High pressure Raman spectroscopy of single-walled carbon nanotubes: Effect of chemical environment on individual nanotubes and the nanotube bundle

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Abstract

The pressure-induced tangential mode Raman peak shifts for single-walled carbon nanotubes (SWNTs) have been studied using a variety of different solvents as hydrostatic pressure-transmitting media. The variation in the nanotube response to hydrostatic pressure with different pressure transmitting media is evidence that the common solvents used are able to penetrate the interstitial spaces in the nanotube bundle. With hexane, we find the surprising result that the individual nanotubes appear unaffected by hydrostatic pressures (i.e. a flat Raman response) up to 0.7 GPa. Qualitatively similar results have been obtained with butanol. Following the approach of Amer et al. [J. Chem. Phys. 121 (2004) 2752], we speculate that this is due to the inability of SWNTs to adsorb some solvents onto their surface at lower pressures. We also find that the role of cohesive energy density in the solvent–nanotube interaction is more complex than previously thought.

Keywords: A. Fullerenes; A. Nanostructures; A. Surfaces; C. High pressure; C. Raman spectroscopy

1. Introduction

Since their discovery by Iijima [1], carbon nanotubes—both multi-walled nanotubes (MWNT) and single-walled nanotubes (SWNT)—have been the focus of much scientific interest due to their extreme strength and novel electronic properties. They are considered to be a possible replacement for silicon-based semiconductors [2], they have applications in materials science due to their extreme mechanical strength [3], and they have attracted much theoretical interest since they represent a possible experimental realization of exotic low-dimensional phenomena [4]. Several different methods for growing SWNTs have been developed, but solid SWNT material produced by these methods generally consists of tangled bundles of tens to hundreds of aligned SWNTs instead of individual tubes [5]. Raman spectroscopy is a leading experimental method for the study of SWNTs due to resonance between the excitation photon energy and the electronic band gap of the SWNT making it possible to obtain a Raman spectrum from a single SWNT [6]. The deformation of carbon nanotubes under high hydrostatic pressure has been studied using Raman spectroscopy [7,8] and has yielded a wealth of information about SWNTs.

The penetration of the nanotube bundle by liquids and adsorption of these onto the surface of the nanotube has been discussed previously in the literature. Early high pressure studies of nanotubes considered only mechanical deformations of the nanotubes as explanations for the observed Raman shifts. Amer et al. [9] were the first to suggest that adsorption of solvents onto the surface of the nanotube plays a role.

Venkateswaran et al. [10] performed molecular dynamics calculations in which they considered the response of the SWNT to hydrostatic pressure for three different cases—(I)
the entire bundle being subjected to external hydrostatic pressure, (II) individual nanotubes subjected to hydrostatic pressure, and (III) the pressure medium entering the interstitial channels in the nanotube bundle and exerting a \( \sin^2 \theta \) force profile on the nanotubes. Their calculations predicted a substantial pressure-induced blue shift in the R band (100–200 cm\(^{-1}\)) peak with model I and a much weaker pressure dependence with models II and III. Experimentally, they observed the large pressure-induced blue shift predicted by model I so concluded that the pressure media used in their experiments do not enter the interstitial channels in the nanotube bundle.

However, they did not consider the microscopic details of the interaction between solvent molecules and the nanotubes. The work of Amer et al. [9], and that presented in this paper, shows that the solvent–nanotube interaction has a large effect on the behavior of the nanotubes under pressure, so we believe that the issue of penetration of the nanotube bundle by liquids needs to be revisited.

In this study, building on the work of Amer et al. [9] and Wood et al. [11], we report the response of SWNTs to hydrostatic pressure in pressure media with a variety of cohesive energy densities and molecular sizes ranging from hexane and argon to water. We draw tentative conclusions about the effect of solvent cohesive energy density and molecular size on the nanotube bundle structure and individual nanotubes, and discuss the consequences for possible applications of carbon nanotubes as molecular sensors of hydrostatic pressure and chemical environment.

We discuss the specific issue of penetration by different pressure media of the interstitial spaces in the nanotube bundle in the light of our results. This possible effect is of interest since it has been suggested as a possible experimental realization of a quasi-1-dimensional liquid [8].

2. Materials and experimental details

The SWNTs used in this study were Carbolex AP Grade nanotubes commercially available from Sigma-Aldrich. They are as-produced single-walled, closed-ended nanotubes grown by the arc method. Their average diameter is 1.4 nm and they are found in ropes of approximately 20 nm diameter (50 tubes). Purity is 50–70%. Catalyst impurities are present consisting of Ni and Y nanoparticles encapsulated in carbon shells, and also small amounts of amorphous carbon (information supplied by manufacturer). The sample has been studied by TEM to confirm the presence of bundled SWNTs and carbon encapsulated metallic nanoparticles.

All Raman spectra were recorded at room temperature using a Renishaw 1000 Raman microprobe system. Scattered light from the sample was collected in the backscattering geometry, passed through a holographic notch filter and a diffraction grating and was detected with a Peltier cooled charge coupled device (CCD) camera. The 514.5 nm excitation of a 50 mW argon laser was used. The laser power reaching the sample in this system is \( \approx 1 \) mW.

The high pressure Raman measurements were performed in a gasketed Mao-Bell type diamond anvil cell (DAC) and the hydrostatic pressure was measured using the R line emission of a small chip of Ruby placed in the DAC. This allows calibration of the pressure to within 3% [12]. Solid SWNT material was loaded directly into the DAC.

High pressure Raman spectra were taken with a variety of pressure media, namely: Hexane, butanol, propan-2-ol, ethanol, methanol, 4:1 methanol–ethanol mixture, 5:4:1 distilled water–methanol–ethanol mixture and distilled water. Since some of these pressure media are not commonly used, the line width of the ruby R-lines was monitored following the methodology in [13] to ensure that a hydrostatic environment was being maintained.

Static scans were centered at 1600 cm\(^{-1}\) and the integration time was varied between 3 and 30 min depending on the strength of the Raman signal. All high-pressure spectra were fitted to two Lorentzian curves (using the least squares curve fitting software on Microcal Origin) after deduction of a polynomial or exponential baseline. The SWNT radial breathing mode at \( \approx 200 \) cm\(^{-1}\) could not be observed due to the use of a holographic notch filter on the spectrometer.

A separate experiment was performed using liquid argon as a pressure medium to study the same SWNT material. In this a 632.8 nm 20 mW HeNe laser was used. A standard MCDAC was used for the higher-pressure part of the experiment and an MCDAC in the Zen configuration [14] was used to attain the lower pressures. Due to the different lineshape and weaker Raman signal from the SWNTs in this experiment, a single Lorentzian was used to fit the spectra.

3. Results

Table 1 summarizes our results. We find a linear shift of the G band peaks with hydrostatic pressure (pressure coefficient 1), followed by a linear shift with a lower pressure coefficient (2). With some solvents, we also observe a further softening of the pressure-induced shift at higher pressures. We find that the pressure coefficient in the low-pressure regime does not vary significantly between different solvents. The pressure coefficient in the higher-pressure regime (2) and transition pressure do vary between solvents, but show no apparent correlation to the cohesive energy density or molecular size of the solvents used. See Table 1.

With hexane and butanol, we also observe a new effect—a flat Raman response to increasing pressure to 0.7 and 0.4 GPa, respectively, as shown in Figs. 1–4. This effect is irreversible (Fig. 2).

The results with liquid argon (Fig. 5) show a pressure coefficient in the low-pressure regime of 13.2 cm\(^{-1}\) GPa\(^{-1}\) compared to 9.0–10.6 cm\(^{-1}\) GPa\(^{-1}\) with the other solvents (see Table 1), followed by a plateau commencing just below 2 GPa. Caution must be exercised in the comparison of these results with the data taken using other solvents due to
differences in the experimental procedures used and excitation laser wavelength—as described earlier. In particular, the procedure of loading the DAC with liquid argon necessitated an initial hydrostatic pressure of 0.8 GPa to seal the DAC so data points below this pressure were taken when decreasing the pressure. Therefore, were an irreversible effect similar to that shown in Fig. 2 exist with SWNTs in argon, this experiment would not reveal its existence.

Fig. 6 shows the frequencies of the two G band peaks plotted against the cohesive energy density [11] of the various solvents listed in Table 1. We see a small shift to higher wavenumber depending on the choice of solvent but a large shift (≈ 5.5–7 cm⁻¹) from the value in air upon immersion in any of the solvents we used. The significance of this result is discussed later.

For each the cohesive energy density (CED) of the solvent is shown. With all solvents we observed a linear pressure-induced shift of the main tangential mode Raman peak, followed by a breakpoint (transition pressure) and linear shift at a lower rate. Pressure coefficients 1 and 2 give the rate of shift with pressure in the low and high-pressure regimes. The transition pressure is the pressure at which the breakpoint occurred. 514.5 nm laser excitation used, except for the results with liquid argon for which 632.8 nm laser excitation was used. W—water; M—Methanol; E—Ethanol.

Table 1
The results of the high pressure experiments with all solvents are summarized

<table>
<thead>
<tr>
<th>Solvent</th>
<th>CED [11,15] (GPa)</th>
<th>Pressure coeff. 1 (cm⁻¹ GPa⁻¹)</th>
<th>Pressure coeff. 2 (cm⁻¹ GPa⁻¹)</th>
<th>Transition pressure (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid argon</td>
<td>Negligible</td>
<td>13.2±1.6</td>
<td>0.5±0.2</td>
<td>1.7</td>
</tr>
<tr>
<td>Hexane</td>
<td>0.22</td>
<td>10.0±0.1</td>
<td>8.2±0.5</td>
<td>1.4</td>
</tr>
<tr>
<td>1-butanol</td>
<td>0.55</td>
<td>9.9±0.1</td>
<td>5.9±0.3</td>
<td>1.9</td>
</tr>
<tr>
<td>2-propanol</td>
<td>0.55</td>
<td>9.0±0.6</td>
<td>7.0±0.2</td>
<td>1.4</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.68</td>
<td>10.5±1.9</td>
<td>5.3±0.5</td>
<td>1.2</td>
</tr>
<tr>
<td>4:1 M:E</td>
<td>0.83</td>
<td>10.6±0.2</td>
<td>5.1±0.1</td>
<td>1.2</td>
</tr>
<tr>
<td>Methanol</td>
<td>0.87</td>
<td>9.1±0.1</td>
<td>5.3±0.1</td>
<td>1.2</td>
</tr>
<tr>
<td>5:4:1 W:M:E</td>
<td>1.56</td>
<td>10.0±0.1</td>
<td>5.8±0.2</td>
<td>0.7</td>
</tr>
<tr>
<td>Water</td>
<td>2.29</td>
<td>9.5±0.1</td>
<td>8.2±0.3</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Fig. 1. Pressure-induced tangential mode Raman peak shifts of SWNTs immersed in hexane and 4:1 methanol-ethanol solution are shown to 8 GPa. The flat Raman response of SWNTs in hexane to 0.7 GPa is visible. Data taken when increasing pressure. Laser excitation 514.5 nm.

Fig. 2. Flat tangential mode Raman response to 0.7 GPa of SWNTs in hexane from Fig. 1 is shown in more detail. Data taken when reducing the pressure from 1.2 GPa show the effect to be irreversible.

Fig. 3. Various spectra of the G band in hexane are shown. The flat Raman response to 0.7 GPa followed by discontinuous step and linear increase are visible. These spectra form some of the data in Figs. 1 and 2.
Conclusions and discussion

In conclusion, we have studied the hydrostatic pressure-induced shift of the Raman G-band peak in a variety of solvents. We observed an initial blue shift of 9.0–10.6 cm$^{-1}$/GPa$^{-1}$ with hydrostatic pressure, followed by a softening at transition pressures ranging from 0.7 to 2 GPa, linear shift with smaller pressure coefficient, then in some cases further softening of the pressure-induced shift at very high pressures. The transition pressure and pressure coefficient of the blue shift in the high-pressure regime appear to vary significantly with choice of solvent but show no apparent correlation to the cohesive energy density or molecular size of the solvents used. We do not at present have an understanding of what causes this variation but there are many factors that could play a role, including shear stresses caused by the pressure medium not being perfectly hydrostatic, and changes in the molecular dynamics of the solvent–nanotube interaction at high pressure caused by different solvents slowly vitrifying or suddenly solidifying in the DAC. The solvent–nanotube interaction could also affect the electronic band structure of the nanotube analogously to the interaction between nanotubes in the bundle [16].

The transition at ~2 GPa to a lower pressure coefficient occurs also when SWNTs are subjected to high pressure with no pressure medium present [17], supporting the hypothesis that the change is due to collapse of the nanotubes [7]. However, our work shows that the transition pressure is dependent on which pressure-transmitting solvent is present so we can conclude that the choice of solvent affects the susceptibility of the nanotubes to collapse.

The results clearly show that the Raman spectra of SWNTs (both in response to hydrostatic pressure and at ambient pressure) are highly sensitive to the solvent in which the nanotubes are immersed. The experiment with liquid argon as the pressure medium (Fig. 5) is further evidence for this due to the higher pressure induced blueshift (13.2 cm$^{-1}$/GPa$^{-1}$) and plateau commencing at ~1.7 GPa. Merlen et al [18] found a similar plateau commencing at 10 GPa with open-ended SWNT.

Since the photon penetration depth in graphite is about 60 nm [9], incident laser photons penetrate deep into the nanotube bundle. The Raman spectrum of SWNTs therefore contains contributions from tubes at the center of the bundle as well as from those at the edge of the bundle—so our results show that the choice of solvent affects the
tubes at the center of the bundles. We believe this suggests that all the solvents used in our experiments are able to penetrate the interstitial spaces between the tubes in a bundle. The large (≈ 5.5–7 cm⁻¹) shift in the Raman peaks on immersion in any solvent used (Fig. 6) is further evidence for this.

Our results also show that the effect of the cohesive energy density of the various solvents used is different from the equivalent hydrostatic pressure—the main G band peak shifts at a rate of 0.8 cm⁻¹ GPa⁻¹ with cohesive energy density (Fig. 6) but at 9.0–10.6 cm⁻¹ GPa⁻¹ with hydrostatic pressure (see Table 1). We accept that the large molecular sizes of hexane and butanol in particular could make it hard for them to penetrate the interstitial spaces, but heterogeneity in the size of these spaces due to the diameter distribution of the tubes and defects in the nanotube lattice could aid the process. It has, however, been previously noted by Venkateswaran et al. [10] that methanol and ethanol molecules should be small enough to penetrate the interstitial spaces in the nanotube lattice. In addition, Sood et al. [19] noted that the observed small upshift in the R band upon immersion in a liquid would be consistent with the alcohol solution entering the interstitial spaces and inhibiting the radial vibration of the nanotubes.

Amer et al. [9] recently suggested that the nanotube G band Raman peak shift with hydrostatic pressure is predominantly due to adsorption of molecules of the solvent onto the surface of the nanotubes, drawing their conclusion from a series of experiments in which SWNTs immersed in different proportions of methanol and water were studied using high pressure Raman spectroscopy. They observed plateaus in which a flat Raman response to increasing pressure was seen, and attributed these to adsorption of one solvent onto the nanotube surface being completed and then adsorption of another solvent commencing. The plateaus observed with liquid argon as a pressure medium support this hypothesis since the open-ended nanotubes used in Ref. [18] would offer more adsorption sites for the argon, allowing the G band to continue shifting to a higher pressure than in our work—as observed. However, Raman shifts under pressure have also been observed when nanotubes were compressed under non-hydrostatic conditions with no pressure medium [17] so adsorption of solvents onto the surface of the nanotubes cannot provide a complete explanation for the observed behavior. The effect observed by Amer is different to that in Figs. 1–4 since they found it to be fully reversible with no discontinuous change in the nanotube Raman shift.

We speculate that the flat nanotube Raman response to low hydrostatic pressures with hexane (Figs. 1–3) and butanol (Fig. 4) could be explained by the large molecular size of the solvents preventing their adsorption onto the surface of the nanotubes at lower hydrostatic pressures. The shift in the Raman peak upon immersion in any solvent of (≈ 5.5–7 cm⁻¹) is evidence against the simpler explanation that hexane and butanol find it harder to penetrate the interstitial channels in the nanotube bundle at lower pressures.

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References