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Chirality-dependent mechanical response of empty and water-filled single-wall carbon nanotubes at high pressure

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ABSTRACT

The mechanical stability of single-walled carbon nanotubes (SWCNT) at high pressure was studied by high-resolution resonant Raman and wavelength-dependent fluorescence-excitation (PLE) spectroscopy resolving the vibrational and electronic resonances of 18 individual chiralities and furthermore even resolving the different behavior of empty (closed, pristine) and water-filled (opened) SWCNTs (diameter range = 0.6-1.42 nm). We find that water-filling exerts a stabilizing counter pressure on the SWCNT walls, leading to an increasing difference between the radial breathing mode frequencies of water-filled and empty SWCNTs at elevated pressures. For small diameter SWCNTs ($d < 1\text{nm}$) with a chiral angle of $\sim 12^\circ$, in particular for the (7,2) chirality, an anomalous behavior is observed, revealing an increased mechanical instability for these SWCNTs. We furthermore ascribe the longstanding contradiction between experiments and theory on the collapse pressure of SWCNTs to the presence of filling in most experiments to date, while empty SWCNTs follow the theoretically predicted collapse behavior.

1. Introduction

Single-wall carbon nanotubes (SWCNTs) are intensively studied for their peculiar electronic and optical properties that depend critically on their specific one-dimensional chiral structure, as described by the chiral indices (n,m) . [1] Being hollow cylindrical structures of sp^2 -hybridized carbon atoms, all located at their surface, they combine a high mechanical resilience with a low density and a high sensitivity to environmental changes. While the axial strength and stiffness of SWCNTs are in the order of 1TPa and 50GPa, [2] respectively, the radial mechanical stability is lower and strongly dependent on the SWCNT diameter, [3] with large diameter SWCNTs ($d > \sim 5\text{nm}$) even collapsing at ambient pressure. [4] For the further development of SWCNT nanocomposites and nano electro-mechanical devices (NEMS) it is important to understand this radial mechanical stability of SWCNTs.

The radial mechanical stability of SWCNTs has previously been studied by probing their vibrational, electronic and structural properties at high pressure *via* resonant Raman scattering (RRS) [5-7], optical absorption spectroscopy, [8] fluorescence-excitation (PLE) experiments [9, 10] and X-ray diffraction. [11] The various observations have been attributed to pressure-dependent cross-sectional deformations, from circular to oval and even peanut-shaped structures. However, in most of these low-resolution high pressure optical studies of SWCNTs, the intrinsic changes of the SWCNTs' vibrational and electronic properties are entangled with ensemble averaging over multiple chiral species that complicate the interpretation of the data. Furthermore, different pressure transmitting media [5] (PTM), interactions between SWCNTs (bundles versus individualized SWCNTs [10]) and filling of the SWCNTs (e.g. argon [5], fullerenes [6, 12] or even

another nanotube, i.e. double-walled CNTs[7, 8]) can influence the results of the pressure behavior. As such, a longstanding disagreement between various experiments and theoretical results exists: while models showed that for individual 1.4nm diameter SWCNTs the collapse pressure should be of the order of 1-3GPa[13, 14] most experiments found signatures of the collapse at much higher pressures (i.e. ~10-20GPa).[5-8]

To enable high-resolution (chirality-resolved) optical spectroscopy of SWCNTs, the SWCNTs need to be solubilised with bile salt surfactants in aqueous solution,[15] which, unlike other surfactants, provide an extremely homogeneous surrounding for the SWCNTs and thus also an increased resolution in optical spectroscopy. This has allowed us to spectrally resolve the features of empty (closed) and water-filled (opened) SWCNTs in bulk solutions, with water-filled SWCNTs showing a hardening (i.e. shift to higher frequency) and broadening of the radial breathing mode (RBM) vibrational frequency and a red-shift and broadening of the electronic transitions.[16-18] In earlier (high pressure) studies of surfactant-solubilised SWCNTs,[8, 10] harsh sonication was applied, thereby opening a significant fraction of the SWCNTs, creating a mixture of empty (closed) and water-filled (opened) SWCNTs.[16, 18-20]

In this work, we compare high-resolution spectroscopy at high-pressure of bile-salt solubilised empty and water-filled SWCNTs to study the effect of the inner environment on the pressure response of 18 different individual SWCNT chiralities. The high-resolution spectroscopy even allows discriminating the RBMs of empty and water-filled SWCNTs within the same experiment in a mixed sample[17]. We further combine the high-pressure RRS-study with excitation wavelength-dependent high-pressure PLE

experiments to correlate intensity changes in RRS with changes in the resonance conditions.

2. Experimental

2.1. Sample preparation

Various dispersions of SWCNTs synthesized by two different methods, i.e. High pressure CO-conversion (HiPco; Carbon Nanotechnologies Inc, batch R0495C)[21] and arc-discharge[22] (further abbreviated as Arc, Nanoledge, batch P00508D), covering different diameter ranges, were individualized in a 1% wt/V sodium deoxycholate (DOC, 99 %, Acros Organics) surfactant solution in D₂O (99.8 % atomD, CorteCnet) according to reference [15]. Samples were prepared either from raw HiPco (Arc) SWCNTs by gentle stirring (no sonication), thus also containing pristine, empty SWCNTs in addition to water-filled SWCNTs (HiPcoM and ArcM, with "M" for "mixed"), or from chemically purified SWCNTs by sonication, thus obtaining 100% water-filled SWCNTs (HiPcoF and ArcF, with "F" for "filled").[16] Empty SWCNTs were extracted from the mixed dispersions with density gradient ultracentrifugation (DGU), resulting in solutions with nearly 90% closed (empty) SWCNTs (ArcE and HiPcoE, with "E" for empty).[19, 23] A more detailed description of the sample preparation can be found in the Supplementary section S1, which also includes the determination of the amount of empty and filled SWCNTs present in the various samples by Raman spectroscopy (Supplementary Figs. S1 and S2).[16-19]

2.2. Characterization techniques.

RRS spectra were collected in backscattering geometry with a Dilor XY800 triple monochromator system. The laser excitation was chosen to selectively excite several SWCNT chiralities, either from an Argon laser (514.5nm), a Krypton laser (647.1 nm) or a tunable Rhodamine6G dye-laser (568.5 nm), pumped by the Argon laser. All Raman spectra were corrected for detector sensitivity, spectrometer efficiency and spectrometer wavelength calibration ($<0.1 \text{ cm}^{-1}$). For the spectra obtained at 514.5nm a high-pressure cycle was performed on the DOC/D₂O solution (without SWCNTs present) to perform a baseline subtraction (including a small, but non-negligible fluorescence background from the diamond when excited with this laser wavelength).

Wavelength-dependent PLE spectra were acquired in backscattering geometry in a sensitive dedicated setup, comprising a high pressure Xenon lamp for excitation and a liquid-nitrogen cooled CCD for detection and were calibrated for spectrometer response, lamp intensity and filter transmission. The PLE maps were fitted using a 2D fitting function, comprising Voigtian line shapes for the emission spectra, while the excitation spectra are fitted by a superposition of a Gaussian line shape corresponding to the excitonic E₂₂ transitions, a Gaussian phonon sideband 0.2 eV above the E₂₂ excitation with similar line width, and the underlying band-to-band transitions were modeled as $1/\sqrt{E-E_{22}}$ and convoluted with a Gaussian line shape with similar width as the excitonic profiles.[24]

2.3 High pressure diamond anvil cell.

High pressures (up to 20 GPa) were achieved inside a diamond anvil cell. The diamond anvils sit on both sides of the sample chamber, which consists of a circular hole ($d = 200\ \mu\text{m}$) drilled through a pre-indented stainless steel gasket (Fig. 1b). The DOC-D₂O solution was used as the pressure transmitting medium (PTM). The pressure was probed by the shift of the R1 fluorescence line of a small ruby chip immersed in the PTM.[25] Before loading the solution sample inside the cell, the solution was partially evaporated, to raise the concentration of both the SWCNTs and the DOC-concentration ($\sim 4\ \text{wt/V}$). This DOC concentration is sufficiently low to avoid the formation of complex elongated micellar phases[26, 27], and sufficiently high to form a more isotropic glassy state upon freezing[28] and to avoid SWCNT bundling during the pressure cycle. While for pure water, hydrostaticity is lost at the solidification pressure of 1 GPa, the presence of the DOC surfactant extends the quasi-hydrostatic conditions to higher pressure. This was experimentally evidenced by (i) a sudden red-shift of the ruby line followed by a smoother blue-shift, meaning a sudden drop and recovery of pressure at this point and (ii) a change of slope of the G-band pressure evolution (see Fig. 5 and below). The PTM solidification point changed slightly from sample to sample, due to the varying DOC concentrations, but occurred at pressures of $\sim 2 \pm 0.3\ \text{GPa}$.

3. Results and Discussion

Surfactant-solubilised SWCNTs are complex systems that require a combination of different spectroscopic techniques, and a range of samples with different diameter ranges and filling states, for a reliable characterisation: In resonant Raman spectroscopy,

complementary information is obtained from the G band[29] (yielding a general indication of the collapse of SWCNTs) and radial breathing mode (RBM ; providing detailed information resolving each individual chirality[29] and its filling state[17]) spectra. PLE spectra furthermore provide information on the shifts of electronic transitions,[18, 30] that influence the resonances in Raman spectroscopy.

3.1. Chirality-dependent evolution of the RBMs with pressure.

Figure 1a and Supplementary Figure S3 present the normalized Raman spectra in the RBM region for the (mixed) HiPcoM sample excited at 568.5 nm at different pressures. Three different chiralities can be observed, *i.e.* (6,5), (6,4), and (7,2), each of them showing a bimodal distribution of empty and water-filled SWCNTs, as was previously studied in reference [17]. Both peak positions and linewidths are dependent on chirality and filling state, and are in excellent agreement with those found before in SWCNT samples from different sources.[17] The RBMs of the empty and water-filled SWCNTs can also be clearly resolved at elevated pressures in this mixed solution, at least up to 3-4 GPa. With increasing pressure, all the Raman bands of the SWCNTs shift towards higher frequencies, including the high-frequency G-band, while at the same time intensity attenuation and broadening takes place. To accurately determine this pressure-dependent hardening of the RBMs of empty and water-filled SWCNTs, the Raman spectra presented in Fig. 1a were fitted using a combination of two Lorentzians for each chirality, corresponding to the RBMs of the empty and water-filled SWCNTs (see also Supplementary section S2). The so-obtained peak positions and their error bars are presented in Fig. 1c, while the differences between water-filled and empty RBM

positions, $\Delta v_{\text{RBM}} = v_{\text{RBMfilled}} - v_{\text{RBMempty}}$ are plotted in Fig. 1d; clearly showing that Δv_{RBM} increases with pressure. Both the evolution of v_{RBM} and Δv_{RBM} also show a dramatic difference between different chiralities, with especially the (7,2) SWCNT behaving very differently (see below).

Similar experiments were performed by exciting the HiPco SWCNTs at 647.1 nm, in resonance with the (10,3), (7,5), (7,6), (8,3) and (9,1) chirality, i.e. with an average diameter of $d_{\text{av}} = 0.82 \pm 0.1 \text{ nm}$, and (14,2), (13,4), (12,6), (16,1) and (13,7) SWCNTs ($d_{\text{av}} = 1.26 \pm 0.1 \text{ nm}$), and by exciting the Arc SWCNTs at 514.5 nm, in resonance with the (15,2), (14,4), (13,6), (12,8) and (11,10) chiralities ($d_{\text{av}} = 1.32 \pm 0.08 \text{ nm}$). In this case however; separate experiments were performed on the filled (HiPcoF, ArcF) and the empty SWCNT sample (HiPcoE, ArcE), allowing for separate monitoring of the RBMs of the empty and filled SWCNTs up to much higher pressures (12-14 GPa for the thinnest SWCNTs). The Raman spectra were fitted analogously to these for the 568.5 nm excitation (see Supplementary Section S2), and the peak positions at different pressures are presented in Fig. 2. For the largest diameters, the RBM peak positions of the filled SWCNTs (and those of empty at slightly higher pressure) cannot be resolved spectrally for individual chiralities, due to broadening and overlap with other chiralities. However, even at the lowest pressures, the RBMs of the filled SWCNTs harden more than those of the empty SWCNTs (Supplementary Fig. S4 and Table S1), in line with observations for the thinner SWCNTs, showing that the internal water exerts an additional restoring force on the SWCNT walls.

The RBM peak positions were fitted as a function of pressure using a second-degree polynomial: $v_{\text{RBM}} = v_0 + \alpha P + \beta P^2$, with v_0 the RBM-frequency in the solution at ambient

pressure (Supplementary Fig. S1-S2). Values for α and β can be found in the Supplementary Table S1 and are also presented in Fig. 3 as a function of diameter and chiral angle. Those experiments in which the SWCNTs could only be followed in a limited pressure range, do not allow for the second order coefficient to be determined and a linear fit was performed ($\beta=0$, see also Supplementary Fig. S5).

The shift of the RBMs with pressure can arise both from the C-C bond hardening and from the mechanical interaction (sterical hindrance) with the external and/or internal environment, exerting an additional restoring force for the radial motion, which increases with pressure. In fact, by comparing with the G-band data we can conclude that the latter effect actually dominates for the RBMs (see below and Supplementary section S4). Indeed, theoretical calculations show that excluding the interaction with the environment results in much lower values for α ($\sim 1.4 \text{ cm}^{-1} \text{ GPa}^{-1}$ for $d=1.22 \text{ nm}$). [31] Simply modeling the interaction with the environment by a Lennard-Jones-type potential (similarly as was previously done to include interactions with other SWCNTs in bundles [31, 32]), we find that the magnitude of the linear shift (α) can be perfectly reproduced (see Supplementary section S4 for this modeling).

For small-diameter SWCNTs, linear coefficients for the RBMs lie between $\alpha \sim 5\text{-}9 \text{ cm}^{-1} \text{ GPa}^{-1}$ well in agreement with previous experiments on debundled SWCNTs, [10] with α increasing for larger diameters. More importantly, we find that for all the investigated chiralities (see also Supplementary Table S1), filled SWCNTs have larger pressure slopes than their empty analogues ($\alpha_{filled} > \alpha_{empty}$), clearly showing that the water molecules serve as an internal support for the SWCNTs.

Remarkably, Fig. 3a shows, for small diameter SWCNTs ($d < 1$ nm) an abrupt minimum for a chiral angle of $\sim 12^\circ$ (i.e. (7,2) and (10,3) chirality). In particular for the empty (7,2) SWCNT, the RBM frequency is hardly changing with pressure (α close to zero), and even softening at pressure above 1.5GPa (Fig. 1 and Supplementary Figure S3), indicating a strongly reduced mechanical stability of these SWCNTs, which softens the RBM even at moderately elevated pressure and thus compensates for the usual hardening observed for other SWCNTs. While prominently present for small diameters (e.g. also for the (10,3) chirality a lower value of α is observed), the chiral angle dependence becomes less significant for the larger diameters (e.g. (13,4) and (14,4)). This particular reduced mechanical stability for small diameter empty SWCNTs with a chiral angle of 12° may be related to an increased torsional instability of thin-diameter chiral SWCNTs, as predicted theoretically to occur for intermediate chiral angles and small diameters ($\propto 1/d^3$).[33] Indeed a coupling between the radial compression and such a torsional mode could provide another degree of freedom to yield under pressure. An analogous coupling of the torsional mode with *axial* strain has been demonstrated theoretically to peak at chiral angles $\leq 15^\circ$. [34] Since the empty (7,2) chirality has a reduced mechanical stability, the effect of water in its interior is much more important than for the other chiralities, resulting in a dramatic difference between the pressure slopes of the RBMs of the empty and water-filled (7,2) SWCNTs.

The quadratic components observed here, clearly present for some chiralities even at low pressures under hydrostatic conditions (*i.e.* below the solidification of the PTM at ~ 2 GPa) are much larger than would be induced by the intrinsic anharmonicity of the C-C bonds, which is known from the high-frequency Raman modes of graphite,[35] and from

the corresponding G-band of the SWCNTs studied here. Furthermore also the anharmonicity of the van der Waals interaction with the environment is negligible for the experimentally observed β -values (see Supplementary section S4). This large quadratic component thus most likely originates from the interaction with the molecular (i.e. non-continuum) structure of the SWCNT environment resulting in an inhomogeneous application of the pressure on the SWCNTs, thus lowering the SWCNTs' symmetry and resulting in a further softening of the RBM vibration which depends quadratically on pressure (analogous to the effect of bundling[31]). This molecular nature of the surrounding medium indeed has the largest effect for the smaller diameter SWCNTs ($|\beta|$ decreasing with diameter). Interestingly, also the internal water molecules further add to this effect (Fig. 3c-d).

3.2. G-band evolution under hydrostatic conditions (< 2GPa)

While the RBMs of filled SWCNTs shift faster with pressure than their empty analogues, the opposite behavior is observed for the high frequency G-bands (tangential vibrations). These modes are related to the graphite E_{2g} optical in-plane vibration, which for graphite gives one single mode in the Raman spectrum as transverse and longitudinal optical phonons are equivalent.[29] In SWCNTs, this mode splits into two modes, G^+ and G^- , as a consequence of the curvature of the tube wall, i.e. weakening of the C-C bonds through rehybridization of the carbon orbitals, leading to a softening of the SWCNT G-band with respect to the graphite G-peak.[29] This softening is more pronounced for vibrations perpendicular to the tube axis (transverse optical phonon, TO) compared to the vibrations along the tube axis (longitudinal optical phonon, LO). For semiconducting

SWCNTs, the LO and TO phonons are the origin of the G^+ and G^- peaks, respectively. The inset of Fig. 4 presents a typical G-band RRS spectrum obtained at ambient pressure and $\lambda_{\text{ex}} = 514.5\text{nm}$ (ArcE sample), for which the G^+ and G^- peaks are indicated.

Under hydrostatic conditions (*i.e.* below the PTM solidification), both peaks harden similarly, with the G-bands of the filled SWCNTs hardening more slowly than the empty ones (Fig. 4). Since this G-band hardening originates from the hardening, and hence shortening of the C-C bonds due to the SWCNT compression, the faster G-band shift for *empty* SWCNTs indicates a higher compressibility. Note that this is completely opposite to the behavior of the RBMs, since as discussed before, the interaction with the environment actually dominates for the radial modes (RBMs), while it is unimportant for the tangential modes (G-band), because the counter pressure exerted by the environment acts in the radial direction, and explains the faster pressure-induced RBM hardening for *water-filled* than for empty SWCNTs. Indeed the relative change in RBM frequency (*i.e.* $(d\nu/dp)/\nu$) is an order of magnitude larger than the relative change in G-band frequency, so the effect of C-C bond hardening is almost negligible for the RBMs.

3.3. Collapse of empty SWCNTs.

At elevated pressures, theoretical calculations predict a diameter-dependent ovalization and collapse of the SWCNTs.[3, 13, 14, 36, 37] While absolute theoretical values of the collapse pressure depend on the specific models used (e.g. individual SWCNTs with[14] or without[13] interaction with the environment, or bundled SWCNTs[3, 36]), all calculations predict a diameter-dependence with inverse cubic law, *i.e.* $P_c \sim d^{-3}$. Using the formula from recent DFT calculations[36], $P_c = 24.6/(0.4 + d)^3$, we find for the specific

SWCNT average diameters in our study collapse pressures of $P_c \sim 4\text{-}6$ GPa for the $d=1.26\text{-}1.32\text{nm}$ SWCNTs, $P_c \sim 11\text{-}17$ GPa for $d_{av}=0.82\pm0.1\text{nm}$ SWCNTs and $P_c \sim 16\text{-}22$ GPa for the smallest diameters ($\lambda_{ex}=568.2\text{nm}$).

In semiconducting SWCNTs, the G^- (TO) frequency depends more strongly on the diameter and chirality of the SWCNTs compared to G^+ (LO).[38] Thus, structural (radial) deformations are expected to affect G^- the most (as well as the RBM vibration). As the G-band is a superposition of the signals from different SWCNTs in resonance, we explicitly choose a sample with a narrow diameter range (ArcE and ArcF) having only a limited number of semiconducting chiralities (5 chiralities, $d_{av}=1.32\pm0.08\text{nm}$) in resonance for a given laser wavelength. Figs. 5a-b present the peak positions of G^+ and G^- as a function of pressure for the ArcE (Fig. 5a) and ArcF (Fig. 5b) samples excited at 514.5nm, and a representative set of RBM (Fig. 5c-d) and G-band (Fig. 5e-f) spectra.

For the empty SWCNTs, above the PTM solidification (indicated by the dashed green region in Fig. 5a), the slope of the G-band is strongly reduced and in particular for G^- nearly vanishes. Furthermore, the G-bands broaden significantly, with the FWHM of the G^+ Raman peak remaining nearly constant below 2GPa, and increasing by more than a factor of 3 in the pressure range of 2-3.8GPa (Supplementary Figs. S6-S8). Due to this significant broadening, the relative intensity of G^- and G^+ changes drastically with (peak) intensity ratio G^-/G^+ going from 0.13 at ambient pressure, 0.23 at 2.5GPa up to 0.52 at 3.8GPa. In contrast, the RBMs of empty SWCNTs don't show any noticeable change in slope nor an increased broadening due to the PTM solidification (Supplementary Fig. S7), thus indicating that the PTM solidification does not influence the radial compression with pressure significantly. In contrast with the RBMs, the G-band is much more

sensitive to the electronic structure of the nanotube wall, which can more easily be influenced by local inhomogeneous interactions with the molecular (frozen) environment, resulting in the observed broadening.

Most importantly, at $\sim 3.85\text{GPa}$, the RBMs of these empty SWCNTs (in the ArcE sample) abruptly disappear (Fig. 5c), a clear indication of the collapse of these empty SWCNTs at this pressure. From this point on, G^- hardly shifts (or even slightly softens) while the slope for G^+ increases again and both G-band features broaden significantly, thus cannot be distinguished anymore. Therefore it is better to consider only the center of gravity (ν_{COG}) of the G-band region and interpret the overall effects on the high-frequency modes considering them as a single feature. Figure 6 compares ν_{COG} of the G-band from empty and filled ARC SWCNTs up to the highest pressures (20GPa). First of all, the discussed changes in the G-band slope after PTM solidification for the empty SWCNTs are also clearly reflected in $\nu_{COG}(P)$. Secondly, the disappearance of the empty RBMs at 3.85GPa is further supported by a change of the slope for ν_{COG} at this point, and continues to harden up to highest pressures, similarly as observed in graphite.[35] Our experiments thus clearly show that isolated, empty SWCNTs with $d_{av}=1.32\pm0.08\text{nm}$ collapse at 3.85GPa, and that this collapse occurs abruptly, agreeing extremely well with the theoretical predictions.[3, 7, 14, 36, 37, 39]

3.4. Filled SWCNTs at high pressure.

In contrast with the empty SWCNTs, the slope and line width of the G-bands of the filled SWCNTs *increases* at the PTM solidification (in particular for G^+ , see also Supplementary Fig. S6), combined with a much larger broadening of the RBMs than the

empty SWCNTs (Figs. 5c-d, compare red curves). This can be explained by the fact that the SWCNT wall is compressed between the frozen external water and internal water, which induces strong inhomogeneous electronic (and sterical) interactions with the highly polar water molecules, typically resulting in a red-shift of the electronic resonances (dielectric effect[18, 19]). At the same pressure, also a new lower-frequency RBM peak suddenly appears, which can be explained by an additional SWCNT chirality coming into resonance (indicated by the red arrow in Fig. 5d). Indeed, taking into account the pressure-induced hardening of the RBMs as well as the expected red-shift of the electronic resonances, this RBM can be assigned to either the (16,5) or (13,8) chirality.

Strikingly, at ~3GPa, a new vibrational feature splitting off from the RBMs is observed for the filled SWCNTs (indicated by the green arrow in Figs. 5c-d), in addition to their RBMs. The same feature can also be observed for the empty sample, though at a much smaller relative intensity and thus most probably originating from a small fraction of filled SWCNTs in this empty sample. This new feature cannot just arise from an RBM of a smaller diameter SWCNT coming into resonance as (i) the Arc samples do not contain such smaller diameter SWCNTs and (ii) the feature shifts much more rapidly than the RBMs with pressure ($\alpha \sim 16 \text{ cm}^{-1}\text{GPa}^{-1}$, far outside the range that can be explained theoretically, see Supplementary Fig. S7). At the same time, the RBM Raman signal (of the filled SWCNTs) itself is strongly attenuated and broadened. We therefore propose this new feature to arise from a lower symmetry radial vibrational mode of a radially distorted SWCNT. The higher pressure slope is then logical because it is composed of two contributions: (1) the bond-hardening with pressure (this effect is the same as for the symmetrical RBM), and (2) the further progressive SWCNT deformation

(increasing the splitting from the symmetrical RBM). While theoretical calculations show that the phonon density of states spreads out and becomes much more complex for deformed SWCNTs,[7] this well-defined new Raman feature has never been reported.

In contrast to the RBMs of the empty SWCNTs (which disappear at 3.85GPa due to the collapse), this new feature and the broadened RBM can be followed up to much higher pressure (gradually broadening and disappearing in the noise at the highest pressures). The pressure derivative for the G-band of the filled SWCNTs changes sign at 14 ± 2 GPa, which has previously been assigned as the signature of the collapse.[5, 40] Above 17GPa, ν_{COG} of the empty and filled SWCNTs coincide, providing indications that these larger-diameter water-filled SWCNTs have collapsed at about 17GPa.

Our results therefore show that the discrepancy between theory and experiments regarding the collapse pressure of SWCNTs, originates from the fact that previous studies have not been performed on closed (thus empty) individualized SWCNTs. Indeed, in previous work generally higher collapse pressure have been observed for SWCNTs deliberately filled with e.g. fullerenes[6, 12] ($P_C \sim 8$ -12GPa), iodine[41] ($P_C \sim 8$ -10GPa) and argon[5] ($P_C > 40$ GPa), as well as for DWCNTs[7, 8] ($P_C \sim 25$ GPa), indicating that filling enhances the mechanical stability of the SWCNTs.

3.5. Irreversible damage after the pressure cycle.

Further evidence of the collapse of larger diameter SWCNTs at ~ 3.8 GPa, can be found by comparing the RBM spectra before and after each pressure cycle to high pressure and back (12-13GPa for the HiPco samples, Fig. 7). For the (initially) empty SWCNTs very drastic changes can be observed. First of all, the largest empty SWCNTs observed at

647.1nm, *i.e.* $d_{av} = 1.26 \pm 0.1$ nm, have an expected collapse pressure of $P_C \sim 4.4$ GPa, taking into account $P_C \sim d^{-3}$ and the observed collapse pressure for $d_{av} = 1.32 \pm 0.08$ nm SWCNTs. Indeed, we find that after a pressure cycle up to 13 GPa, the RBM signals of empty SWCNTs are completely absent for these largest diameters (Fig. 7), indicating that once collapsed the empty SWCNTs undergo severe structural damage therefore not showing a RBM signal anymore.

Secondly, the intermediate diameter empty SWCNTs in this study ($d_{av} \sim 0.82 \pm 0.1$ nm, expected $P_C \sim 16$ GPa) become water-filled after the pressure cycle (none of the SWCNTs remain empty); indicating that these initially empty SWCNTs have been irreversibly damaged, but have not collapsed yet (note that even a single defect large enough to pass a water molecule is sufficient to fill the entire SWCNT). Finally, for the (6,5) and (6,4) chiralities ($d_{av} = 0.71 \pm 0.03$ nm, Fig. 7b, expected $P_C \sim 25$ GPa) a significant fraction remains empty after a pressure cycle up to 12 GPa, which is much lower than the expected collapse pressure and thus no structural damage has been caused yet. The exception on the rule is again the (7,2) chirality which only shows RBMs of filled tubes after the pressure cycle. This can be explained by its lower mechanical stability, as we already inferred from its exceptionally low α -value (Figure 3), thus it can be expected that this particular chirality does not follow the $P_C \sim d^{-3}$ law, and rather collapses at a much lower pressure, resulting in irreversible structural damage to the empty SWCNTs, as we observe.

For all water-filled SWCNTs, peak positions and line widths remain unchanged after the cycle, even for the largest diameters, indicating that these HiPco SWCNTs have not fully collapsed at the highest pressures in this particular experiment yet (13 GPa being the

highest pressure). We do observe an overall decrease of the RRS intensity combined with small changes in the relative intensities for the different chiralities (Fig. 7a, HiPcoF), showing that also the water-filled SWCNTs are structurally damaged to some extent.

For all SWCNTs, RRS intensity changes drastically with increasing pressure. The relative intensity of the different empty and water-filled SWCNT chiralities can be directly extracted from the RBM fits as a function of pressure (Supplementary Fig. S9 for $\lambda_{\text{ex}}=647.1\text{nm}$). At low pressure, intensity reduces similarly for all SWCNTs. At slightly higher pressure the intensity of the largest diameter empty SWCNTs approaches zero as they collapse. For the thinner diameters, the intensity starts to level off in this range and RBMs can be monitored during the entire pressure run. It is important to realize that also a change of the electronic transitions of the SWCNTs with pressure and a reduction of the optical path length during compression (typically the gasket reduces in thickness by $\sim 50\%$ and expands laterally) may affect the intensity changes in RRS (but with an identical factor for all SWCNTs). To check the importance of these electronic shifts, we also performed PLE experiments as a function of pressure.

3.6. Pressure induced electronic changes.

The bile salt surfactants[15] allow for studying the very characteristic PLE spectra[30, 42] of the individualized semiconducting SWCNTs, which would be quenched in SWCNT bundles. PLE-spectra of the mixed HiPco1 sample were obtained at ambient pressure, 0.51 GPa, 1.65 GPa, 3.4 GPa and after pressure release at 0.9 GPa and are presented in Fig. 8. At higher pressure, the electronic resonances shift and broaden, and the PL intensity is drastically reduced. After a pressure cycle up to 3.4 GPa and back,

irreversible changes of the PL intensity and line shape are observed, indicating significant structural damage of the SWCNTs even at these low pressures. To determine the shifts of the electronic transitions, the PLE maps were fitted two-dimensionally[24], obtaining at each pressure the wavelengths of the first (λ_{11} , emission wavelength) and second (λ_{22} , excitation wavelength) electronic transitions of the SWCNTs (Fig. 8f and 9, see experimental section 2.2).

At low pressures (up to 1 GPa), the evolution of E_{11} and E_{22} shows distinct behavior for $(n-m) \bmod 3=1$ and $(n-m) \bmod 3=2$ SWCNTs, in agreement with calculations[37] and experimental studies up to 1 GPa.[9, 43] At higher pressures however, we observe an overall downshift in energy for all SWCNTs, which can be ascribed to the compression of the surfactant layer around the SWCNTs, thereby increasing the dielectric constant of the environment. E_{11} and E_{22} show comparable shifts (in energy), but since the linewidth of both transitions is comparable in wavelength units (thus larger for E_{22} when expressed in energy units), this shift is most significantly noticed for λ_{11} (Fig. 8f). Furthermore, the line width of all resonances broadens drastically, i.e. almost by a factor of 3 at 3.4GPa, ensuring that all of the SWCNTs observed at 0 GPa remain in resonance in these experiments up to 3.4GPa. Therefore we can conclude that the strong intensity decrease of the RBMs observed below 3GPa (Supplementary Fig. S9) cannot be ascribed to a loss of resonance conditions. More important are the increased environment influences induced by pressure and eventually also the creation of defects in the SWCNT walls, resulting in both an overall broadening and weakening of the PLE intensity. And in particular this broadening, allows for the observation of the RBMs up to much higher pressures (even up to 12 GPa for the thinnest diameters).

4. Conclusion

In this work, we combined high resolution resonant Raman and PLE experiments on individualized empty and water-filled SWCNT chiralities to study the effect of water filling on their pressure stability. The RBM frequencies of water-filled SWCNTs harden faster with pressure than those of empty SWCNTs, showing that an additional restoring force for the RBM stabilizes the filled SWCNTs. This is further substantiated by the fact that the RBMs of filled SWCNTs are observed up to much higher pressure and show less irreversible damage during the pressure cycle. The empty SWCNTs collapse at much lower pressure and show more damage after the pressure cycle.

The chirality-dependent study of the pressure slopes of the RBMs reveals a clear minimum for small diameter ($d < 1\text{nm}$) SWCNTs with a chiral angle of $\sim 12^\circ$, in particular for the (7,2) chirality, indicating a reduced mechanical stability of these SWCNTs, suggesting an increased torsional mechanical instability for these particular chiralities. For SWCNTs with an average diameter of 1.32nm , we find that empty SWCNTs abruptly collapse between 3.45GPa and 3.85GPa , in agreement with theoretical predictions. In contrast to this abrupt collapse for empty SWCNTs (*i.e.* no intermediate ovalization stage), the filled SWCNTs clearly show a modification of the radial cross-section at about 3GPa , which results in the observation of a new Raman-active radial vibrational mode that blue-shifts about twice as fast with pressure as the normal RBM vibration. The collapse of the same-diameter filled SWCNTs occurs at much higher pressure (in the range of $14\text{-}17\text{GPa}$). Thus, the longstanding contradiction between theory and

experiments on the collapse pressure originates from the fact that previous studies have been performed (often unwittingly) on filled SWCNTs.

Our results imply that the optimal preparation of carbon nanotubes for reinforced composite materials calls for a gentle procedure to open the SWCNT ends (to fill them and increase their radial stability), while avoiding shortening the tubes or other damage to the tube walls, which would reduce their tensile strength.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at ...

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FIGURES:

Fig. 1: (a) Normalized RRS spectra (black) of the RBM evolution with pressure for the HiPcoM sample ($\lambda_{\text{ex}} = 568.5 \text{ nm}$, spectral resolution 0.34 cm^{-1}) in resonance with the (6,5), (6,4), and (7,2) SWCNTs (see also Fig. S3 for a more detailed version of panel 1a). Fits (green) are a superposition of Lorentzian peaks for the RBMs from empty (red) and water-filled (blue) SWCNTs. At higher pressures, additional vibrations/SWCNTs (grey) come within the field of view (at lower frequencies). (b) Picture of the diamond anvil cell. The metallic gasket placed in between the diamonds has a centered hole which defines the sample chamber; (c) Pressure-induced evolution of the RBM vibrations of the empty (red, hollow symbols) and water-filled (blue, filled symbols) (6,5) (circles), (6,4) (triangles) and (7,2) (stars) SWCNTs obtained from the fits given in panel (a). Red and blue lines represent a fit of the data points with a second-degree polynomial (see text and Fig. S5). Error bars

on the individual data points are presented in green (empty SWCNTs) and cyan (water-filled SWCNTs).; (d) Shifts of the RBM positions (experimental and fitted) of filled SWCNTs with respect to empty ones, i.e. $\Delta\nu_{\text{RBM}} = \nu_{\text{RBMfilled}} - \nu_{\text{RBMempty}}$. The error bars for the (6,4) at the highest pressures increase because of the proximity of the (7,2) RBM signals. Details on the fit procedure can be found in the SI, section S2 and Figures S3-S4.

Fig. 2: Evolution of RBM frequency with pressure for empty (red, open circles) and water-filled (blue, filled circles) SWCNTs: (a) HiPco SWCNTs with average diameter $d_{\text{av}} = 0.82 \pm 0.1 \text{ nm}$ excited at 647.1nm, (b) HiPco SWCNTs with average diameter $d_{\text{av}} = 1.26 \pm 0.1 \text{ nm}$ from the same experiment (excited at 647.1nm), for which the different chiralities can only be resolved up to 2GPa and (c) Arc SWCNTs with average diameter $d_{\text{av}} = 1.32 \pm 0.08 \text{ nm}$ excited at 514.5nm, chirality-resolved only up to 1GPa (see also Fig. S4). Linear (dashed lines, $\beta=0$) and 2nd degree polynomial (solid lines) fits for the different chiralities are presented.

Fig. 3: Linear coefficients α and 2nd order coefficients β obtained from the fits of the RBM peak positions as a function of chiral angle (a-c) or SWCNT diameter (b-d) for the empty (red, open circles) and water-filled (blue, filled circles) SWCNT chiralities. Error bars arise from a weighted fit of the data points presented in Figures 1c and 2. A clear minimum is observed at a chiral angle of ~12° for small diameter SWCNTs ($d < 1$ nm: (7,2) and (10,3)), as indicated by the dotted line in panel (a), while $|\beta|$ seems to decrease with diameter.

Fig. 4: Variation of the G^+ -peak position as a function of pressure for the empty (ArcE, red open circles) and filled (ArcF, blue filled circles) excited at $\lambda_{\text{ex}}=514.5\text{nm}$. Error bars are presented in magenta and cyan respectively. Red and blue solid lines are linear fits for empty and filled SWCNTs respectively, under hydrostatic conditions. The inset presents the G-band spectrum of empty SWCNTs at ambient pressure, indicating the main two modes: G^+ and G^- (for spectra at elevated pressures, see Figure S8)

Fig. 5: (a-b) Variation of G^+ (circles) and G^- (squares) peak positions as a function of pressure for empty (ArcE, a) and filled (ArcF, b) SWCNTs excited at $\lambda_{\text{ex}}=514.5\text{nm}$ (Error bars are shown in magenta and cyan respectively). The green dashed region corresponds to the PTM solidification (see also Figure 4), which occurs at slightly different pressure for the empty and filled samples due to the slightly different surfactant concentrations (see methods), while the cyan dashed region corresponds to the pressure at which the empty RBMs can no longer be observed (see panel (c)). (c-d) RBM spectra at three different pressures, where the red and blue curves are multiplied by 20 for clarity (signal intensity decreases with increasing pressure). The blue arrow indicates the expected position of the RBM signal at ~3.9GPa, the red arrow indicates an additional RBM observed for the filled SWCNTs after PTM solidification and the green arrow indicates a new feature arising mainly in the filled sample above 2.8GPa while in the empty sample its intensity is drastically reduced and thus could be due to a small amount of filled SWCNTs in the "empty" sample (see also Figure S7). The * indicates a plasma line from the laser. (e-f) Normalized G-band spectra at the same pressures (for other spectra see figure S8).

Fig. 6: Center of gravity of the G-band region (v_{COG}) for empty (red, open symbols) and filled (blue, filled symbols) Arc SWCNTs as a function of pressure.

Fig. 7: Reversibility after each pressure cycle. a) RRS spectra excited at $\lambda_{\text{ex}} = 647.1$ nm before (black) and after (red) a pressure cycle up to 13 GPa and back for initially mostly empty SWCNTs (HiPcoE) and water-filled SWCNTs (HiPcoF). The spectra after the pressure cycle are multiplied by 5. The region of the largest diameters (160-220 cm^{-1}) is additionally multiplied by 10 for clarity. b) RRS spectra excited at $\lambda_{\text{ex}} = 568.5$ nm before (black) and after (red) a pressure cycle up to 12 GPa for the mixed empty/water-filled SWCNTs (HiPcoM). The corresponding chirality assignment is included.

Fig. 8: (a-e) 2D PLE maps obtained at different pressures from the HiPcoM sample. The color scales indicate the loss of intensity at higher pressures, with an almost 10 times decrease in intensity for the spectrum at 3.4 GPa. Chiral indices indicated in panel (a) are obtained using the relations of empty SWCNTs [19]. Panel (e) was obtained after decompression from 3.4 GPa. (f) Peak positions obtained from the 2D fits of the PLE maps, as a function of pressure.

Fig. 9: Shifts of the electronic transitions as a function of pressure for (a) the first (ΔE_{11}) and (b) second (ΔE_{22}) optical transitions. Errors obtained from the 2D fits are also presented. The $(n-m)$ mod 3=1 or 2 SWCNTs are indicated by stars and squares respectively.

Supplementary Data for:

Chirality-dependent mechanical response of empty and water-filled single-wall carbon nanotubes at high pressure

Supplementary Section S1: Sample Preparation

Solutions of individualized SWCNTs were prepared by adding 10 mg of SWCNT powder to 3 mL of a 1% w/V sodium deoxycholate (DOC) solution in D₂O and subsequent stirring for several days. Afterwards the solutions were centrifuged at 16215g for 24 hours (Sigma 2-16KCD centrifuge with swing-out rotor) to remove any residual bundles.

HiPcoM: Mix empty and filled SWCNTs: Raw HiPco SWCNTs (batch R0495C, Carbon Nanotechnologies Inc.) solubilised without sonication, resulting in a mixture of empty and water-filled SWCNTs.

HiPcoF: Filled SWCNTs: Superpurified HiPco SWCNTs (batch SP0356, Unidym) were annealed at 800 °C in vacuum to remove any residuals from the purification (without the vacuum annealing additional unidentified RBM-bands were found in the Raman spectra, most probably corresponding to SWCNTs filled with other molecules than water). Since these SWCNTs are purified, they are 100% opened and thus water-filled upon solubilisation. The solutions were furthermore sonicated for 1 hour in a bath sonicator (BRANSONIC 1510 E-MTH, 70 W, 42 kHz) during the solubilisation procedure to achieve a higher concentration of individualized SWCNTs.

HiPcoE and ArcE: Empty SWCNTs: The empty SWCNTs were extracted from the HiPcoI solution by density gradient ultracentrifugation (DGU).[1] For this purpose, iohexol (tradename 'Nycodenz' obtained from Axis-Shield in powder form) was used as a gradient medium and dissolved in D₂O at appropriate concentrations to obtain the desired density range. Gradients were prepared in 1.3 mL polyallomer centrifuge tubes by starting from a step gradient (low density $\rho=1.186$ g/mL (for HiPco) and $\rho=1.15$ g/mL (for Arc) layer added gently on top of a higher density layer $\rho=1.27$ g/mL), subsequently tilting the tube $\sim 80^\circ$ and rolling it around its axis to form a continuous gradient. The ArcM and HiPcoM SWCNT solutions were added to the top (low density) layer. The surfactant concentration in both layers was kept constant at 0.7%

w/v DOC. Ultracentrifugation was performed using a centrifuge (Kontron Centrikon T-1080) with swing-out rotor (TST 28), operated at 20°C. The solutions were centrifuged for 48h at 28000 rpm (122.000g max). After centrifugation, the empty SWCNTs were fractionated manually from the centrifuge tube using a syringe. The so-obtained solutions were dialyzed in a 1% DOC/D₂O solution using 10KDalton MWCO dialysis cassettes, to remove the density gradient medium (evidenced by optical absorption spectroscopy). Figure S1a shows the specific fraction selected for the empty SWCNTs.

ArcF: Filled SWCNTs: raw Arc-discharge SWCNTs (batch P00508D, Nanoledge) were opened by air oxidation and acid treatment. This procedure has previously been shown to be 100% efficient in opening the SWCNTs.[2] In brief, the SWCNTs were heated in air at 365°C, up to a total weight loss of 50%, to remove other carbonaceous material present in the raw SWCNT sample. In a second step, the sample was treated ultrasonically (bath sonicator: Branson, 1510E-MTH, 70W, 42kHz) in concentrated (37%) HCl at 60°C, to remove the catalytic nanoparticles and open the SWCNTs. Afterwards, the SWCNTs were neutralized by excessive rinsing with deionised water and vacuum filtration (5µm polycarbonate filter, Whatman). Finally, the so-obtained powder was annealed at 800°C for 1 hour in vacuum to remove any residual functional groups which can block the SWCNT-ends. These dispersions in 1% w/v DOC/D₂O were furthermore sonicated for 1 hour in a bath sonicator during the solubilization procedure to achieve a higher concentration of individualized SWCNTs.

Supplementary Fig. S1: a) Photograph of DGU centrifuge tube for HiPco SWCNTs, showing the empty fraction that was selected (red vertical lines). b-c) Raman spectra (black) of samples HiPcoM, HiPcoF and HiPcoE, excited at 568.5 nm (with 0.34cm⁻¹ spectral resolution) (b) and 647.1 nm (with 0.67cm⁻¹ spectral resolution) (c). Lorentzian fits (green) are a superposition of empty (red) and water-filled (blue) SWCNTs. The lower frequency region of the 647.1 nm spectra are multiplied by 10 for clarity. The RBMs of the water-filled tubes in this region (160-220 cm⁻¹) are very broad and overlap significantly, so that different chiralities cannot be resolved.

Supplementary Fig. S2: a) Photograph of DGU centrifuge tube for Arc-SWCNTs, showing (red vertical line) the empty fraction that was selected (indicated by the red line). b) Raman spectra (black) of samples ArcE and ArcF, excited at 514.5nm and obtained with a spectral resolution of 1.9cm^{-1} . Lorentzian fits (green) are a superposition of empty (red) and water-filled (blue) SWCNTs' RBMs.

Supplementary Section S2: Fit Procedure Raman spectra

The Raman spectra at each pressure were fitted according to the following procedure:

(1) The Raman spectra of the different solutions obtained at ambient pressure (Figs. S1-S2), were fitted simultaneously, *i.e.*, with shared peak positions and line widths, but with variable amplitudes, using for each chiral structure two Lorentzians, corresponding to the RBMs of empty and water-filled SWCNTs respectively, as shown previously in ref. [3]. These simultaneous fits were used to (i) assign the number of chiralities in resonance at a particular wavelength and (ii) determine the ratio of empty and filled SWCNTs for each chirality. For example, for the ArcE and ArcF sample, 5 chiralities are in resonance at 514.5nm, and the ArcE sample contains mainly empty SWCNTs, the ArcF sample mainly filled SWCNTs (Fig. S2).

(2) The fitted peak positions were each time used as a starting point to fit the Raman spectra obtained at the next higher pressure. Separate experiments were performed for the empty (ArcE, HiPcoE) and filled (ArcF, HiPcoF) samples, thus their spectra were acquired at different pressures and consequently, simultaneous fits, such as for the solution spectra at ambient pressures, cannot be applied. Since the ArcE and ArcF samples contain mainly empty or mainly filled SWCNTs, respectively, it is clearly reasonable to fit their Raman spectra (514.5nm excitation) with either the RBMs of the empty or the filled SWCNTs, respectively (Fig. S4). Similarly, the HiPcoF spectra were fitted by including only the RBMs for the filled SWCNTs. The HiPcoE sample, however, contains a non-negligible amount of filled (7,5) and (8,3) SWCNTs, and therefore the RBMs of these 2 filled chiralities were also included in the fit. Finally, the mixed HiPcoM sample (568.5nm excitation) was fitted with a combination of empty and water-filled RBM peaks (Fig. 1a and Fig. S3b-c for examples).

(3) The errors on the peak positions obtained from the fit procedure were corrected for the systematic deviations of the model (effectively decreasing the number of degrees of freedom used in the reduction of χ^2) and these error bars were quadratically added with the accuracy of the spectrometer positioning ($<0.1\text{cm}^{-1}$). This yields very conservative error bars, which are sometimes even a factor of 10 larger than those (erroneously) provided by common curve fitting programs. For the fits of the HiPcoE spectra, the fitting accuracy is furthermore validated by comparing the values for the filled (7,5) and (8,3) peak positions with those obtained from the HiPcoF sample.

(4) Finally, the peak positions are fitted using either a linear (when small number of data points are available) or a second-degree polynomial: $\nu_{\text{RBM}} = \nu_0 + \alpha P + \beta P^2$, to determine the pressure coefficients α and β . ν_0 is the peak position at ambient pressure, which was obtained accurately from the simultaneous fits of the Raman spectra of the solutions at ambient pressure. For the linear and second-degree polynomial fits, χ^2 was weighted with the error bars on the individual data points according to $1/\text{error}^2$, thus yielding also conservative error bars for α and β , as presented in Figure 3 and Table S1.

Supplementary Fig. S3: (a) Raman spectra (black) excited at 568.5nm of the RBM-region of the HiPcoM sample, obtained with a spectral resolution of 0.34cm⁻¹. Raman spectra are normalized on the (6,5) (left part of the spectrum) and (6,4) (right part of the spectrum) SWCNTs, and shifted vertically by the pressure they were measured at. Peak positions, as obtained from the fits presented in Figure 1a, of the RBMs of empty (red crosses) and filled (blue crosses) SWCNTs are also presented, as well as the second-degree polynomial fits of these peak positions which are indicated as red and blue dashed lines, respectively. Vertical gray lines indicate the peak positions. The data clearly shows that the (6,5) and (6,4) SWCNTs shift much more drastically with pressure than the (7,2) chiral structure, evidencing the increased mechanical instability for the (7,2) chirality. (b-c) Raman spectra obtained at two different pressures (in black), with their corresponding fits (in green) using a superposition of two RBM peaks for each chirality, corresponding to the empty and water-filled SWCNTs. Other chiralities becoming resonant at higher pressures (cyan peak) are also included in the fits. The magenta arrows indicate the direction of the shifts for the different chiralities which is clearly different for the (7,2) SWCNT.

Supplementary Fig. S4: Raman spectra (black) excited at 514.5nm of the RBM-region for the ArcE (a) and ArcF (b) samples and their fits (in green) using either a superposition of empty (in red) or filled (in blue) peaks. Peak positions and error bars, as obtained from the fits, are presented in panels (c) and (d) for empty and filled SWCNTs, respectively. Linear fits were performed, taking into account the error bars on the individual data points, and values of α are presented in Table S1. Filled SWCNTs clearly shift faster than empty SWCNTs. Instrumental resolution was set at 1.9cm⁻¹ for the solution spectra and 3.8cm⁻¹ for the spectra at high pressure.

Supplementary Fig. S5: Linear (dashed lines) and 2nd order polynomial fits for the empty and filled (6,5), (6,4) and (7,2) peak positions as a function of pressure, showing clearly that for these data a linear fit doesn't accurately describe the data. For both fits, v_0 was kept constant at the value at ambient pressure, while varying α and β .

Supplementary Section S3: RBM Pressure Dependence

Supplementary Table S1: RBM pressure derivatives of the different SWCNT chiralities. Peak positions and their respective error bars, are obtained from fits of the Raman spectra at each pressure. When sufficient data points are available (up to high pressure), a second-degree polynomial was fitted to these peak positions, defining both α and β . For the largest diameters only a linear fit was performed. ν_0 is the RBM frequency at ambient pressure (i.e. in solution), which was obtained from the simultaneous fits shown in Figs. S1-S2. Error bars on α and β are conservative estimates of the fitting errors, weighted by the conservative error bars on the individual data points. Data presented between brackets, e.g. for the filled (15,2) SWCNTs, is obtained from a linear fit of only four data points (see Fig. S3) and therefore omitted from Figure 3 in the main text.

(n,m)	Diameter	Chiral angle	E/F	ν_0	α	β
(7,2)	0.64	12.2	E	359.7	0.46±0.13	-0.25±0.05
			F	362.9	2.86±0.19	-0.46±0.05
(6,4)	0.68	23.4	E	335.5	5.64±0.11	-0.36±0.10
			F	337.4	5.75±0.12	-0.39±0.10
(6,5)	0.75	27.0	E	308.6	6.28±0.10	-0.34±0.10
			F	310.0	6.55±0.10	-0.37±0.10
(9,1)	0.75	5.2	E	304.0	4.85±1.16	
			F	305.6	5.94±1.17	
(8,3)	0.77	15.3	E	297.1	6.01±0.29	-0.21±0.02
			F	298.9	6.48±0.09	-0.24±0.01
(7,5)	0.82	24.5	E	282.6	6.16±0.17	-0.19±0.01
			F	284.4	6.19±0.15	-0.20±0.01
(7,6)	0.88	27.5	E	263.6	5.48±0.69	-0.19±0.08
			F	265.1	5.71±0.24	-0.16±0.02
(10,3)	0.92	12.7	E	251.8	3.99±0.75	-0.05±0.08
			F	252.7	4.34±0.65	-0.05±0.04
(14,2)	1.18	6.6	E	198.6	6.01±0.94	
			F	199.4	6.13±0.35	
(13,4)	1.21	13.0	E	195.3	5.17±0.83	
(12,6)	1.24	19.1	E	190.8	5.63±0.95	
(15,2)	1.26	6.2	E	188.7	7.34±0.42	
			(F	192.6	10.4 ± 3.5)	
(14,4)	1.28	12.2	E	185.3	6.16±0.45	
			(F	189.8	10.0 ± 3.2)	
(16,1)	1.29	3.0	E	183.8	6.14±0.95	
(13,6)	1.32	18.0	E	180.9	7.00±0.83	
			(F	184.9	10.0 ± 2.0)	
(12,8)	1.37	23.41	E	174.9	8.42±0.26	
			(F	178.9	11.1 ± 2.9)	
(13,7)	1.38	20.2	E	175.9	8.11±0.91	
(11,10)	1.42	28.4	E	168.7	8.56±0.37	
			(F	172.5	11.0 ± 6.4)	

Supplementary Section S4: Origin of α (and β)

As calculated previously by Venkateswaran *et al.*[4], the C-C hardening of the covalent bonds in the SWCNT wall as a function of pressure for an isolated SWCNT cannot account for the size of the experimentally-observed linear pressure derivatives α , yielding a theoretical value for $\alpha \sim 1.4 \text{cm}^{-1} \text{GPa}^{-1}$ for a (9,9) SWCNT ($d=1.22 \text{nm}$). Rescaling the C-C hardening observed for the G-band in our experiments to the RBM frequencies, we would obtain $\alpha \sim 1.2 \text{cm}^{-1} \text{GPa}^{-1}$ for the RBMs of the ArcE sample, in very good agreement with this theoretically predicted value. However, the experimentally observed linear pressure derivatives for the RBMs are much larger ($\alpha \sim 5\text{-}9 \text{cm}^{-1} \text{GPa}^{-1}$, in the diameter range $d=0.6\text{-}1.42 \text{nm}$).

This much larger pressure derivative α for the RBMs can be explained by the van der Waals interaction with the (external or internal) environment, exerting an additional restoring force on the RBM vibration.[4, 5] To account for this interaction with the environment in the calculation of α , we used a Lennard-Jones-type potential,

$$U_{LJ}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

using the van der Waals parameters for carbon in SWCNTs, $\sigma=0.3534 \text{nm}$ and $\epsilon=0.2906 \text{kJ/mol}$ given by reference [6]. The effect of pressure is included as a static radial force of magnitude $F(P)=PA_c$ acting on each carbon atom, with A_c the SWCNT wall area per carbon atom (i.e. half of a graphene unit cell = 0.0269nm^2).

For this very simplistic model, we neglect the C-C bond hardening and solely calculate the effect of the interaction with the environment, so that the potential acting on the SWCNT carbon atom as a function of pressure becomes:

$$U(r, P) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] + PA_c r$$

The RBM frequency as a function of pressure can then be calculated as

$$\nu(P) = \sqrt{\frac{k_0^{eff} + k(P)}{m_C}}$$

with k_0^{eff} the effective force constant for the radial motion of the carbon atoms in the SWCNT at zero pressure, which can be approximately obtained from the RBM frequency at low pressure ($k_0^{eff} = m_C \nu_{0,RBM}^2$), and m_C the atomic mass of carbon. $k(P)$ can be obtained by taking the second derivative to r of $U(r, P)$, in the minimum of $U(r, P)$.

As such, we obtain for the (6,5) SWCNT $\alpha = 6.05 \text{cm}^{-1} \text{GPa}^{-1}$; and for the (12,8) SWCNT, $\alpha = 10.5 \text{cm}^{-1} \text{GPa}^{-1}$, in excellent agreement with the experimentally observed values, showing that the additional radial restoring force exerted by the environment is indeed the dominant factor determining the pressure slope α of the RBMs. Somewhat surprisingly, α does not depend critically on the used potential $U_{LJ}(r)$ because for different potentials the environment molecules automatically explore regions of similar steepness for a given pressure.

In contrast, applying the same model to β (second order pressure derivative) yields values that are completely negligible compared to the experimentally observed β values. Thus β cannot be explained by the anharmonicity of the C-C van der Waals interaction with the environment or by the anharmonicity of the C-C bonds (because of the comparison with graphite[7]), and must originate from an inhomogeneous application of pressure by the molecular environment which is not accounted for by this very simple model.

Supplementary Section S5: Additional Figures

Supplementary Fig. S6: FWHM of the G⁺ Raman peak obtained from Voigtian fits of the G-band. Under hydrostatic conditions (<2GPa) the line width hardly increases, indicating that the environment easily adapts to the pressure and provides a homogeneous surrounding for the SWCNTs. After PTM solidification, the line width increases (by almost a factor of 3) due to the inhomogeneous interaction with the fixed molecular environment.

Supplementary Fig. S7: Normalized RBM spectra of the ArcE (left panel) and ArcF (right panel) SWCNTs excited at 514.5nm measured with an instrumental resolution of 3.8cm^{-1} . Spectra are normalized and shifted vertically according to the pressure at which they were measured (horizontal dashed lines indicate the pressure values). The RBM spectra of the empty SWCNTs are presented up to 4GPa, as at higher pressures, the RRS intensity becomes of the order of the baseline (from the fluorescence in the diamond anvil cell). The RBM frequencies of the empty SWCNTs gradually increase with $\alpha \sim 7\text{cm}^{-1}\text{GPa}^{-1}$, while for the filled SWCNTs $\alpha \sim 10\text{cm}^{-1}\text{GPa}^{-1}$ (see also Fig. S4). At $\sim 3\text{GPa}$, an additional Raman feature (indicated by the magenta line) splits off from the RBMs of the filled SWCNTs (and a very small fraction of this new feature is also observed in the empty sample, most probably due to a small amount of filled tubes in this empty sample). This new feature shifts with $\alpha \sim 16\text{cm}^{-1}\text{GPa}^{-1}$ and is attributed to a lower symmetry radial vibrational mode of a radially distorted filled SWCNT. The RBMs of the empty SWCNTs disappear above 3.5GPa. The narrow lines observed for the ArcF sample are plasma lines from the laser.

Supplementary Fig. S8: Normalized G-band spectra of the ArcE (left panel) and ArcF (right panel) SWCNTs excited at 514.5nm measured with an instrumental resolution of 3.8cm^{-1} . Spectra are normalized and shifted vertically according to the pressure at which they were measured (horizontal dashed lines indicate the pressure values). Red en blue filled circles indicate the fitted peak positions as presented in Figure 4 in the main text, red and blue stars indicate Center of Gravity (v_{COG}) positions as presented in Figure 6 in the main text. The narrow lines observed for the ArcF sample are plasma lines from the laser.

Supplementary Fig. S9: Normalized intensity of the RBMs of a selection of SWCNTs as a function of pressure. For the (16,1) SWCNTs, at pressures in between 2-4GPa the RBM intensity becomes too low to be experimentally detected, most probably due to the collapse of these larger diameter SWCNTs.

Supplementary Section S6: PLE experiments

The diamond anvil cell gives a strong fluorescence background which is especially important at elevated pressure, where the actual SWCNT emission becomes weaker. Therefore we measured this background independently from the SWCNT emission, by focusing the lamp-beam on a different part in the cell, and subtracted it from the PLE data accordingly to obtain the PLE maps of the SWCNTs. The raw PLE data, i.e. without background subtraction, can be found in Figure S10.

Supplementary Fig. S10: 2D PLE maps obtained at different pressures and spectrum of the background of the diamond anvil cell. For the spectra shown in the main text, this background was subtracted

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