁵ 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 as a function of scattering polarisation angle below.

Before the completion of the polarisation analysis, this letter focuses first on the minutiae of the SM. Fig. 3(a) shows the SM region in more detail. Five clearly distinguishable

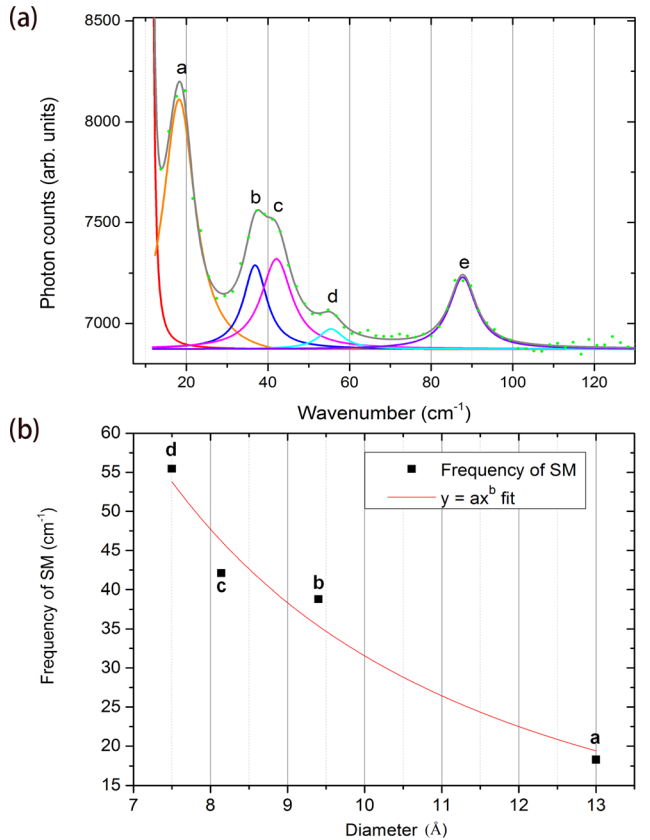


FIG. 3. (a) Enlarged extreme low frequency Raman region revealing distinctive squash modes of vertically aligned SWNTs with polarisation angle equals to 90°. (b) Resonant frequency of SM dependent on diameter. See Table I for detailed assignments.

peaks can be identified and are listed in Table I. Additionally, Fig. 3(b) shows our experimental results (squares) in comparison to a diameter dependent 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 $r^{-1.95 \pm 0.03}$.²⁵ As a result, this relation has been used as an additional model to assign Raman peaks to different SWNT diameters in Table I.

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 SWNTs in the aligned sample.

Fig. 4 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

TABLE I. 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 ^a
b 38.31	5.96	8.14–9.40	(7,6)	0.008	261 ^a
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)	0.065	315
			(10,0)	4.637	295
e 88.79	8.12	≪7.05/bundle			

^aWere not found experimentally in the RBM region because of their extremely low relative intensity.

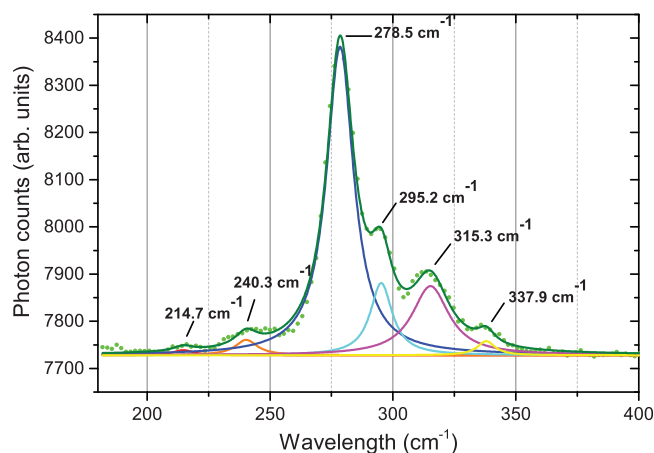


FIG. 4. Raman spectrum and peak fitting results of the RBM region of vertically aligned SWNTs.

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.³³ 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.²⁸ More chiralities can be detected using different excitation energies. The assignments of the modes are consistent with those of Dresselhaus *et al.*³⁴

Only two peaks have solely been assigned using tight-binding theory.^{26,35,36} However, their low Raman intensity (RI) and as a consequence their invisibility in the RBM region has been predicted^{26,35,36} 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.

Finally, we compare the polarisation dependent anisotropy of the aligned samples (array) in the G-mode (A_{1g}), RBM, and SM regions with the theoretical predictions. The polarisation dependent Raman scattering intensity is plotted against the analyser angle ($0^\circ = p$ -polarization (Z), $90^\circ = s$ -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 (A_{1g} representation) behavior as predicted by Saito. Recording both regions makes it possible to choose the stronger signal depending on the analyser setting. Finally, the relative shifts in wavelength when chirality/diameter of the tubes is changed (a measure of their sensitivity with respect to environmental changes) is larger for the SM region as the relative shifts scale as

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

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

In summary, we report an experimental direct polarisation dependent detection of SWNT Squash Modes (E_{2g}) in the ultra-low frequency Raman region $17\text{--}100\text{ cm}^{-1}$. We have assigned different chiralities of our SWNT samples by peak fitting the highly resolved Raman spectra and cross-correlating

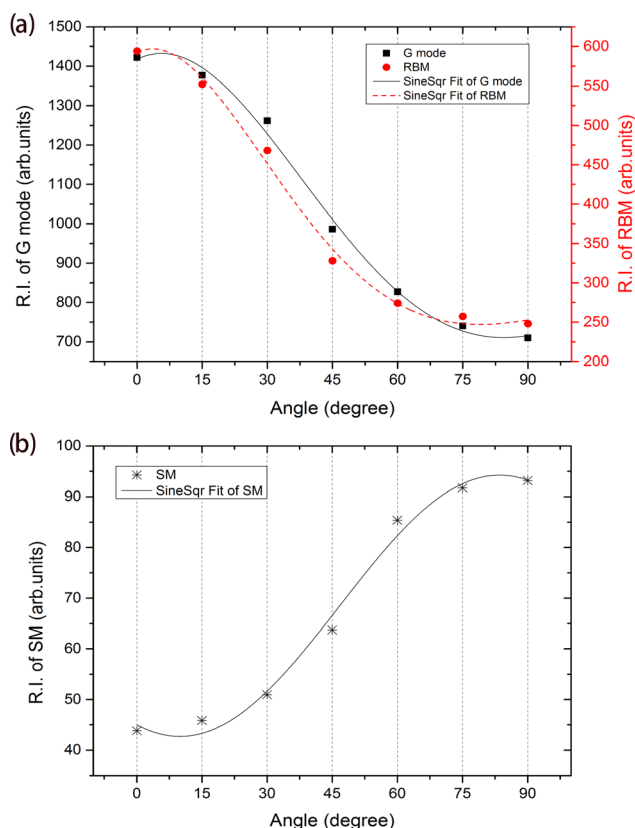


FIG. 5. Polarization dependent RI of the (a) G-mode and RBM, and (b) SM.

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 RBM frequency. Finally, the polarisation dependent anisotropy 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. The intensity of SMs was predicted to be close to the G-mode,²⁵ but as result show, is of the order of the significantly weaker RBM mode. For future work, the ability to experimentally access the extreme low frequency Raman region, as demonstrated above, impacts strongly on our ability to answer fundamental questions in physics related to electron-photon interactions, magneto-resistance, and superconductivity in low dimensional systems.²⁷

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